Advanced Low Energy Enzyme Catalyzed Solvent for CO_2 Capture

Final Scientific/Technical Report

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Abstract

A proof-of-concept biocatalyst enhanced solvent process was developed and demonstrated in an integrated bench-scale system using coal post combustion flue gas. The biocatalyst was deployed as a coating on M500X structured packing. Rate enhancement was evaluated using a non-volatile and non-toxic 20 wt% potassium carbonate solution. Greater than 500-fold volumetric scale-up from laboratory to bench scale was demonstrated in this project. Key technical achievements included: 10-fold mass transfer enhancement demonstrated in laboratory testing relative to blank potassium carbonate at 45°C; ~ 7-fold enhancement over blank in bench-scale field testing at National Carbon Capture Center; aerosol emissions were below detection limits (< 0.8 ppm); 90% capture was demonstrated at ~19.5 Nm^3/hr (dry basis); and ~ 80% CO_2 capture was demonstrated at ~ 30 Nm^3/hr (dry basis) for more than 2800-hrs on flue gas with minimal detectible decline in activity. The regeneration energy requirement was 3.5 GJ/t CO_2 for this solvent, which was above the target of 2.1 GJ/t CO_2. Bench unit testing revealed kinetic limitations in the un-catalyzed stripper at around 85°C, but process modeling based on bench unit data showed that equivalent work of less than 300 kWh/t CO_2 including all CO_2 compression can be achieved at lower temperature stripping conditions. Cost analysis showed that 20% potassium carbonate in a basic solvent flow sheet with biocatalyst coated packing has economic performance comparable to the reference NETL Case-12, 30% MEA. A detailed techno-economic analysis indicated that addition of catalyst in the stripper could reduce the cost of capture by ~6% and cost of avoided CO_2 by ~10% below reference NETL Case-12. Based on these results, a directional plan was identified to reduce the cost of CO_2 capture in future work.

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1.0 Executive Summary

Akermin was awarded funding in October 2010 through the DOE National Energy Technology Laboratory (NETL), existing plants division, to further develop a proprietary immobilized enzyme technology based on carbonic anhydrase that enhances rates of CO_2 absorption into various carbonate-based solvents that have low regeneration energies. All project milestones have been completed as of the end of October 2013. This report comprises the final progress report for this project under DE-FE0004228.

Akermin's work plan consisted of four main areas of development that are summarized below:

1. Identification of a preferred enzyme;
    - Akermin evaluated a broad range of carbonic anhydrases from various suppliers and evaluated them for suitability for immobilization (sufficient purity), high activity in the target solvent (potassium carbonate); stability at high pH, thermal stability suitable for long-term bench unit demonstration at 40°C, and availability on a multi-kilogram scale to support development and demonstration activities. Akermin selected Carbonic anhydrase from Novozymes A/S Denmark as the most suitable enzyme for development and established a supply arrangement with the company.

2. Optimization of the immobilization polymer/enzyme system;
    - Akermin investigated several approaches to immobilize carbonic anhydrase on random and structured packing. Significant enhancement factors (up to 20-fold) were achieved with several carbonic anhydrases using a micellar polymerization system based on polyhydromethylsiloxane-*graph*-polyethyleneglycol (PHMS-*g*-PEG) polymer. Yet a relatively quick decline in activity (within 1 hr), which was most likely caused by product inhibition of the enzyme, prompted Akermin to explore an alternative immobilization approach based on silica gel. This immobilization method (that was eventually deployed in the bench unit) demonstrated up to 17-fold enhancement of CO_2 capture at room temperature and 10-fold enhancement at 45°C relative to blank potassium carbonate in laboratory testing.

3. Definition of operating limits through analysis of lab-scale reactor data and process modeling;
    - Lean feed temperature was fixed in the range 40 to 45°C.
    - The 20% w/w K_2CO_3 equivalent concentration was selected to provide suitable margin over possible precipitation conditions.
    - Lean and rich limits were identified based on detailed equilibrium data review including literature reports and laboratory testing. A sufficiently lean loading, typically <0.38 mol/mol K_2CO_3 equivalent or less, is needed to achieve 90% capture in the flue gas application. The rich loading, typically ~ 0.68 - 0.70 mol/mol K_2CO_3, is limited by equilibrium with as fed flue gas.
    - Bench unit test plan was designed with a parametric study component to quantify regeneration energy with varied lean loading and reduced reboiler pressures; to determine

flow rates required for 90% capture with and without biocatalyst; and to provide long-term performance evaluation at a fixed gas and liquid flow condition.

- Achievable regeneration energy was determined to be ~ 3.5 GJ/t CO_2, which was above the target of 2.1 GJ/t CO_2. It was constrained by kinetic limitations below about 85°C, and depended on lean loading requirement. Even so the lower temperature regeneration conditions explored in bench unit testing were shown to reduce equivalent work in detailed process modeling.
- A small set of techno-economic cases were specified for detailed costing based on results from bench unit testing, process modeling results, and engineering judgment.

4. Scale-up to a bench-scale unit capable of interfacing directly to a commercial slip-stream.
    - The immobilization approach yielding the best performing biocatalyst samples in a small single pass reactor (SPR) tests were adapted to coating 0.5-L sections of M500X structured packing. The scale up of biocatalyst formulation was successfully demonstrated achieving ~ 7-fold enhancement in field testing relative to blank packing in 212 mm inside diameter by 8-m tall packed column with 40°C lean feed of 20% K_2CO_3 at ~ 0.28 mol/mol K_2CO_3 as fed.
    - Further improvements in biocatalyst formulation resulted in up to 17-fold enhancement of the overall mass transfer coefficient at room temperature in the presence of the catalyst compared to blank packing, and 10-fold enhancement relative to 45°C blank.

Key objectives of this project included demonstrating biocatalyst-enhanced absorption in a bench scale pilot plant, achieving approximately 90% CO_2 capture with 30 Nm^3/hr (dry equiv) coal combustion flue gas, operating up to six months, and completing a techno-economic analysis.

Figure 1 shows that approximately 80% CO_2 capture was demonstrated with long-term stable performance at the design gas flow rate. Biocatalyst testing in bench unit achieved 90% CO_2 capture at approximately 20 Nm^3/hr with the design liquid-to-gas ratio, which represents a 7-fold higher gas flow at 90% capture than would be achieved with blank (un-catalyzed) packing in the same column. Therefore, significant enhancement was feasible and reliably demonstrated at bench unit scale with biocatalyst coated packing. Capture performance below the originally planned 90% removal at the design flow rate is attributed to a lower than expected area efficiency and slightly lower than expected activity of the catalyst generated under scaled-up conditions.

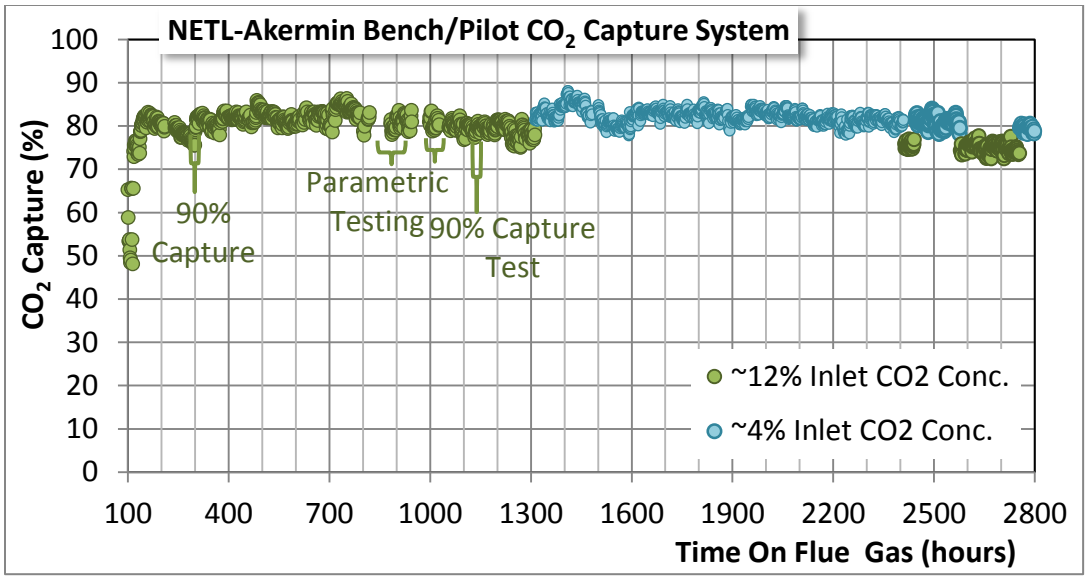

Figure 1: CO_2 capture data for bench unit at National Carbon Capture Center with coal flue gas

A techno-economic assessment (TEA) was performed with the assistance of the Pacific Northwest National Laboratories, and a review of the TEA was provided by the power engineering firm WorleyParsons. The economic evaluation by PNNL focused on three absorber and stripper column heights that are linked to catalyst performance cases. All cases used 20% potassium carbonate (K_2CO_3) with the same lean and rich loading conditions and the same basic solvent flow sheet, see Appendix A. While the energy performance was equivalent, the amount of enhancement provided by the immobilized biocatalyst was varied to understand its effect on the size and cost of the absorber and stripper used in the design. The cost of capture with a 10-fold acceleration of capture in absorber and no acceleration of desorption in stripper was approximately the same as the reference NETL Case-12. However, by also deploying catalyst in the stripper resulted in a reduction in cost of capture by 5.8% relative to the reference case, and a reduction in avoided cost of CO_2 by 10.4%.

This work shows that CO_2 capture in environmentally benign aqueous solutions enabled by immobilized biocatalysts was technically feasible and, and the cost of CO_2 capture was comparable to NETL case-12, version 2 with biocatalyst deployed in the absorber only. It was shown that the best economic performance could be achieved with regeneration at the lowest practical regeneration temperature — a feature that is attributable to minimizing equivalent work by using lower temperature steam to regenerate the low heat of reaction solvent. Bench unit testing and rate based modeling of the stripping process for 20% K_2CO_3 revealed a kinetic limitation at around 80 to 85°C, which also depended on the lean loading. For this reason, the regeneration temperature was limited in the TEA to around 87°C. It was found that this kinetic limitation depends on the size of the stripper for a given extent of lean solvent regeneration. This project did not deploy enzyme into the stripper according to the original scope of work, as it was intended that biocatalyst coating packing in the absorber would be sufficient to leverage a conventional

solvent flow sheet. However, directional trends suggest alternative flow sheets with novel methods of CO_2 stripping should be explored to enable regeneration of this solvent or other solvents at lower temperatures/pressures aided by catalyst.

The main conclusion of this work is that non-volatile, environmentally benign solvents, such as 20% potassium carbonate aqueous solution, can be enabled by biocatalyst in a conventional solvent flow sheet. In this case the biocatalyst was deployed as a coating on structured packing. This concept was found to be technically feasible and economically competitive with the most recent reference case, NETL Case 12, revision 2. However, further process innovation and development is needed to reduce energy penalty and cost of capture toward achieving the DOE's goal of less than 35% increase in levelized cost of electricity.

Key technical achievements:

- Developed understanding of overall biocatalyst enhancement and its temperature dependence.
- Demonstrated up to 20-fold enhancement in overall mass transfer coefficient relative to room temperature blank K_2CO_3 using biocatalyst coated structured packing.
- Demonstrated over 12-fold enhancement in overall mass transfer coefficient in laboratory closed loop reactor at 45°C compared to blank K_2CO_3 (non-catalyzed system at the same temperature) using the most recent biocatalyst formulation on structured packing.
- Identified potential to reduce total equivalent work by ~20% (including CO_2 compression) based on bench unit stripper size and performance data with ~85°C reboiler with potassium carbonate.
- Demonstrated 90% capture in 275-liter packed column absorber with ~32-second space time, which represents a 7-fold increase in flow relative to blank packing at same temperature.
    - Absorber: ~20.9-cm diameter column x 8-m packing
    - Liquid/Gas ratio: ~ 9 liters liquid/dry Nm^3 gas, 12% CO_2 in flue gas,
    - Solvent: 20% K_2CO_3, 40°C lean feed, lean loading of 0.28 mol/mol,
- Demonstrated ~2800 hours on coal flue gas at the National Carbon Capture Center with steady performance of ~ 80% CO_2 capture using biocatalyst coated absorber packing.
- Reliable operation was demonstrated (99% available relative to flue gas supply).
- Negligible heat stable salts accumulation (< 1.6% of solvent capacity per year).
- Greater than 99.9% purity of CO_2 product measured by NCCC.
- Zero volatility in K_2CO_3 system, potassium aerosol carry-over below detection limit.
- Negligible detectible corrosion rates using 304-stainless steel.

2.0 Technical Summary

Task 1 – Project Management and Planning (Akermin)

Subtask 1.1 – Project Management and Planning

The Recipient shall finalize the Project Management Plan within 30 days after award and manage project activities in accordance with the plan. The Project Management Plan will be updated as necessary. The program manager will be responsible for coordinating project activities between Akermin and its sub-contractors (Battelle and PNNL).

Project management plan was submitted to NETL and updated as required throughout the project. A project extension was granted during budget period one to allow more time to complete the 10-fold enhancement milestone. A project extension was granted in budget period two to extend field testing biocatalyst in the bench unit through the end of September 2013. The revised project end date was September 30, 2013. Testing at NCCC continued though the end date. A project closeout meeting was held at NETL on November 22, 2013. This report represents the final deliverable for this project.

Subtask 1.2 – Briefings and Reports

The Recipient shall monitor and coordinate the technical and financial activities of the project and will prepare and deliver reports and briefings as outlined in Sections D and E below.

Akermin submitted eleven quarterly reports and provided project continuation applications as required to document technical progress and financial status of the project.

Subtask 1.3 – Finalize Agreement with the National Carbon Capture Center

The Recipient shall obtain an executed host site agreement with the National Carbon Capture Center (NCCC) to provide a bench-unit testing slot at the power systems development facility adjacent to Plant Gaston, an Alabama Power pulverized coal-fueled generating plant operated by Southern Company Services. The Recipient shall also obtain the required National Environmental Policy Act approvals for testing at the NCCC.

The Technical Collaboration Agreement (TCA) between Akermin and NCCC was fully-executed by all parties on May 17, 2012. The updated NEPA environmental questionnaire for testing at the NCCC was submitted to DOE on August 22, 2012.

Task 2 – Enzyme Selection (Lead Organization: Akermin)

Subtask 2.1 – Enzyme Stability Studies

Evaluate the tolerance of select free enzymes to temperature, pH, and ionic strength. Akermin anticipates evaluating up to four different enzyme varieties under anticipated operating conditions

of approximately 40°C, pH 8-10, and high ionic strength (up to 4 M solutions). Select a preferred enzyme for long-term development based on stability at operating conditions and long-term scale-up expression potential.

Akermin has completed this subtask and has selected carbonic anhydrase (CA) developed by Novozymes. Akermin evaluated the stability of several carbonic anhydrases, including bovine carbonic anhydrase (bCAII), human carbonic anhydrase (hCAII, and hCAIV), and genetically-engineered CAs from Novozymes and other suppliers. Among the enzymes tested the CA from Novozymes was by far the most stable.

Figure 2 shows that soluble Novozymes CA retains full activity at room temperature for over 3 months when incubated as 1 mg/ml solution in 0.5 M K_2CO_3/0.5 M $KHCO_3$ buffer pH near 10. The enzyme demonstrates a half-life of 120 days (4 months) at 40°C, 12 days at 60°C and less than 1 day at 70°C. A pH-stat method was used to assay CO_2 hydration activity, as described in the next section under Task 2.2.

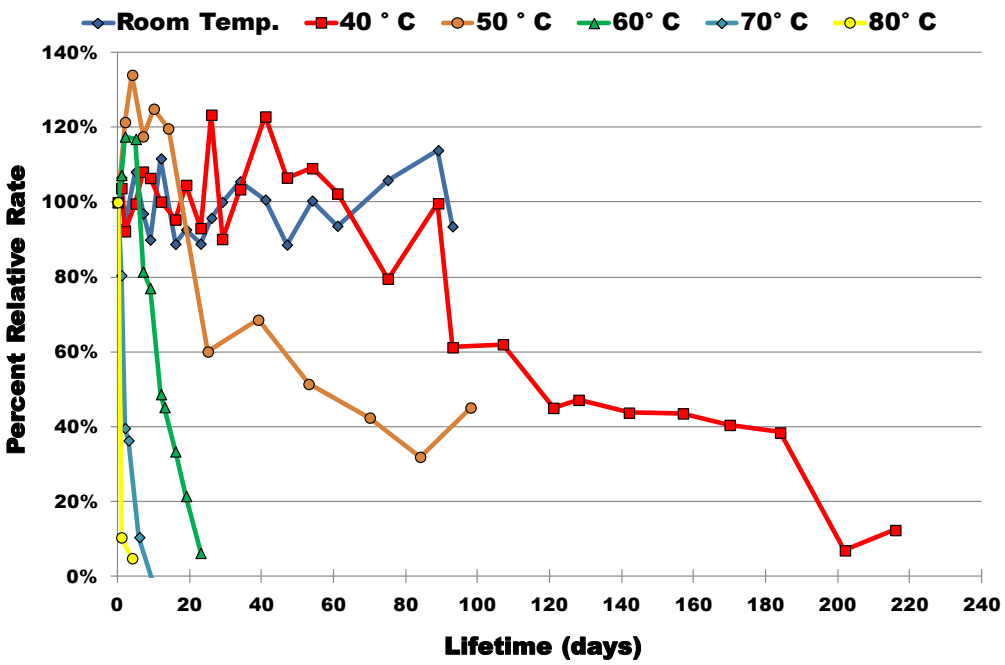

Figure 2: Thermal stability studies with dialyzed, soluble, Novozymes CA.

Effect of impurities on CA activity

Flue gases include nitrogen oxides, sulfur oxides, and heavy metals as a result of impurities typically present in coal during the combustion process. Although these impurities are anticipated to be at the ppm level prior to entry into a CO_2 capture reactor, the volume of gas output from a coal-burning power plant

is expected to result in the accumulation of significant amounts of aqueous nitrates, sulfates, and trace metals. These impurities pose a technical risk to sustained operation of an immobilized CA reactor due to potential inhibition of enzyme activity. Key project objectives included evaluating the impact of contaminants such as nitrogen oxides, sulfur oxides, and heavy metals common to coal-fired flue gases.

The tolerance of free enzyme to nitrate, nitrite, sulfate, and sulfite anions was evaluated using the pH stat assay, performed at 8°C to improve sensitivity and reproducibility. Nitrate and nitrite anions demonstrated little or no inhibitory potency against the engineered CA at molar concentrations, as illustrated in Figure 3 for nitrate. In the case of sulfate, no inhibition was observed at concentrations approaching the solubility limit of approximately 300 mM in carbonate/bicarbonate solutions. These values are consistent with those reported in the literature [1], taking into account the pH-dependence for CA inhibition by anions [2]. Based upon these results, significant inhibition of immobilized CA is not anticipated by these anions.

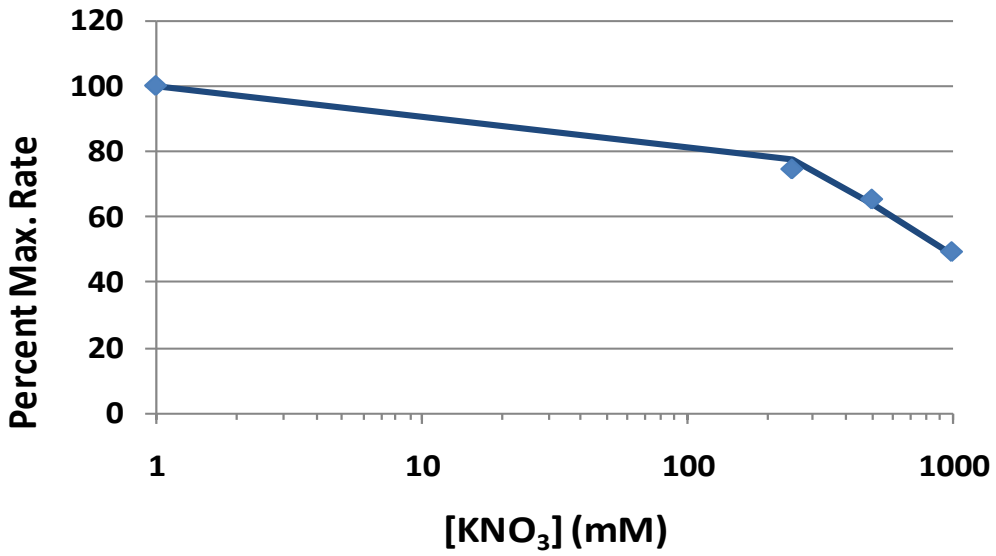

Figure 3: Inhibition of Novozymes CA by Potassium Nitrate

Inhibition of free enzyme by divalent metals was evaluated by the addition of stock solutions containing the metal chloride or nitrate salts to the assay mixture. Note that chloride anion is not an inhibitor of the engineered CA at concentrations as high as 2.0 M. As illustrated in Figure 4, Hg(II) demonstrated an IC_{50} of 0.13 mM against the CA. This value is consistent with inhibition constants reported for mercury, obtained with various human CA isoforms using the PNPA esterase assay [3].

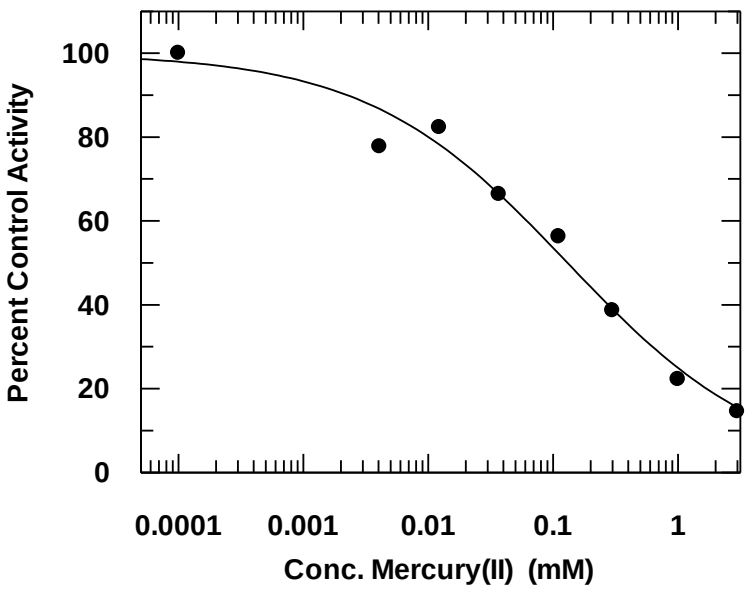

Figure 4: Inhibition of Novozymes CA by Hg(II)

The inhibition constants and/or observed activity at a defined concentration for each contaminant examined are provided in Table 1.

Table 1: Inhibition of CA by Various Contaminants Present in Flue Gas

Contaminant	Anticipated in flue gas (DOE FOA 000785)	Soluble Product	IC50 (mM)
NO_X	53 ppmv	Nitrate (NO_3^-)	~ 1000
		Nitrite (NO_2^-)	> 2000
SO_X	46 ppmv	Sulfate (SO_4^{-2})	> 500
		Sulfite (SO_3^{-2})	>100
Chloride	< 1ppm*	Chloride (Cl^-)	> 2000
Heavy Metals	1.3 ppbw	Mercury Hg^{+2}	0.14

*Expected to be negligible after caustic scrubber.

The accumulation of metal cations in the aqueous phase of a CO_2 absorber will likely be limited by the precipitation of insoluble metal salts due to the presence of counter–ions, such as hydroxide, carbonate, chloride and sulfate. Table 2 provides the solubility product constants (K_{sp}) of several metal salts of interest. Note that the solubility product constants for many hydroxide salts are approximately 10^{-15}, which is often lower than that of the chloride or sulfate salts. Consequently, the concentration of hydroxide anions at pH 9 is sufficient to limit the soluble accumulation of many divalent metal hydroxides to low micromolar concentrations.

Table 2: Solubility Product Constants for Various Metal Salts of Interest

Compound	Formula	K_{sp} (25 °C)
Cadmium arsenate	$Cd_3(AsO_4)_2$	2.2×10^{-33}
Cadmium carbonate	$CdCO_3$	1.0×10^{-12}
Cadmium hydroxide	$Cd(OH)_2$	7.2×10^{-15}
Lead(II) carbonate	$PbCO_3$	7.40×10^{-14}
Lead(II) chloride	$PbCl_2$	1.70×10^{-5}
Lead(II) hydroxide	$Pb(OH)_2$	1.43×10^{-20}
Lead(II) sulfate	$PbSO_4$	2.53×10^{-8}
Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}
Mercury(II) hydroxide	HgO	3.6×10^{-26}

From: http://www.ktf-split.hr/periodni/en/abc/kpt.html

Subtask 2.2 Establish Enzyme Assay

An enzyme assay will be designed and implemented for rapid and accurate evaluation of enzymes from various sources or potential suppliers for specific activity and enzyme purity as needed for quality assurance.

Akermin has completed this subtask. Akermin uses a 96-well plate for rapid enzyme screening according to CO_2 dehydration reaction that is followed with colorimetric absorbance with a pH sensitive dye.

For precise determination of CO_2 hydration activity, Akermin adopted a potentiometric pH-stat assay [4] [5] that is based on the automatic titration of Tris buffer with potassium hydroxide (KOH). To perform the assay, 50 mL of 30 mM Tris (pH 8.6) is delivered into a water-cooled vessel, containing a stir bar, and placed on a stir plate. A circulating chiller is used to cool the solution in the vessel to 6°C. The assay is initiated by feeding a 10% CO_2 gas stream (balance N_2) into the chilled solution through a sparging stone

at 1 SLPM. As the pH drops, due to capture and hydration of CO_2 to HCO_3^- and H^+, the auto-titrator adds a solution of 0.2 M KOH to maintain a constant pH of 8.6. Based on the reaction stoichiometry, the rate of base addition to maintain static pH during the course of the reaction is directly proportional to the rate of CO_2 capture in the same time period.

Akermin implemented improved temperature control and enhanced procedural specifications to further improve the method's sensitivity and reproducibility. The potentiometric titration proved to be the most direct and accurate method for determining the carbonic anhydrase (CA) enzyme activity in solution. However, it is worth noting the limitations of this assay. It cannot be used to test performance in typical capture solutions due to the high ionic strength, and the fact that these capture solutions are not buffers. It cannot be used to any utility to screen immobilized enzyme. The pH stat assay is, however, a useful screening tool for soluble enzyme activity.

Hence, for immobilized enzyme activity characterization, Akermin assembled several small single-pass reactors (SPR) that are each comprised of a small (about 1.6 cm inside diameter) packed-column reactor typically loaded with 1109 pieces of model spherical packing (65-g bare packing, 3.66 mm diameter before coating). A gas consisting of 15% CO_2 blended with nitrogen is fed at the bottom, and a single pass of lean solution consisting of 20 wt% K_2CO_3 at ~ 25% conversion to bicarbonate, or approximately pH 10.1, is fed from the top. The reactor is typically operated at room temperature, and the solution is not recycled. This single pass approach significantly increased the laboratory throughput and eliminated potential interference of the leached enzyme. A high liquid-to-gas (L/G) ratio (about 50 ml solution/L gas) was selected to keep the equilibrium partial pressure constant over the reactor (low liquid phase conversion)—in order to facilitate calculation of overall mass transfer coefficient.

The same test conditions were used for monitoring lifetime performance of the selected immobilized enzyme system.

Subtask 2.3 – Evaluate and partner with enzyme supplier for expression.

Evaluate capabilities, commitment and approach of various enzyme suppliers toward providing enzyme expression at sufficient quantities for the program within a reasonable cost and performance expectation, as well as long-term development interest. Select an enzyme provider for this project.

Akermin has concluded this task as of the end of budget period one as planned. Novozymes has supplied Akermin with multi-kilogram quantities of enzyme to support all research activities and supply for the bench unit.

Task 3 – Enzyme Immobilization and Characterization (Lead Organization: Akermin)

This task is central to Akermin's technology offering—immobilization and stabilization of enzymes for industrial deployment. There are two key milestones addressed by the immobilization development activities described herein:

Milestone A1: Greater than 80% enzyme retention demonstrated in a flow system.

Milestone A3: Lab-scale CLR demonstrates 10X absorption rate enhancement.

The first key metric above concerns the degree of physical enzyme retention in the immobilization matrix. The second key metric concerns achieving an order-of-magnitude (10X) improvement in overall mass transfer coefficient for absorption so that the required column size may be similarly reduced for a given CO_2 capture target.

Subtask 3.1 – Evaluate and Down-select Polymer System

Investigate various coupling chemistries (epoxide, succinimide, 4-toluenesulfonyl, 4-nitrobenzenesufonyl, etc.) to tether enzyme into the hydrophilic regions of the micellar polymer and compare to micellar polymers without these functional groups. Down-select to define the enzyme-to-polymer coupling chemistry.

Akermin initially selected a polyhydromethylsiloxane-*graph*-polyethyleneglycol (PHMS-*g*-PEG) micellar polymer system for immobilization due to high permeability to carbon dioxide. Akermin explored various coupling chemistries as described above. Akermin showed that tethering of the enzyme is possible via two different approaches: introduction of a tethering site into the micellar polymer, or functionalization of the enzyme with allyl groups that attach to the micellar polymer during cross-linking. It was also shown that once the enzyme is covalently tethered, physical enzyme retention as high as 90% is achieved, exceeding our milestone-A1 requirement of >80% physical retention.

To further improve observed activities, Akermin investigated using the vinyl-functionalized CA itself as the cross-linker in the micellar polymer film, resulting in more hydrophilic films with good enzyme retention at higher enzyme loadings. This approach was essential to achieving high enzyme retention in the PHMS micellar polymer system with high peak activity.

Figure 5 shows enzyme retention results in a study with allyl-PEG-succinimide functionalized Novozymes CA; approximately 30 wt% PEG with medium cross-link density using either non-functionalized Novozymes CA (Sample #1) or allyl-PEG-succinimide functionalized Novozymes CA (Sample #4).

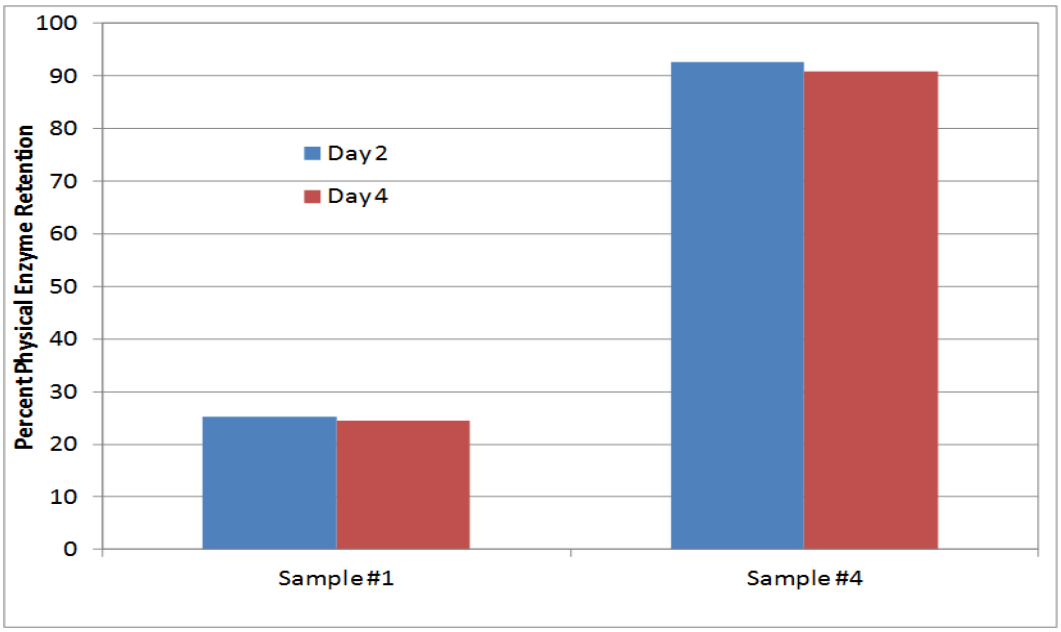

Figure 5: Physical enzyme retention in PHMS-g-PEG micellar polymer using functionalized (sample 4) and non-functionalized (sample 1) Novozymes carbonic anhydrase

Later in the program, Akermin began working with a complimentary immobilization strategy called sol-gel encapsulation. It represented an extension of our siloxane-based chemistry to form a hybrid organic/inorganic highly porous network around the enzyme. A distinct advantage of this approach is that the film has intrinsic porosity and what appears to be (based on scanning electron microscopy) a high specific surface area. Also, it was discovered that the enzyme did not need to be covalently tethered into the porous matrix to maintain good physical enzyme retention, unlike the PHMS-*g*-PEG micellar polymer approach.

Figure 6 shows the enzyme retention of a porous silica coating derived from sol-gel encapsulation of CA for one thousand hours (42 days) of continuous liquid flow. The results show that approximately 87% of the enzyme remained in the sample after 100 hours on-stream and >80% of the enzyme still remained after 400 hours. It is worth noting that the initial enzyme leaching follows a logarithmic trend appearing to slow after several days.

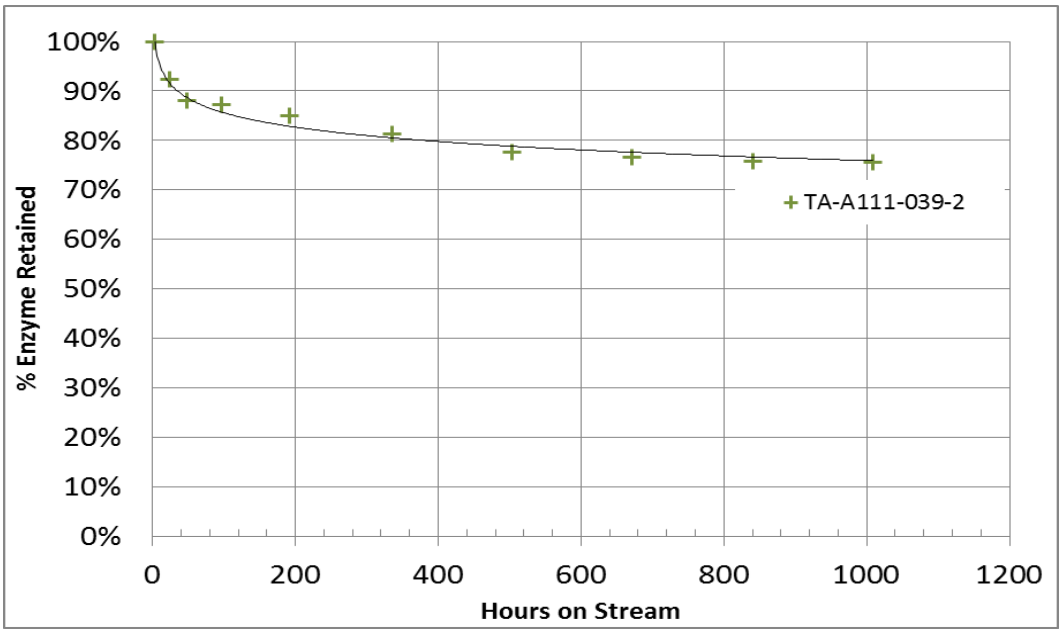

Figure 6: Enzyme retention of sol-gel immobilized CA in continuous liquid flow.

Subtask 3.2 – Develop and Optimize Polymer System (Sr. Scientist, Polymers)

Design and execute a systematic study of polymer system design parameters: overall hydrophilic content (30-60 wt%), grafting densities and molecular weight of the hydrophilic groups (0.5-5 kDa), grafting densities of functional moieties for enzyme tethering, enzyme loading (2-10 wt%), and cross-linking density. Vary the hydrophilic content (by increasing the grafting density and/or molecular weight of the hydrophilic groups) and determine the impact on the ionic transport of the polymer, as this may provide more or less hydrophilic channels. Investigate the impact of key process variables (e.g., grafting density, molecular weight, solution viscosity, deposit method, etc.) on the polymer's mass transport characteristics including the thickness and permeability of the polymer layer.

Akermin's critical focus was on the development and optimization of the immobilized enzyme polymer system for coating absorber column packing. Many variations of cross linking, film additives, enzyme loading, and film thickness were explored, but as previously noted, a key breakthrough occurred when allyl-functionalized enzymes were used as cross-linkers in the PHMS-g-PEG system. Enhancement factors in the range of 7 to 17X were achieved at peak performance with Novozymes CA, and peak enhancement factors as high as ~20X (>90% CO_2 capture in the standard SPR test) were observed, as shown below in Figure 7.

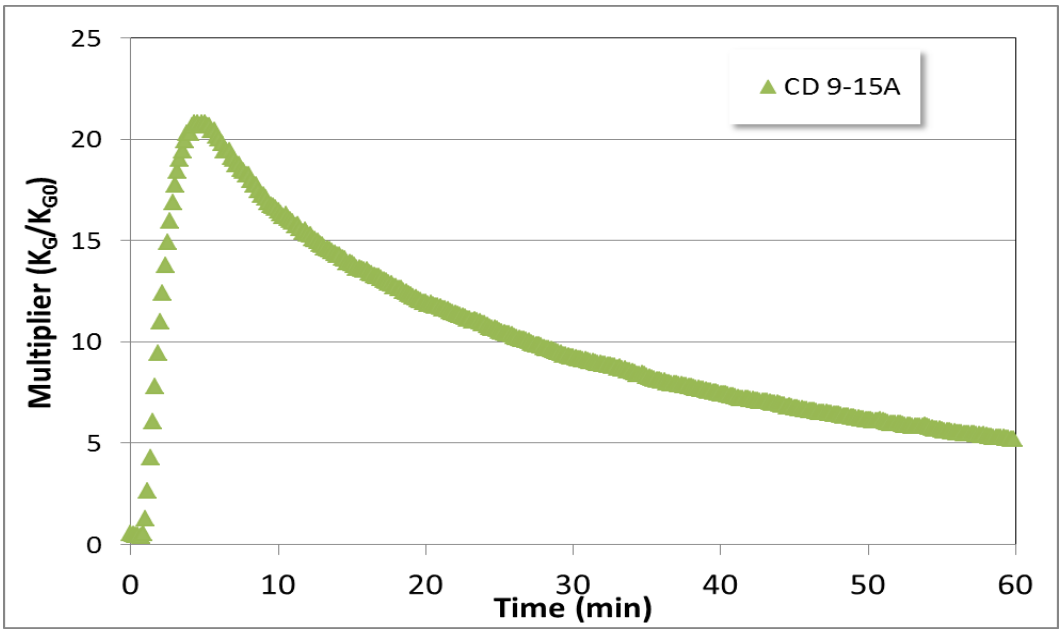

Figure 7: Multiplier demonstrated with micellar ~17 wt% allyl-functionalized CA in PHMS-g-PEG cross-linked at room temperature with 22 wt% polyquaternary ammonium salt as a function of time.

Certain trends in activity began to emerge in the detailed studies of the PHMS-*g*-PEG system. As seen with the data in Figure 7 above, the CO_2 conversion peaks rather quickly but then slowly decays over time. It was hypothesized, and various washing experiments indicate, that this decay is reversible and is likely caused by bicarbonate build up in the film. Akermin explored various methods to improve diffusion to eliminate this bicarbonate build-up in the PHMS-g-PEG matrix—including adding pore forming materials and/or charged additives into the polymer films as well as changing the cross-link density of the matrix. None of these modifications, however, completely eliminated the performance declination observed with this immobilization strategy.

In contrast, the encapsulation of Novozymes CA into porous silica coatings eliminated the enhancement decline that was observed with the PHMS-*g*-PEG system. The silica sol-gel immobilization technique yielded much more consistent performance over time. As shown in Figure 8 below, enzyme-containing silica coated on to 3.66 mm Tipton spheres tested in Akermin's single-pass reactor (SPR) demonstrated steady performance with more than 10-fold enhancement in overall mass transfer coefficient and steady CO_2 capture rates >80% for more than 24 hours. The blank CO_2 capture was approximately 14.9% (bare support, no enzyme). Equal mass of bare support was used in the blank and immobilized enzyme film cases.

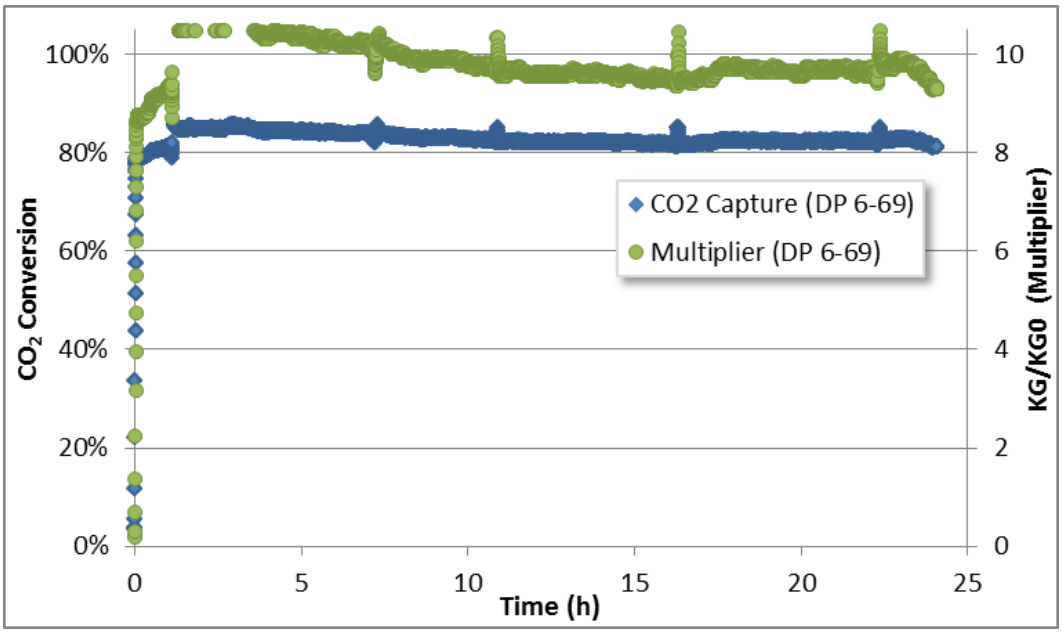

Figure 8: Performance of sol-gel immobilized enzyme in SPR.

After initial activity testing of a replicate sample (DP-7-29A) in the SPR, it was transferred and monitored continuously in the closed-loop reactor (CLR) at 30°C; results presented in Figure 9 below indicated a peak multiplier of >10X (initially), and average enhancement of approximately 9X over 100 hours on stream. The average mass transfer coefficient (per packing area) $K_{G\ (Pack)}$ = 0.162 mmol/(s m^2 packing kPa), blank under equivalent conditions gives $K_{G,P}$ = 0.0178. Test conditions were 15% CO_2 feed at 400 SCCM gas, 20 ml/min of 20 wt% K_2CO_3 at ~30°C and average CO_2 loading X_C = 0.26 moles CO_2/K_2CO_3 equiv. (carbonate converted to bicarbonate); and the average CO_2 capture was 80%, whereas the same number of blank (bare, uncoated) Tipton spheres had 13.2% CO_2 capture under these conditions. Multiplier calculation for random packing takes into account an increase in packing diameter with coating, which increases surface area for the same number of packing pieces.

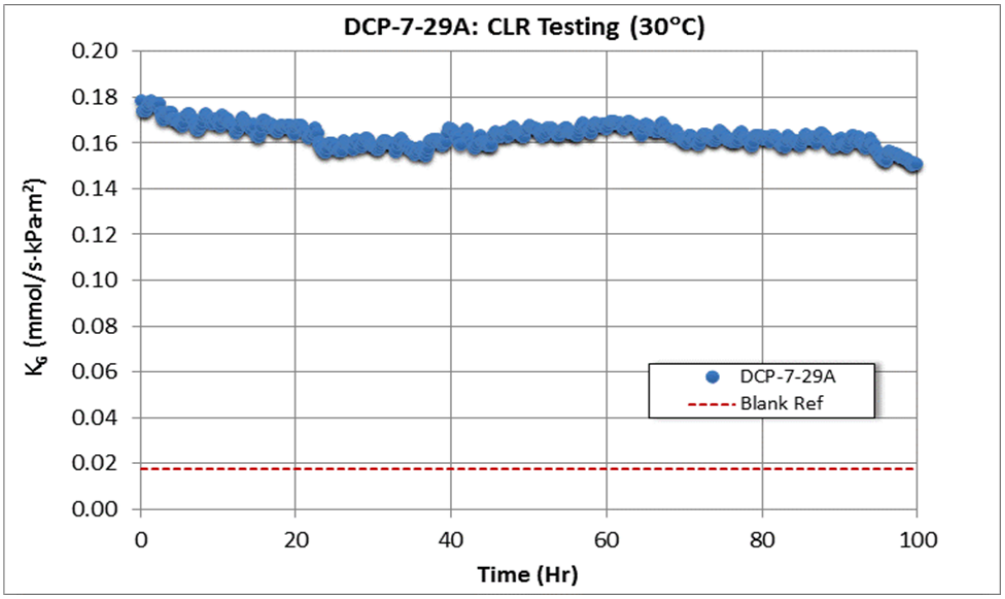

Figure 9: Performance of sol-gel immobilized enzyme vs. blank in a closed loop reactor (CLR).

Akermin selected the porous enzyme-containing silica coating (generated via sol-gel encapsulation of CA) for further development toward demonstration of immobilized enzyme enhanced performance in the bench unit based on results of this task. The sol-gel formulation was optimized to retain >87% enzyme over a period of 100 hours of continuous liquid flow, while also achieving the target 10-fold improvement of the overall mass-transfer coefficient, thus meeting key milestones A1 and A3, respectively. Optimization of the sol-gel system to further improve its performance, to verify repeatability of the synthesis method, and to adapt the techniques for scale-up to 275 L of structured packing for the bench unit is discussed in Subtasks 5.2 and 9.2.

Subtask 3.3 – Characterize Immobilized Enzyme System (Sr. Scientists, Polymers, Analytical)

Quantify immobilized enzyme retention, thermal stability of enzyme, overall porosity and pore size distribution, CO_2 diffusion/permeability through micellar polymer, percent activity retention compared to free enzyme, and enzyme dispersion. Akermin will employ advanced analytical techniques to assist in characterizing the micellar polymers developed and to evaluate interactions between the polymer and enzyme such as proton NMR, Fourier transform infrared spectroscopy (FTIR) and electron microscopy, and fluorescence microscopy. Down-select and define the preferred and alternate micellar polymer system for lab-scale testing in the batch and closed loop reactors and eventual scale-up to the bench-scale unit.

Akermin used a variety of techniques to characterize the immobilized enzyme system. Fourier transform infrared (FTIR) spectroscopy was used to confirm the presence of enzyme and PDMS in the silica coating. An overlay of three spectra is shown in Figure 10. The upper most spectrum in the figure represents lyophilized carbonic anhydrase. The middle spectrum represents silanol-terminated PDMS.

The bottom spectrum represents the silica coating, which contains diagnostic peaks indicating the presence of the enzyme as well as PDMS in the immobilization matrix.

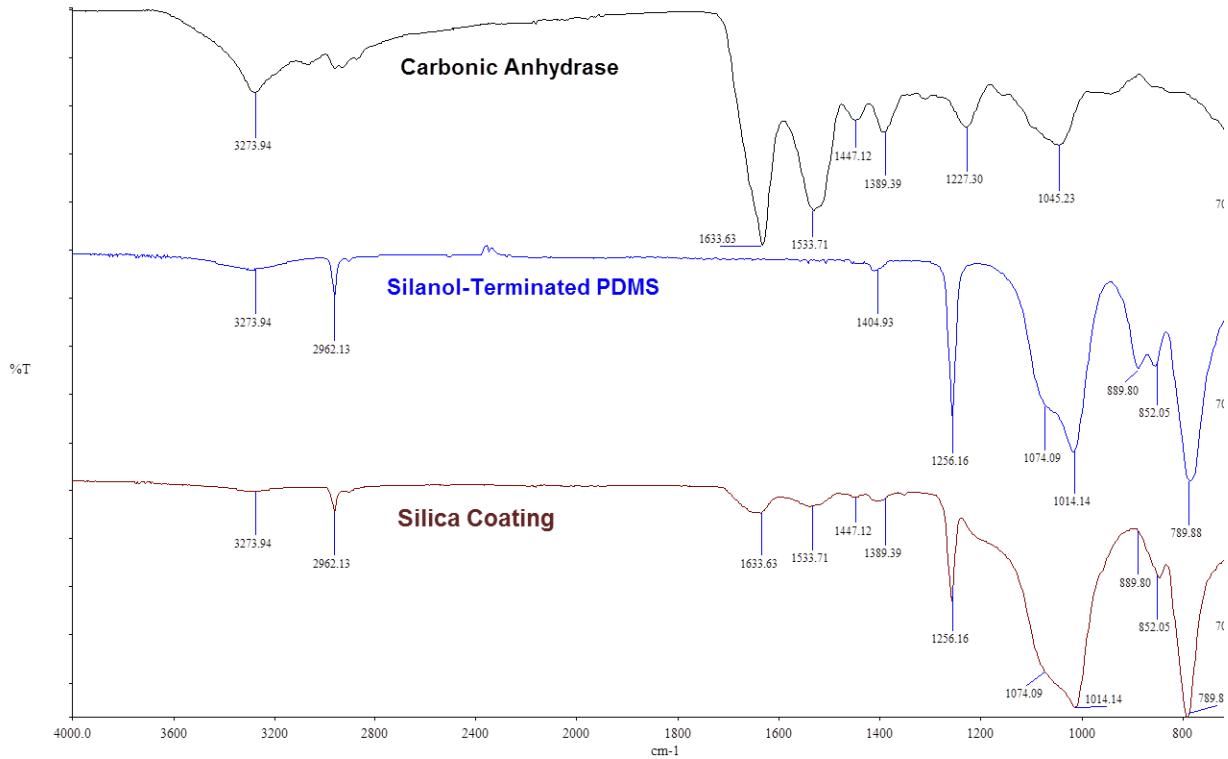

Figure 10: FTIR spectra of lyophilized carbonic anhydrase, silanol-terminated PDMS, and the silicate coating

Scanning electron microscopy (SEM) and gas sorption techniques were utilized to evaluate surface morphology, surface area and pore volume of coating materials. An example SEM is shown in Figure 11 at 1,000X magnification (A) and 25,000X magnification (B). It is clear in the images that the silica-based coatings have a high surface area made up of clusters of small silica particles. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis of the N_2 gas sorption isotherms were used to quantitate the surface area and pore size of the materials. Coating material was harvested from packing and the powder was submitted for gas-sorption analysis. Results from these tests indicated surface areas ranging around 15 m^2/g of material with pore volumes of approximately 0.118 mL/g.

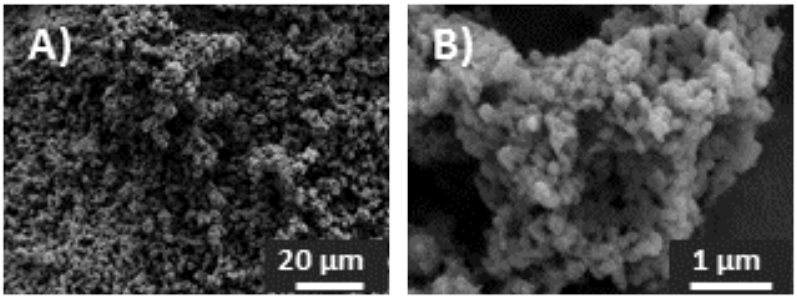

Figure 11: Representative SEM images of the enzyme-containing silica coatings

Immobilized enzyme activity was quantified in the SPR under standard test conditions, as described in Task 4. The SPR was utilized to perform short duration tests of a multitude of immobilized enzyme-coated packing samples—thus the SPR was a powerful rapid screening tool for quantifying mass transfer enhancement on coated packing, accelerating development.

Enzyme retention was quantified by UV absorbance at 280 nm. Solutions used for hydrating samples were evaluated to quantitate the mass of enzyme lost during the hydration process. The difference in quantity of enzyme leached from the initial concentration of enzyme loaded in the sample was used to calculate the percent enzyme retention. An example of this technique used to track enzyme retention with time is shown in Figure 6 of Subtask 3.1. Hydrations solutions were exchanged and analyzed by 280 nm absorbance to ensure that enzyme leaching had ceased prior to analysis in the SPR. Solutions from SPR tests were also evaluated to determine whether soluble enzyme was present in the test solution and contributing to the overall CO_2 capture.

As the silica-based immobilization system exhibited a high surface area, retained a majority of the enzyme, and performed at a steady state, with no signs of transport issues over time; it was selected as the preferred system for enzyme immobilization and was used for all subsequent laboratory development and bench-scale testing.

Subtask 3.4 – Lifetime Testing of Immobilized Enzyme

Perform lifetime activity studies with the preferred immobilized enzyme. Goal is to achieve lifetime activity milestones at intended operating condition (temperature, ionic strength, and pH) that are defined in the Project Management Plan. The intended conditions will be defined based on an agreed specification that is consistent with PNNL's initial model.

Akermin completed a 200 day endurance test of its immobilized enzyme with sample DCP-7-29A on September 7, 2012(Figure 12). As of the 200th day, the sample demonstrated approximately 45% CO_2 capture and retained about 46% of its initial overall mass transfer coefficient. Constant conditions were used for this test, but the test was interrupted from time-to-time due to unforeseen circumstances. Loss of coating over time was tracked by observing the packed column height with time. Losses of coating may have occurred due to handling the column containing the random packing (handling necessitated because of test interruptions), or may have experienced natural sloughing in the continuous liquid stream. Data

trends suggest an apparent correlation between retained coating thickness and retained biocatalyst performance, which suggests the specific activity of the coating was approximately constant.

The endurance test conditions: standard formulation coating on 65 g of 3.66 mm Tipton ceramic spheres, 20 ml/min liquid, 20 wt% K_2CO_3, pH 10, 45°C, 400 SCCM gas, 15% CO_2 in nitrogen, 1.07 bar total pressure. The initial packed volume was approximately 67 ml total with a gas void fraction of about 35% wetted basis (about 47.5% dry basis). Using 80% CO_2 capture as the starting position, the initial overall mass transfer coefficient relative to packing area, K_{GP} (start) = 0.167 mmol CO_2/second-kPa-m^2 packing, or approximately a 12-fold multiplier over the blank under these conditions.

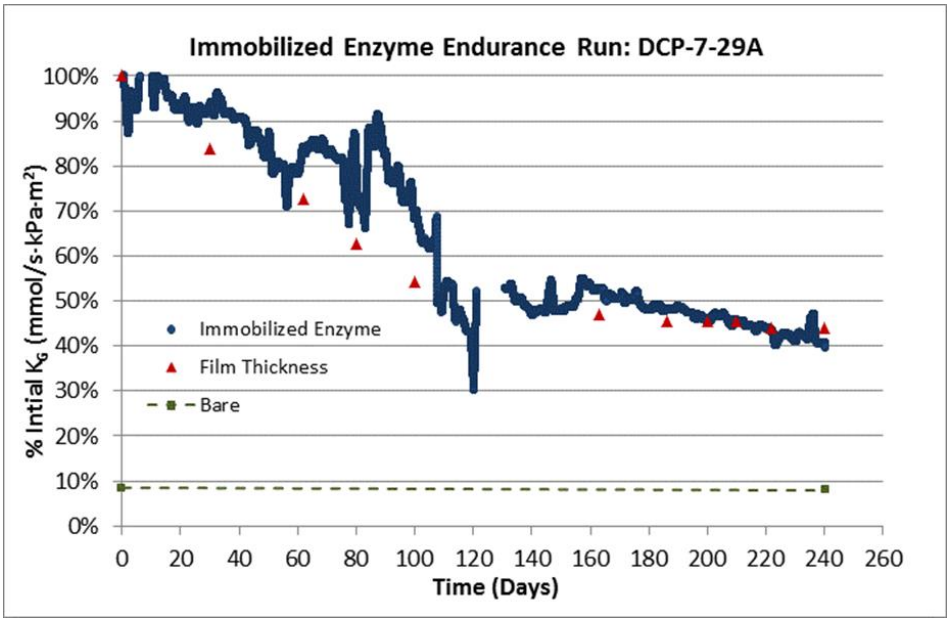

Figure 12: Akermin's lifetime study with immobilized enzyme through 240 days (October 18, 2012).

Task 4 – Semi-Batch Reactor Studies (Lead Organization: Akermin)

The objective of this task is to develop methods for quantifying the performance of immobilized enzyme systems relative to blank potassium carbonate and conventional solvents such as methyl diethanolamine (MDEA) and monoethanolamine (MEA). Semi-batch reactor studies were initially proposed based on its similarity to the pH-stat assay, but the form of gas-liquid contact was not ideal for gaining meaningful and repeatable area-specific mass transfer results for coated packing. The gas-sparged batch reactor did not provide a good representation of the gas-liquid contact conditions of the typical packed column absorber; therefore method development was needed to quantify immobilized biocatalyst coated packing performance in this project.

A packed column reactor setup was proposed going forward since it would be most similar to the coated packing system to be deployed in a bench unit within this project. Several key methods were developed

in this task to extract representative mass transfer coefficient measurements in laboratory packed column reactors as a function of CO_2 loading.

The following describes the test reactors, the standard test conditions, and presents the background theory used to analyze the laboratory data to determine mass transfer coefficients and bio-catalytic enhancement relative to blank controls, and methods used to accurately quantify CO_2 loading with continuous pH monitoring.

Single Pass Reactor System and Standard Test Conditions

Akermin designed a small (approximately 50 to 75 ml) packed column referred to as the single pass reactor (SPR) system. A process flow diagram of the system can be found in Figure 13. It is suitable for rapid screening of biocatalyst coating formulations deposited as coating on model spherical random packing. The Akermin SPR method provides for quantification of area-specific mass transfer coefficients using a first-order plug flow reaction engineering model. This is quite useful in that the mass transfer coefficients determined in the laboratory data are directly translatable to the design of larger-scale packed column systems based on solid understanding of the area efficiencies.

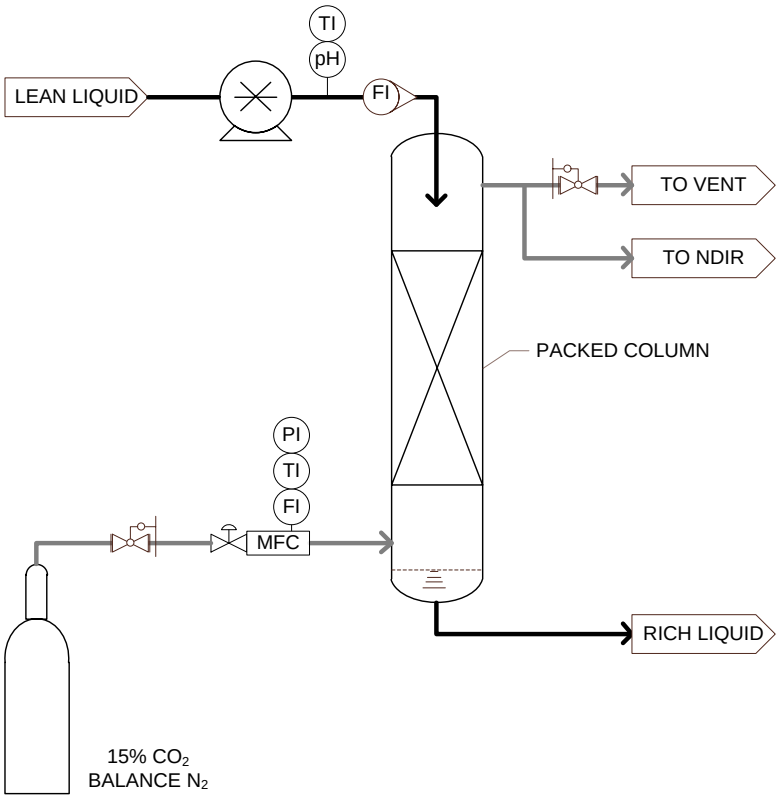

Figure 13: Process Flow Diagram for Akermin Single Pass Reactor

The SPR standard test conditions include feeding 200 SCCM of a gas mixture (15% CO_2 in nitrogen) at the bottom of a 1.59-cm ID packed column with approximately 7 kPa(g) back pressure; the local ambient pressure in Saint Louis is ~1 bara. The SPR column is filled with model spherical packing (Tipton corp., 3.66 mm ± 0.15 silica spheres). The standard fill equated to 65-g of bare spheres (about 1109 pieces), and the typical packing fraction was approximately 39.5% (solid fraction). Meanwhile, 25 ml/min liquid flow is delivered to the top of the column at about 25°C. When higher temperatures were required for specific tests, a water jacket was added to hold the column at the desired temperature and the liquid feed was preheated before delivery to the column. The high liquid-to-gas (L/G) ratio is important for data analysis, so that the CO_2 loading in the liquid, and thus the equilibrium partial pressure, is essentially constant in the column. The liquid hold up under the specified gas and liquid flow conditions was approximately 13.4%. The packing fraction (solid fraction) was approximately the same for coated and bare packing. Tests were conducted with the same number of packing spheres (e.g., ~1109 pieces, or 65-g bare), which simplifies analysis of the mass transfer coefficient multiplier.

When using the same number of model packing spheres, and because the void fraction is the same, the increase in column height is related to the increased diameter of the packing. Therefore, the coating thickness (and the coated particle diameter) can be estimated as follows (Equation 1 below):

$$t_{coating} = \frac{d_{bare}}{2}\left[\left(\frac{H_{coated}}{H_{bare}}\right)^{1/3} - 1\right] \tag{1}$$

Closed Loop Reactor System, Standard Test Conditions

Akermin also adapted an existing closed loop reactor (CLR) system found in Figure 14 to support testing of 22 mm units of structured packing in a 5.40 cm ID column (about 500 cm^3 per section). Structured packing was Mellapack M500X that was found to have 360 m^2/m^3 surface area due to discrete orthogonal cuts in the packing sheets relative to the small diameter encircling the packing. The CLR was typically operated with 2.18 SCCM gas flow at 7 kPa(g) back pressure, 1 bara local ambient pressure, and 218 ml/min liquid flow at 45°C (unless otherwise specified). Typically only one section of Sulzer packing was used to screen catalyst performance, but equivalent performance was found with two layers of packing tested with the same liquid flow and equivalent gas space time, which is characteristic of an apparent first-order process. The packing was found to have a dry void fraction of 98% (2% solid volume in bare, uncoated condition) and liquid hold up under the standard test conditions was approximately 9 to 10%; the loss of void fraction due to biocatalyst coating was typically in the range of 10 to 20%, depending on thickness.

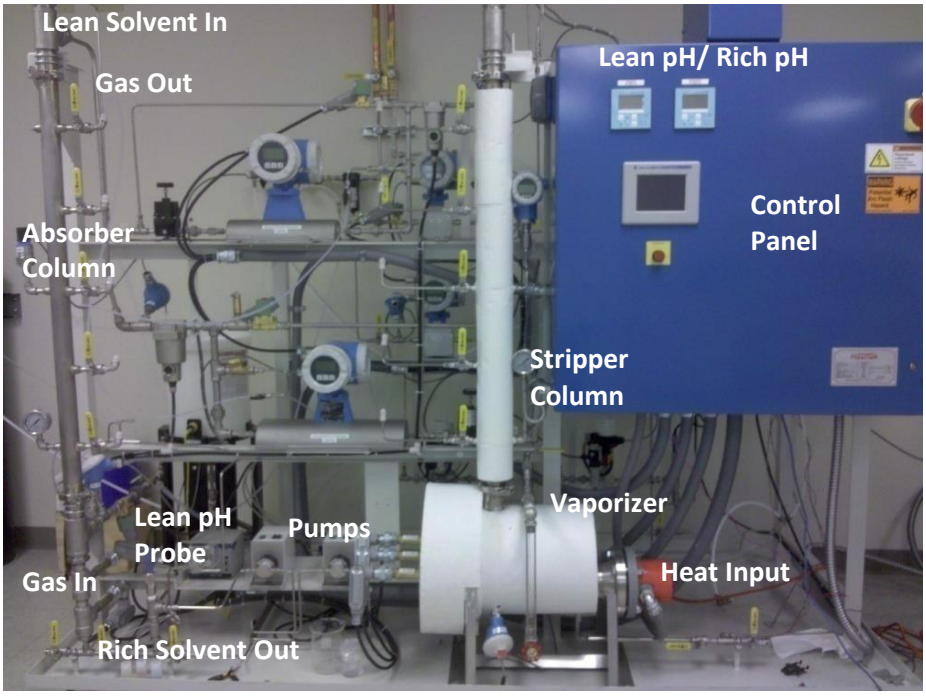

Figure 14: Akermin's Lab-Scale Closed Loop Reactor System

CO_2 loading from pH data

The absorption of CO_2 into aqueous solutions has several steps beginning with rapid physical absorption (defined by Henry's law) followed by slower chemical hydration reaction (which may occur in many steps by various mechanisms, for example with or without catalyst). Butler, in his work "Carbon Dioxide Equilibria" describes hydrated CO_2 as a polyprotic acid having two important equilibria: the first being the deprotonation of carbonic acid (pK_{a1}^{0} = 6.35 at 25°C and zero ionic strength), the second being the deprotonation of bicarbonate (pK_{a2}^{0} = 10.33 at 25°C and zero ionic strength). [6] Clearly, at relevant pH conditions, the second acidity dominates. Therefore, CO_2 loading in bicarbonate solutions can be calculated from on-line pH measurements using the Henderson-Hasselbalch equation using known equilibrium data for the second acidity (pK_{a2}) of hydrated CO_2. [6] The *pKa* for the second acidity equilibrium (pK_{a2}) is calculated for the relevant temperature (T) and base concentration (m, molality) which is determined from reference data (e.g., $pK°_{a2}$ = 10.33 at 25°C and zero ionic strength) corrected based on relevant activity coefficient data. [7], [8], [9] Equation (2) below includes the generalized stoichiometric parameter n to represent the number of bicarbonate ions formed per mole of base converted, which for the carbonate base ($CO_3^{=}$), n = 2.

$$X_C = \frac{10^{(pK_{a2}-pH)}}{n + 10^{(pK_{a2}-pH)}} \tag{2}$$

X_C is the CO_2 loading reported as the state of base conversion to bicarbonate. In the above analysis, the concentration of carbonic acid is negligible due to the relevant pH range for this application; therefore, first acidity is neglected. Akermin used the theory above to determine pK_{a2} from prepared solutions of K_2CO_3 and $KHCO_3$ (each >99.5% pure from Sigma Aldridge) for a range of equivalent molality K_2CO_3 at 50% converted to bicarbonate. Figure 15 and Figure 16 provide the necessary data to calculate CO_2 loading from pH measurements with known equivalent K_2CO_3 concentration and temperature of pH measurement. Results are comparable with literature reported data. [7] [8]

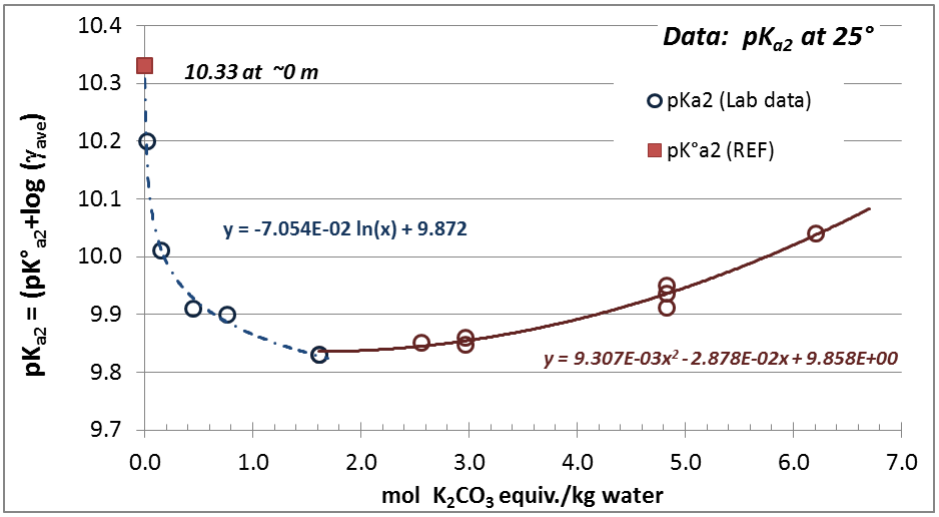

Figure 15: Equilibrium data for second acidity (pK_{a2}) of hydrated CO_2 in aqueous K_2CO_3 at 25°C

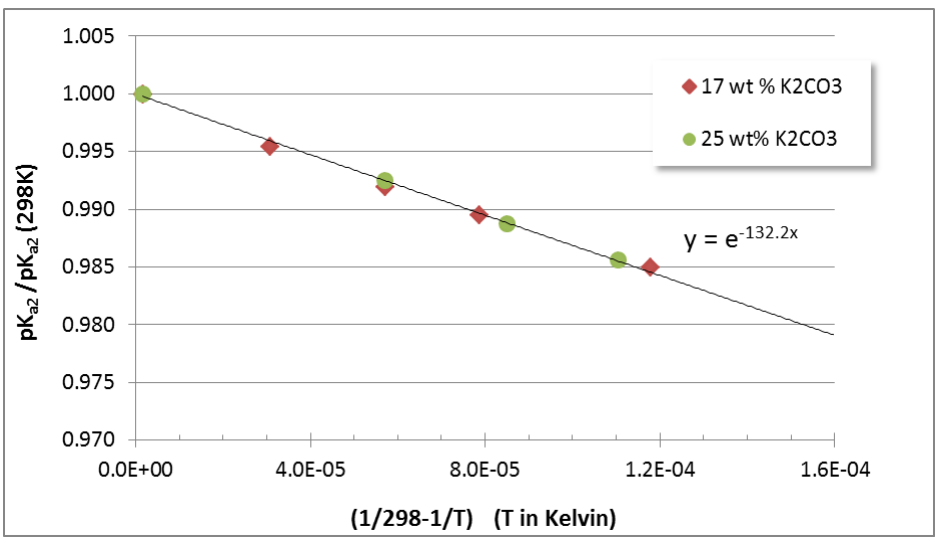

Figure 16: Shift in equilibrium second acidity of hydrated CO_2 in aqueous K_2CO_3 as a function of temperature (pK_{a2} relative to pK_{a2} at 25°C)

Quantification of Mass Transfer Coefficients from CO_2 Capture Data

The overall mass transfer coefficient can be deduced from a simple application of a plug-flow reactor design equation using a reversible first-order rate law, observed in Equation 3.

$$F_{A0}\frac{dX_A}{dV} = -k_1(C_A - C_A^*) \tag{3}$$

In the above expression, F_{A0} is the molar flow rate of the limiting reagent (in this case CO_2 assuming excess lean liquid feed relative to gas feed rate considering equilibrium limits), X_A is the conversion of *"A"* (i.e., the CO_2 capture), V is the total packed volume, k_1 is the volumetric average mass transfer coefficient, C_A is the concentration of A in the gas phase, and C_A^* is the concentration of *"A"* that would be realized at the equilibrium limit for the given liquid state conditions ($C_A^* = P_{CO_2}^*/RT$, and depends on solution CO_2 loading, capture solvent concentration, and temperature).

The solute *"A"* is assumed to be dilute to simplify analysis. A review of this method using non-dilute gas assumptions shows that the error in enhancement factors is <9% when CO_2 capture <90% and feed is 15% CO_2 or less. The equilibrium partial pressure is approximately constant over the column per experiment design with high liquid-to-gas (L/G) ratios. With the above assumptions, the mass transfer coefficient can be calculated from an integrated form of the first-order plug flow reactor design equation, see Equation (4) below. Experiments are designed so that the lean-to-rich CO_2 spread is small, reactors operate near isothermal, and so the equilibrium partial pressure is constant.[1]

$$k_1 = \ln\left[\frac{X_{CO_2}^* - X_{CO_2}}{X_{CO_2}^*}\right]/\tau \tag{4}$$

The CO_2 capture (X_{CO_2}) is defined as the flow of CO_2 absorbed divided by flow of CO_2 fed. It is readily calculated from a mole balance using dry basis mole fraction data, as observed in Equation 5.

$$X_A = \frac{y_{A0} - y_A}{y_{A0}(1 - y_A)} \tag{5}$$

[1] The same approach described here is applicable to the design and analysis of a packed column with a larger lean-to-rich swing in CO_2 loading from top-to-bottom by summing volume (or space time) determined from discrete sections of approximately constant equilibrium partial pressure.

The feed gas (y_{A0}) and treated gas (y_A) are typically measured in the laboratory using a calibrated non-disperse infrared analyzer (Quantek Model 906). Measurements in the field bench unit were taken with highly accurate Emerson XStream.

Similarly, $X^*_{CO_2}$ is the equilibrium CO_2 capture limit calculated from Equation (5) above when letting the exit (dry basis) mole fraction, y_A, equal the equilibrium partial pressure divided by the system absolute pressure (dry basis). Finally, τ is the gas space-time, which is simply the total packed volume divided by actual volumetric flow rate: $\tau = V_{total}/v_0$.

Under certain lean loading conditions, where the equilibrium CO_2 capture approaches unity (e.g., >0.95), then the volumetric mass transfer coefficient can be approximated by the irreversible equivalent form in Equation 6.

$$k_1 \cong \ln\left[1 - X_{CO_2}\right]/\tau \tag{6}$$

The above approximation can be quite useful when taking the ratio of $\ln\left[1 - X_{CO_2}\right]$ for quick comparison of test data collected under equivalent lean conditions and the same space time to estimate relative enhancement.

Mass Transfer Coefficient (K_G) Relative to Packing Area:

The volumetric mass transfer coefficient (k_1), which is based on the measured CO_2 capture and gas space time, is related to the overall area-specific mass transfer coefficient per packing area ($K_{G,P}$) with knowledge of the installed packing area (A_p) and the volume fraction of gas in the reactor (i.e., the gas void fraction (ϕ_{void})). This relationship is observed in Equation 7.

$$K_{G,P} = \frac{k_1}{\phi RTa_p} = \frac{\ln\left[\frac{X^*_{CO_2} - X_{CO_2}}{X^*_{CO_2}}\right]}{\frac{V}{v_0}\phi_{void}RTa'_p} = \ln\left[\frac{X^*_{CO_2} - X_{CO_2}}{X^*_{CO_2}}\right]\frac{v_0}{\phi_{void}RTA_p} \tag{7}$$

The volume fraction of gas in the reactor is calculated from the solid fraction and liquid hold up ($\phi_{void} = 1 - \phi_{solid} - \phi_{liquid}$). R is the ideal gas constant, T is the average temperature in the reactor, and a'_p is the packing specific area (m^2 packing surface area per m^3 packed volume). A_p is the total packing area ($A_P = Va'_p$). v_0 is the actual volume flow rate of gas. For structured packing, the packing specific area is assumed to be the same after coating with biocatalyst—essentially the same parallel sheets of metal are coated. For coated spherical packing, the area increases with the square of coated sphere diameter.

Similarly, V is the volume of packing (typical uses internal diameter of column) and v_0 is the actual volumetric gas flow at the inlet of the column. Strictly, for a non-dilute gas application, a small correction would be added to account for volume contraction with absorption, but for the test conditions relevant to this project it is a very minor correction.

Quantification of Gas-Liquid Interfacial Area Efficiency:

The area efficiency of a given test reactor (or test condition) can be determined by comparing the mass transfer coefficient determined per packing area (K_{GP}) to the interfacial mass transfer coefficient measured in the wetted wall column (K_{GI}) for the reference solvent tested under equivalent conditions, see Equation 8. Wetted wall data by PNNL is available for 17% K_2CO_3 at 30°C, 12% MDEA at 35°C, and 30% MEA at 40°C, see summary results in Table 3 below.

$$K_{G,I} = K_{G,P}/\eta_e \tag{8}$$

The area efficiency η_e in the various reaction systems was determined as described by conducting a test in the laboratory packed column reactor using un-catalyzed (blank) solvents at the same temperature, concentration, and CO_2 loading conditions. The standard test conditions in the SPR (using 1109 pieces of 3.66 mm diameter Tipton spheres, or a total area of approximately 0.047 m^2) yields an interfacial area efficiency of about 29 to 31% for K_2CO_3 and MDEA; data supporting this calculation can be observed in Table 3. Area efficiency analysis for the CLR system with Sulzer M500X structured packing is presented in Subtask 5.1, Table 6.

Table 3: Mass transfer data in SPR compared with regressed PNNL wetted wall column data.

Description	CO_2 Loading (n/n K^+)	CO_2 Capture (%)	Equilib. Capture (%)	Space Time (%)	Wet Void Fraction (%)	$K_{G,P}$ (mmole/ kPa m^2 s)	$K_{G,I}$ (mmole/ kPa m^2 s)	η_e (area eff.)
17% K_2CO_3, 30°C	0.109 0.199 0.272	13.7% 11.6% 9.9%	98.8% 94.6% 86.3%	8.2	33.8%	0.024 0.020 0.020	0.081 0.073 0.066	29.0% 27.4% 30.9%
12% MDEA, 35°C	0.114 0.201 0.310	26.7% 20.6% 16.0%	96.9% 90.9% 80.3%	8.3	33.8%	0.051 0.041 0.036	0.147 0.139 0.129	35.0% 29.8% 27.7%
30% MEA, 40°C	0.37 0.40	85.8% 80.8%	98.3% 97.8%	8.2	33.8%	0.332 0.281	0.888 0.728	37.4% 38.6%

Mass Transfer Multiplier

It is convenient to test under the equivalent space time and equivalent liquid flow rates so the area efficiency can be assumed equal in the structured packing system. The gross surface area of coated structured packing is essentially the same as the base steel area. However, the ratio of K_G measured in the structured packed column under equivalent test conditions depends on void fraction as observed in Equation 9. The void fraction is impacted by the amount of coating deposited, which is not known with a high degree of certainty.

$$\frac{K_{G\ (catalyzed)}}{K_{G\ (blank)}} = \frac{\ln\left[\frac{X^*_{CO_2} - X_{CO_2}}{X^*_{CO_2}}\right]_{catalyzed}}{\ln\left[\frac{X^*_{CO_2} - X_{CO_2}}{X^*_{CO_2}}\right]_{blank}} \frac{\phi_{blank}}{\phi_{catalyzed}} \tag{9}$$

As a practical matter, however, the loss of void fraction due to coating is not beneficial to the volumetric performance of the structured packing. Therefore, the more relevant multiplier (M) for structured packing, where volume efficiency is the relevant metric impacting volume of the column, is most appropriately determined from the ratio of volumetric mass transfer coefficients under equivalent test conditions, as observed in Equation 10.

Multiplier for structured packing data:

$$M = \frac{k_{1\ (catalyzed)}}{k_{1\ (blank)}} = \frac{\ln\left[\frac{X^*_{CO_2} - X_{CO_2}}{X^*_{CO_2}}\right]_{cat}}{\ln\left[\frac{X^*_{CO_2} - X_{CO_2}}{X^*_{CO_2}}\right]_{blank}} \tag{10}$$

In the above expression, X_{CO_2} is experimentally determined, while $X^*_{CO_2}$ is known from equilibrium partial pressure data. However, under the standard test conditions where CO_2 loading is low and equilibrium capture limit approaches unity, Equation 10 can be simplified to Equation 11.

Simplified multiplier for structured packing under lean conditions:

$$M = \frac{k_{1\ (catalyzed)}}{k_{1\ (blank)}} \cong \frac{\ln\left[1 - X_{CO_2}\right]_{cat}}{\ln\left[1 - X_{CO_2}\right]_{blank}} \tag{11}$$

In contrast to structured packing, the void fraction of the random packing with and without coating remains approximately the same. Also, the standard tests employ the same number of model packing spheres, which is an important consideration for the following analysis. Taking into account the increase in the height of the column due to coating (see Equation 1), the enhancement in overall mass transfer coefficient can be expressed as Equation 12 below.

SPR Multiplier for random spherical packing, same number of pieces, lean conditions:

$$Multiplier, M = \frac{ln\left(1 - X_{CO_2}\right)_{coated}}{ln\left(1 - X_{CO_2}\right)_{bare}} \left(\frac{d_{bare}}{d_{coated}}\right)^2 \tag{12}$$

Subtask 4.1 –Establish Baseline Rates for MEA Solvents

Operate lab-scale, semi-batch reactor with MEA concentrations from 15 to 30 wt% to establish an absorption rate baseline for comparison with specific carbonate systems of interest.

A key objective of this task was to quantify the mass transfer enhancement needed in K_2CO_3 to be comparable with the reference 30% MEA solution, as specified in the NETL reference case studies.

To provide a practical comparison between rates in two different solvents, it is important to consider the preferred CO_2 loading ranges for each solvent for the given gas treating application. The typical lean loading determined for K_2CO_3 in a coal flue gas application is approximately 0.15 mol/mol K^+ and the equilibrium rich loading is nearly 0.35 mol/mol K^+ (these loadings are equivalent to 30% and 70% converted to bicarbonate, respectively). Likewise, the optimal lean CO_2 loading for MEA is approximately 0.22 and the typical rich loading is approximately 0.45 mol CO_2/mol MEA [10].

Table 4 below summarizes the regressed mass transfer coefficient data at the respective lean, rich and median CO_2 loadings. See Subtask 4.3, Figure 18, for a plot of mass transfer coefficient data. Results indicate that MEA (30% at 40°C) in its preferred lean loading condition is about 30-fold faster than 20% K_2CO_3 at 30°C in its preferred lean loading condition for a flue gas application. However, MEA is just 16-times faster at the median CO_2 loading compared to that in the median CO_2 loading of K_2CO_3. Notably, 1 gram soluble Novozymes CA per liter solution gives a median mass transfer enhancement that is 12-times faster than blank K_2CO_3 at 30°C—or about 75% of MEA at its median preferred loading.

Table 4: Regressed mass transfer coefficient results at optimal lean*, median, and max rich loading†

Test Solution	CO_2 Loading (mol/mol)	K_{Gl} (mmol/s m^2 kPa)	K_{Gl} relative to K_2CO_3 at lean, median, or rich
20% K_2CO_3, optimal lean	0.15	0.075	(lean reference)
20% K_2CO_3, median	**0.25**	**0.066**	**(median reference)**
20% K_2CO_3, typical rich	0.35	0.058	(rich reference)
1 g CA/L soln, 20% K_2CO_3, optimal lean	0.15	0.95	12.6 (lean/lean)
1 g CA/L soln, 20% K_2CO_3, median	**0.25**	**0.79**	**12.0 (median/median)**
1 g CA/L soln, 20% K_2CO_3, typical rich	0.35	0.67	11.5 (rich/rich)
30% MEA optimal lean	0.22	2.33	31.0 (lean/lean)
30% MEA, median	**0.34**	**1.10**	**16.6 (median/median)**
30% MEA, typical rich	0.45	0.52	8.9 (rich/rich)

*Optimal lean loading for flue gas application based on modeling or literature review.

†Typical rich loading based on practical considerations including equilibrium limitations in flue gas application.

Subtask 4.2 –Establish Baseline Rates for Carbonate Solvents

Operate lab-scale, semi-batch reactor in specified carbonate solutions to determine initial rates of CO_2 capture under various pH conditions (9 to 10.5), ionic strengths (1 to 4 mol K^+/L), and temperatures (25-50°C). Determine the initial rates at different solvent compositions, temperatures, and ionic strengths for the non-catalyzed carbonate system.

Data presentation in this section focuses on 20% K_2CO_3 (w/w equivalent as pure). The effect of varying K_2CO_3 concentration on blank mass transfer coefficient was small and differences were difficult to quantify. The highest practical concentration is desirable to minimize energy and reduce cost of capture. In this case, 20% K_2CO_3 was specified for the bench-unit deployment considering the bicarbonate precipitation limit at elevated CO_2 loading is a key concentration limiting consideration (T_{ppt} ~25°C at 0.40 mol CO_2/mol K^+, or 80% converted) if bicarbonate precipitation is to be avoided.

Experiments were performed in the SPR with 65-g bare Tipton spheres (3.66 mm diameter). Liquid was fed at 25 ml/min comprising 20% K_2CO_3 that had a starting lean pH of about 10.0 at 23°C, which equates to about 30% X_C (conversion to bicarbonate), or 0.15 mol CO_2/mol K^+. A 15% CO_2 mixture in nitrogen gas was fed at a rate of 100 sccm. The liquid was allowed to recirculate without regeneration, and the pH

was allowed to drift close to the equilibrium rich CO_2 loading (0.35 mol/mol K+). Resulting mass transfer coefficient data is presented in Figure 17 below.

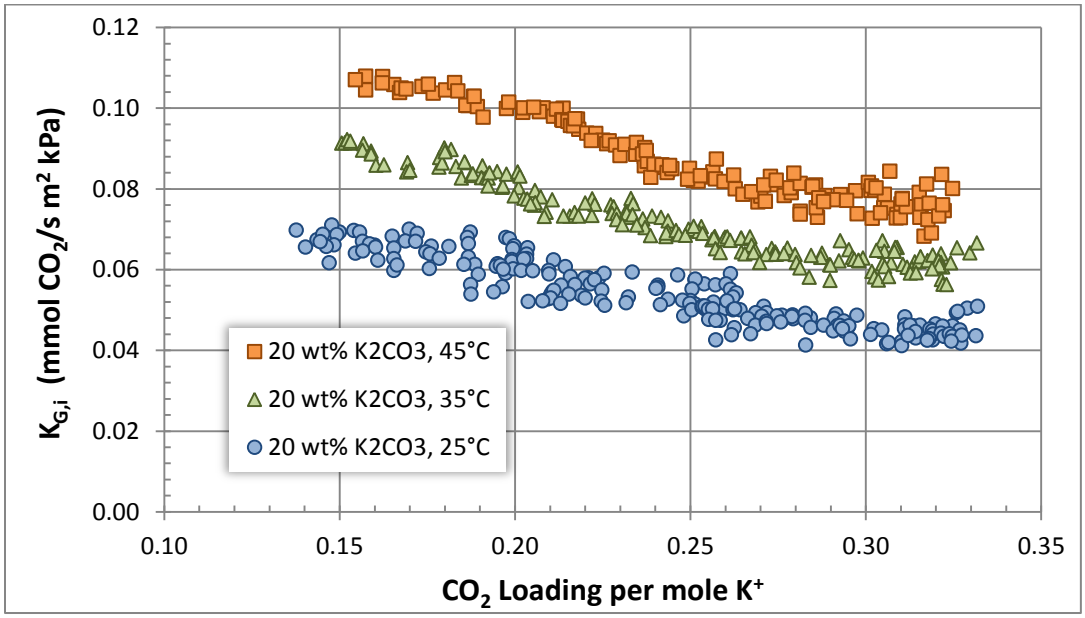

Figure 17: Dependence of mass transfer coefficient on temperature and CO_2 loading for (blank) un-catalyzed 20 wt% K_2CO_3 solutions under standard SPR test conditions.

Figure 17 shows that the overall mass transfer coefficient increases by approximately 65% with 20°C temperature rise. Also, mass transfer coefficients decrease with increased CO_2 loading, as expected.

Subtask 4.3 –Establish Free Enzyme Catalyzed Rates for Carbonate Solvents

Conduct lab-scale, semi-batch reactor experiments similar to Subtask 4.2 with free enzyme. Determine the initial rates at different solvent compositions, temperatures, and ionic strengths (similar to Subtask 4.2) for the enzyme-catalyzed carbonate system.

Soluble enzyme was blended with prepared K_2CO_3 solutions and tested in the SPR using random packing (1109 pieces of 3.66 mm diameter Tipton spheres), or tested in the CLR using 0.5 liters of structured packing (2-inch Sulzer M500X, 360 m^2/m^3 at this diameter). Data for enzyme-catalyzed absorption was plotted along with data for the respective un-catalyzed solvents for the same temperature conditions in Figure 18 below, along with MEA and MDEA reference data.

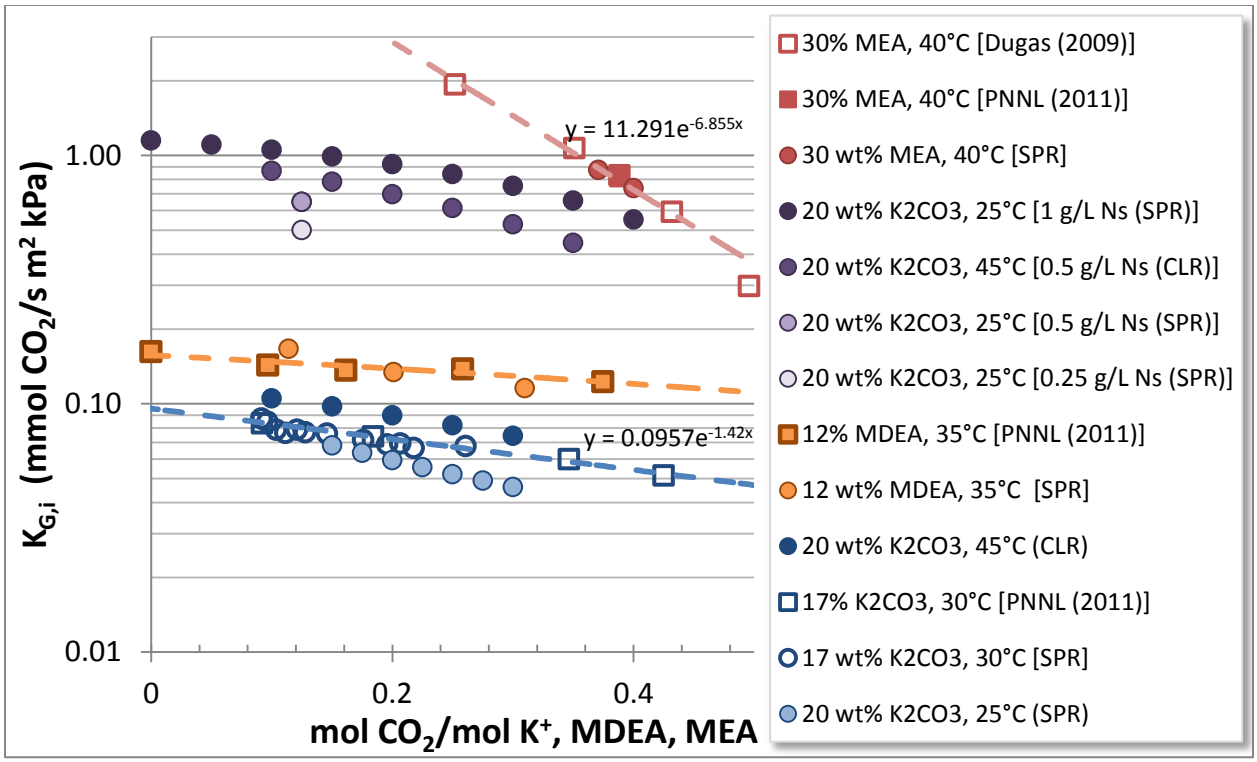

Figure 18: Dependence of catalyzed mass transfer coefficient (K_{GI}) on solvent loading for potassium carbonate and MEA. MEA data from wetted wall column data by PNNL and literature [11]

Mass transfer coefficients per packing area were calculated from Equation 7 and corrected to effective area (gas-liquid interfacial area) using Equation 8. Mass transfer measurements with soluble enzyme demonstrated a square root dependence on enzyme concentration for fixed CO_2 loading, which is consistent with Danckwertz surface renewal theory for mass transfer with homogenous reaction. [12]

The decrease in mass transfer coefficients with increasing CO_2 loading was as expected. Temperature was found to have a much smaller influence on enzyme-catalyzed mass transfer, and the temperature boost appeared to be less significant with increasing enzyme concentration (30% increase in mass transfer coefficient for a 20°C rise for 0.5 g/L Novozymes CA; 10% increase with 20°C rise for 1 g/L). This result is in contrast to the un-catalyzed K_2CO_3 system that exhibits as much as 65% increase of mass transfer coefficients over the same temperature rise. This diminished influence of temperature on catalyzed mass transfer is consistent with the lower activation energies of the enzyme-catalyzed processes.

An examination of Figure 18 revealed that Akermin's data generated with SPR and PNNL's wetted wall column data for MEA compare well with the corresponding published wetted wall column data for MEA. [11] The trends of Akermin's mass transfer coefficients in 17% K_2CO_3 at 30°C and 12% MDEA at 35°C are also consistent with PNNL's wetted wall data.

The influence of K_2CO_3 concentration (17% compared to 20% w/w) on mass transfer coefficient was relatively minor for blank K_2CO_3. Temperature dependence of biocatalyst-accelerated CO_2 capture in K_2CO_3 diminishes with increased concentration of the enzyme in solution.

Subtask 4.4 –Test Immobilized Enzyme Systems

Operate lab-scale, semi-batch reactor in specified carbonate solutions with various immobilized enzyme catalyst systems developed in Subtask 3.3. This is a key test that is used to determine the preferred immobilized enzyme system before the next phase reactor testing. Determine initial rates of CO_2 capture under specific conditions of solvent composition, temperature, and ionic strength. This effort is used as a tool to explore the immobilized enzyme performance relative to free enzyme-catalyzed and non-catalyzed baseline systems. Develop a preliminary estimate of the enzyme loading requirement for the closed loop reactor system consistent with program goals.

Mass transfer data for solvents over biocatalyst coated packing (CSP) are presented in Figure 19. Immobilized enzyme data is presented in a similar form as Figure 18 and includes the MEA and blank K_2CO_3 reference cases.

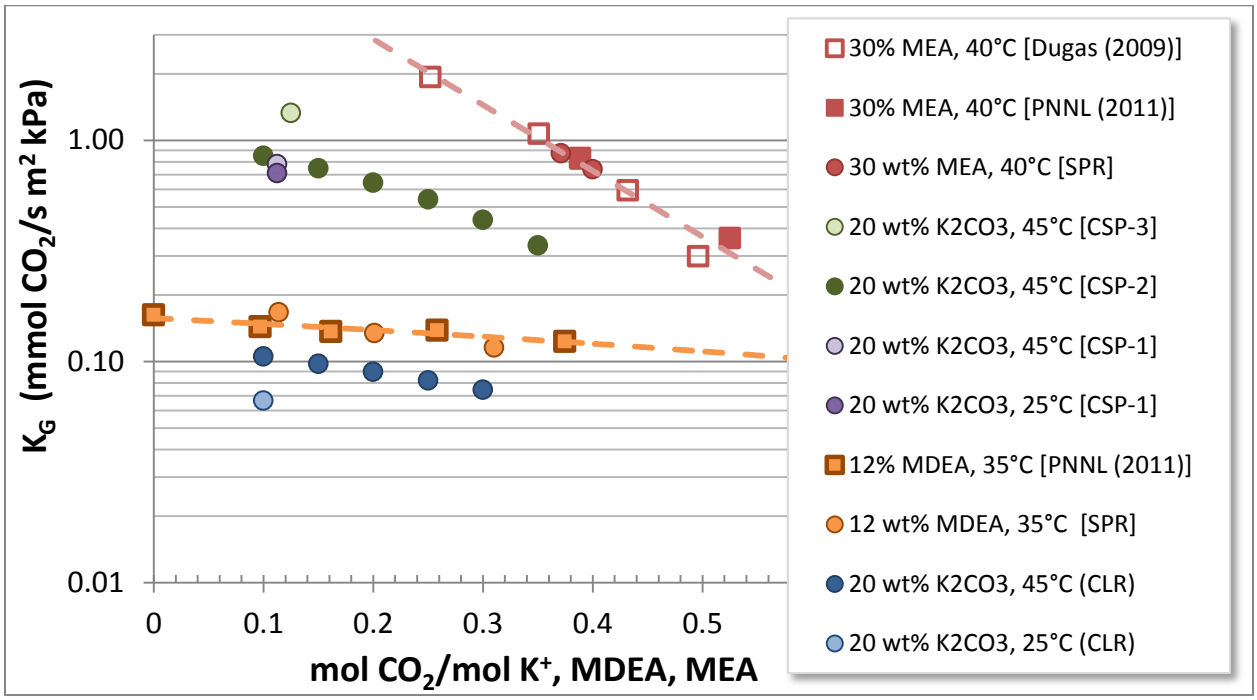

Figure 19: Biocatalyst coated packing performance data compared with blank potassium carbonate and MEA data from wetted wall column data by PNNL and literature [11]

Biocatalyst coated structured packing samples CSP-1 (BMR-3-92) and CSP-2 (LW-145-21B) in

Figure 19 use a similar formulation to what was deployed in the NETL-Akermin bench unit, and as expected both present similar performance. It should be emphasized that performance can be improved further by optimizing the formulation. For example, a more recent sample, CSP-3 (LW-145-60C), had an interfacial mass transfer coefficient of 1.3 mmol/s m^2 kPa at lean conditions, i.e. about 70% better than CSP-1 and CSP-2.

Table 5 provides more specific data for coated structured packing (CSP) samples presented in Figure 19. Similar to the effect on soluble enzyme, temperature has a minimal impact on the mass transfer coefficient for the immobilized enzyme system, showing only about 10% boost in mass transfer coefficient between 25°C and 45°C. This is in contrast with 65% increase in mass transfer coefficient for blank Sulzer packing in CLR.

Table 5: Supporting data for mass transfer enhancement on coated structured packing with varied test temperature.

Coated Packing Ref.	Ave. Temp. (°C)	CO_2 Loading (mol/ mol K^+)	CO_2 Capture (%)	Equil. Capture (%)	Space Time (s)	k_1 (1/min)	Mult. (45° Ref)	Mult. (25° ref)	ϕ_{biocat}	ϕ_{void}
Blank 20% K_2CO_3, 25°C	24.2°	0.119	9.2%	98.7%	14.8	0.40	--	1.0	0.0%	91.0%
Blank 20% K_2CO_3, 45°C	45.8°	0.116	13.5%	96.7%	13.8	0.65	1.0	1.6	0.0%	91.0%
CSP-1	22.2°	0.110	63.1%	99.5%	14.6	4.09	6.3	10.2	17.8%	69.2%
CSP-1	45.6°	0.110	64.2%	98.8%	13.8	4.51	6.9	11.3	17.8%	69.2%
CSP-2	44.5°	0.136	70.6%	95.6%	13.8	5.82	8.9	14.6	14.1%	76.9%
CSP-3	43.6°	0.119	82.6%	96.9%	13.8	8.31	12.8	20.9	10.9%	80.1%

Figure 20 further illustrates this point in that the CO_2 capture of the biocatalyst sample is approximately equal at all temperatures, but the blank reference has a clear improvement in CO_2 capture performance with temperature. The calculated multipliers with temperature are presented for two CSP samples tested in the CLR.

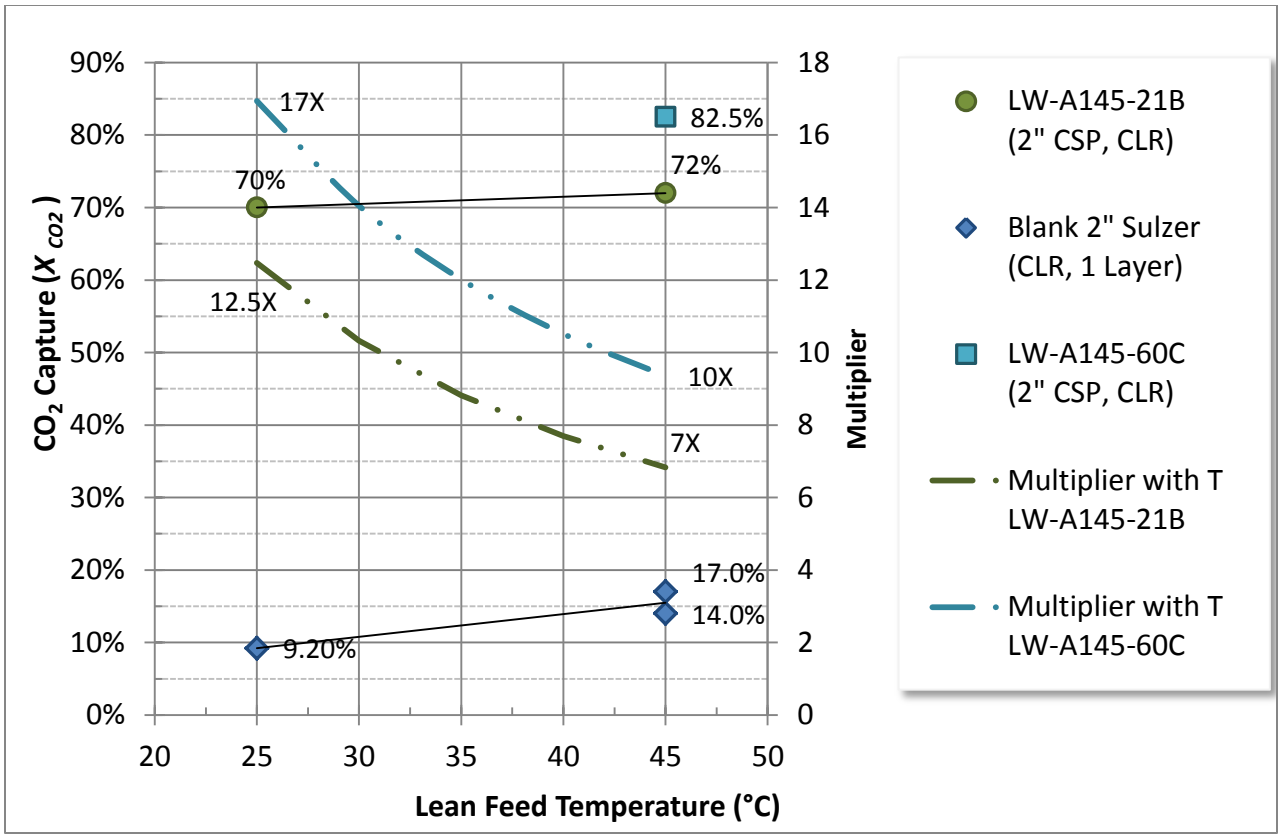

Figure 20: Effect of temperature on CO_2 capture and multiplier performance in 20% w/w K_2CO_3.

Biocatalyst formulations similar to bench unit deployment showed 7-fold enhancement relative to the reference blank at 45°C (equivalent to 12-fold enhancement relative to the blank at room temperature) in the laboratory closed loop reactor (CLR). This enhancement is roughly equal to performance of 0.5 g/L solution of soluble enzyme. The performance of a recently improved formulation resulted in 12.8-fold enhancement relative to the blank at 45°C (equating to approximately 20-fold enhancement relative to the blank at room temperature), which is roughly equivalent to the performance of 1 g/L of soluble Novozymes CA. Laboratory data provided in this subtask, including most recent formulation improvements, demonstrates the potential to deploy an active biocatalyst coating that meets or exceeds the 10-fold enhancement target (at 45°C) specified in the final techno-economic analysis.

Task 5 – Lab-Scale Closed Loop Reactor Operations (Lead Organization: Akermin)

Subtask 5.1 – Demonstrate Baseline Performance in Lab-Scale Flow Reactor

Operate the lab-scale closed loop reactor with different packing materials, solvent concentrations, and temperatures (40-60°C). Establish baseline performance with prepared packing materials containing no enzymes.

In the early phases of this project, Akermin used Sulzer DX laboratory packing—a wire mesh gauze packing typical of laboratory distillation but atypical of large-scale absorption process. [13] More recently, Akermin focused on Sulzer Mellapack 500X, which is a stainless steel structured packing. In larger diameter (e.g., commercial scale) columns, this packing is expected to have 500 m^2/m^3 surface area. However, due to edge effects of orthogonally cut sheets to accommodate 54 mm (2.1-inch) inside diameter laboratory column, the packing specific surface area was about 360 m^2/m^3.

The data in Table 6 was collected in the CLR using 17% K_2CO_3 solutions at 30°C using a feed gas flow rate of 2.0 and 4.36 SLPM with two layers of M500X packing described above. Conditions were selected for direct comparison with the PNNL wetted wall column data. Results indicated an area efficiency of approximately 13.5% at the standard test liquid flow condition. The standard test condition was selected to achieve quantifiable CO_2 capture in the range of 12% to 90% while testing just one or two sections of coated packing.

Table 6: CLR tests conducted with 17% K_2CO_3 at 30°C using 2-layers M500X for comparison with PNNL WWC Data to determine area efficiency

Description	Temp. (°C)	CO_2 Loading (n/n K^+)	CO_2 Capture (%)	Equilib. Capture (%)	Space Time (sec)	k_1 (1/min)	Packing Area (m^2/L)	Wet Void Fraction (%)	$K_{G,P}$ (mmole/ kPa m^2 s)	η_e (area eff.)	$K_{G,I}$ (mmole/ kPa m^2 s)
17% K_2CO_3, 30°C CLR, 4.36 SLPM Gas	30.0	0.101	12.5%	98.6%	14.5	0.56	0.360	89.0%	0.0115	14.1%	
17% K_2CO_3 CLR 2.0 SLPM	29.7	0.105	24.4%	99.3%	31.7	0.53	0.360	89.0%	0.0110	13.5%	
PNNL, WWC (17% K_2CO_3, 30°C)	30.0	0.103	--	--	--	--	--	--	--	--	0.0821

Subtask 5.2 – Produce Immobilized Enzyme Column Packing for Lab-Scale

Investigate coating procedures for applying enzyme-containing micellar polymer layer to commercially-available column packing. Explore surface functionalization of column packing materials to promote adhesion of micellar polymer layer. Scale-up production of coated column packing material to enable lab-scale closed loop reactor testing of immobilized enzyme.

As described in Task 3, Akermin down-selected to a porous silica based immobilization matrix that can be deposited on to various structural supports using solution precursor chemistry, termed sol-gel encapsulation. Initially, this immobilization strategy was used to stir-coat ceramic spheres that were tested as random packing in Akermin's SPR or CLR systems. Results from these early development studies were used to demonstrate enzyme retention over a period of 45 days. This same random packing system was used in endurance activity testing (i.e., lifetime studies; Subtask 3.4) exceeding 200 days on stream, as previously described. To transition to commercially-available structured packing (ideal for low-pressure applications), Akermin had to adapt its promising sol-gel encapsulation methods for deposition onto stainless steel structured packing.

The majority of Akermin's efforts focused on spray-coating methods because of its suitability to scale-up and compatibility with chemical and physical properties of the sol-gel precursors. Two critical developmental steps were achieved to transition the sol-gel immobilization technology to structured packing. The first was the establishment of a robust base coating, or "primer" layer, which enabled adhesion of the CA-containing porous silica coating to the stainless steel structured packing. Akermin developed an in-house deposition method of a silicate primer layer derived from tetraethylorthosilicate (TEOS) followed by thermal curing at elevated temperatures. Akermin also worked closely with Lantec Products, Inc, a coating company affiliated with Sulzer, to identify the most promising formulation of their proprietary silicate coating onto Sulzer packing for use as a primer layer for the bench unit packing. After testing several iterations of Lantec's coatings, Akermin down-selected to the ideal candidate and secured a contract agreement with Lantec to deposit its proprietary coating as the primer layer for the 8" Sulzer packing used in the bench unit.

The second major development involved the generation of long-lived stable colloidal suspensions (stable gels) containing CA. These stable suspensions arrested the condensation step of the sol-gel process allowing the gel to be handled and sprayed over a greater period of time. This development was critical as it simplified scalability and provided a method for generating a robust coating solution that contains all the vital components in one pot.

Several derivative formulations were spray-coated onto individual Sulzer sheets resulting in a homogeneous and uniform coating, as seen below in Figure 21. Further investigation of this coating using SEM analysis (inset) revealed what appeared to be a high surface area porous microstructure, similar to what was previously observed with films stir-coated onto random ceramic packing. This method of spray coating was used to prepare samples of immobilized enzyme on structured packing for testing in the lab-scale CLR.

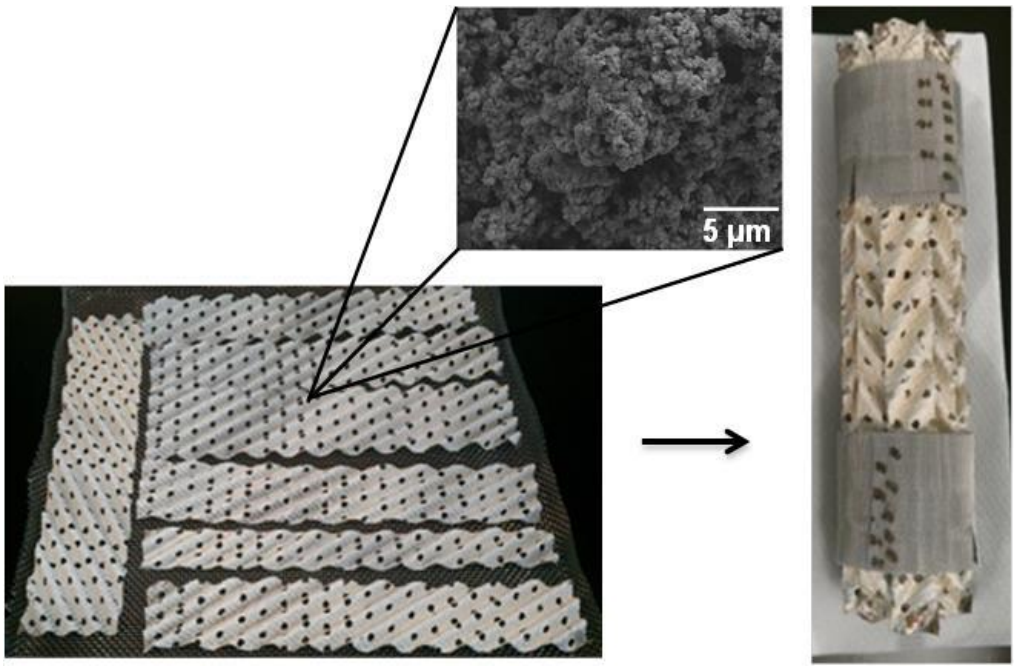

Figure 21 CA-containing porous silica coating on a 2" diameter unit of Sulzer M500X structured packing.

Subtask 5.3 –Demonstrate Enzyme Catalyzed Carbon Capture in Lab-Scale Flow Reactor

Demonstrate an order-of-magnitude (~10x) increase in the rate of CO_2 capture relative to the no enzyme baseline in a lab-scale, closed loop, continuous flow reactor using simulated flue gases (15% CO_2, 85% air).

Akermin demonstrated a key milestone by achieving approximately 10-fold multiplier in overall mass transfer coefficient at ~25°C with an immobilized enzyme sample in a continuous flow CLR, as shown in Figure 22, tested at 10.7 seconds space time, 20 wt% K_2CO_3 and lean pH approximately 10.15. Akermin achieved this critical project milestone on October 24, 2011.

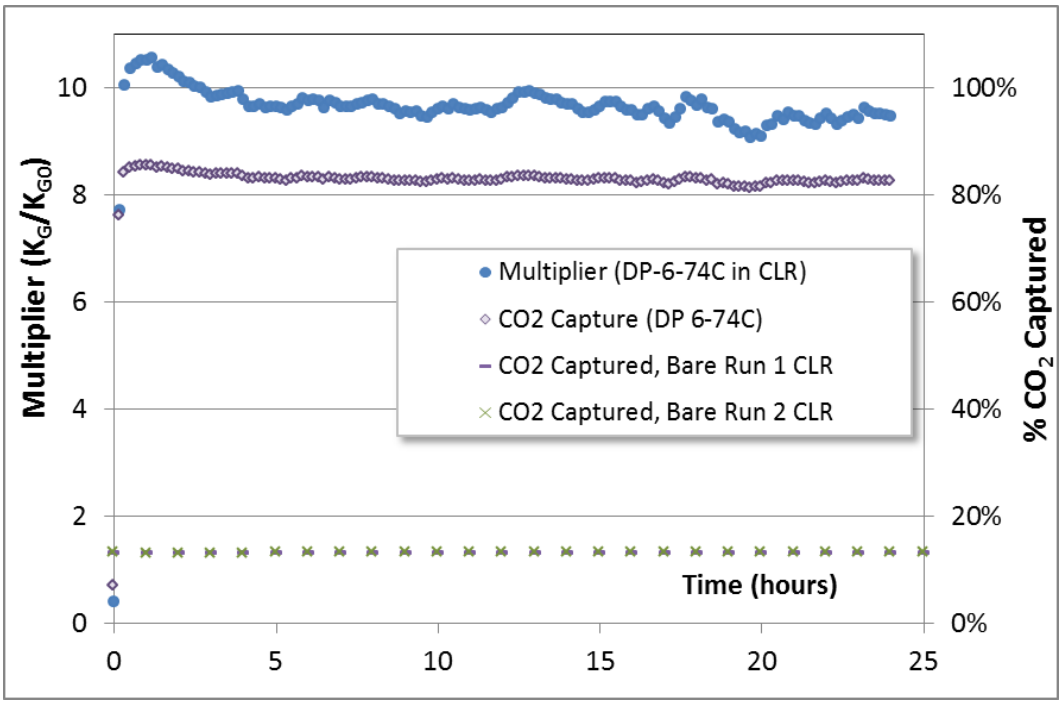

Figure 22: Multiplier and % CO_2 capture in CLR with sol-gel immobilized CA at 25°C

An average of 83.1% CO_2 capture was achieved over a 24 hour period compared to baseline tests with equal weight of bare packing (65 g, 3.66 mm Tipton Spheres in all cases). Bare packing exhibited approximately 14% CO_2 capture at the same flow conditions. Data show that at least an order-of-magnitude (10X) increase in overall mass transfer coefficient relative to a no enzyme baseline (i.e., bare packing) was achieved over a period of at least 24 hours with sample DP 6-74C. The peak multiplier was approximately 10.5X and the average over 24 hours was 9.7X.

The total feed gas flow rate was 400 SCCM, comprised of 15% CO_2 (dry basis) blended with 85% air, which is saturated at approximately 25°C with water before being fed to the counter-flow packed bed reactor. The CLR had ~65 g of bare packing coated with sol-gel containing CA. It was estimated that the sol-gel coating was approximately 200 to 230 microns thick (causing about 25% increase in surface area) and that the void fraction of the packed column was approximately equal to the blank sample (46%). Further, in the test run described above, the liquid feed was 25 ml/min of 20 wt% K_2CO_3 solution that was fed with a pH near 10.15 (or about 22% converted to bicarbonate) and 25°C.

It should be noted that the multiplier discussed here is relative to 25°C standard test. The multiplier will vary as a function of temperature because the biocatalyst system exhibits lower activation energy than the blank carbonate system, as previously discussed.

Subtask 5.4 –Evaluate Trace Contaminant Effects Lab-Scale Flow Reactor

Operate the lab-scale, closed loop, continuous flow reactor under typical operating conditions and challenge the performance by independently and concomitantly adding 20 ppm of SO_2 and NO_2 into the simulated flue gas stream. Determine if there is any enzyme inhibition due to said trace contaminants. Experiments would be conducted where the trace contaminant is added, then removed and added again to quantify the level of reversible inhibition. Short-duration tests would not be adequate to explore heat stable salt formation and its long-term impact, nor detection of slight irreversible denaturing.

The trace contaminant test utilized a 70-ml packed column with enzyme immobilized on 65-g of bare 3.66 mm Tipton spherical packing. Simulated flue gas was fed at 200 sccm (dry equivalent). Initially, the feed gas was 15% CO_2 balanced by nitrogen with no contaminants as baseline (shown in the first blue trace over the first day). The feed gas was then switched to a 15% CO_2 blend with 20 ppm NO_2 and 20 ppm SO_2, balanced by nitrogen. The performance of the sample with this feed gas is shown in the green trace of Figure 23, over a 5 day period. Finally, the feed gas was switched back to the original 15% CO_2 (balanced by nitrogen), which is shown in the final blue trace from about day 6 to day 7. As can be seen in Figure 23, the sample had no loss in activity when exposed to a feed gas containing NO_2 and SO_2 and maintained 90% CO_2 capture over the duration of the experiment.

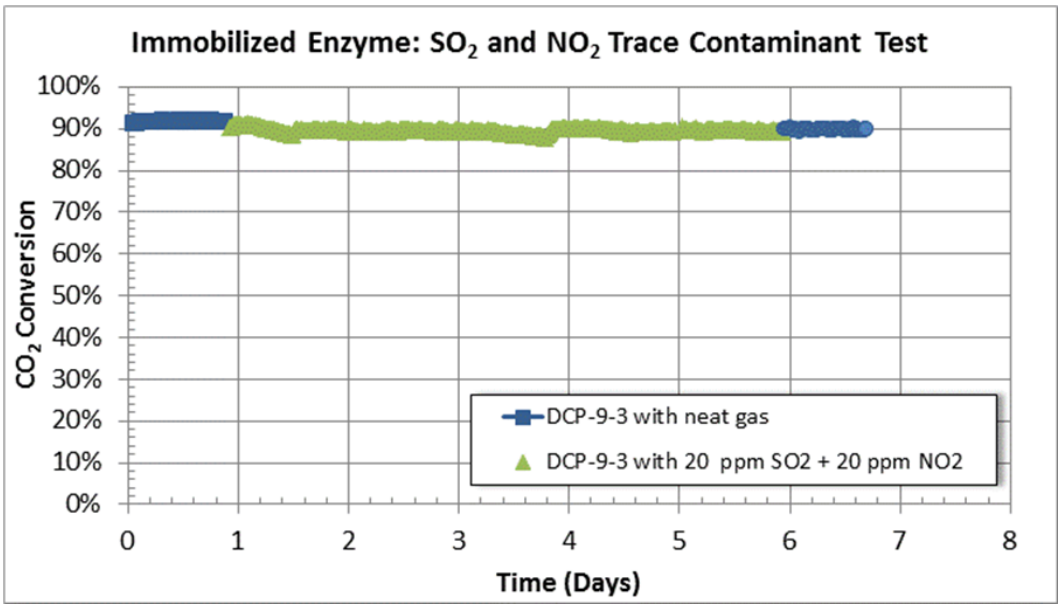

Figure 23: Trace contaminant test of Akermin's immobilized enzyme with 15% CO_2 feed gas and 20 ppm NO_2 and 20 ppm SO_2.

Task 6 – Aspen Plus® Model Development and Techno-Economic Analysis

Subtask 6.1 – Preliminary Techno-Economic Analysis and Model Development

> PNNL will adapt existing advanced power plant modules (supercritical pulverized coal power plant) to include MEA and alternative solvent systems (CA catalyzed and non-catalyzed carbonate chemistry systems) at 550 MWe (net output power). PNNL will prepare cost and performance estimates similar to NETL Case 12, including mass and energy balances and absorber and desorber design model outputs and specifications. The project team will also define assumptions and document the sizing and costing methodology applied to the carbon capture system. Battelle will provide data analysis and reporting support for this task.

The focus of this task was preliminary absorber sizing and preliminary mass and energy balance estimation. At this stage, Akermin worked with PNNL to review several critical process parameters including the equilibrium partial pressure predictions, heat of reaction for CO_2 absorption/desorption, and precipitation of $KHCO_3$ by comparing predictions with laboratory and literature data. A complete capture plant costing and levelized cost of electricity calculation was not performed at this juncture. However, a detailed presentation of the preliminary techno-economic analysis is provided under Subtask 6.3, "Revised Techno-Economic Analysis, Industrial Scale, Wetted Wall Feedback."

A 16-fold improvement in overall mass transfer coefficient in K_2CO_3 with 40°C lean feed temperature would require about 80-ft of M350Y packing for a 550 MWe (net) plant at 80% flooding. Likewise, a 10-fold enhancement results in 130-ft of absorber packing. These enhancement targets are within the range of laboratory coated packing data collected in the Akermin CLR system, see Table 5.

Literature review suggested a trade-off exists between latent duty and sensible duty would result in minimizing regeneration energy at a certain lean loading condition. [7] Preliminary modeling bore this out and indicated regeneration energy would be minimized if the lean loading were just sufficient to meet the treated gas exit partial pressure requirement.

Figure 24 below illustrates a data validated equilibrium curve for 20% K_2CO_3 at 40°C. Horizontal lines represent the feed gas partial pressure and the treated gas partial pressure relative to 90% capture assuming the Case-12 flue gas condition. Two example operating lines are also illustrated. As illustrated here, the lean threshold required to achieve 90% capture is approximately 0.40 X_{CL} (mol/mol K_2CO_3 equivalent), and the maximum rich loading is also limited to about X_{CR} = 0.74. Practically, however, the absorber would operate at near 0.35 lean loading and near 0.70 rich loading (as shown below) to have a small offset from the lean and rich equilibrium limit conditions at 40°C liquid temperature.

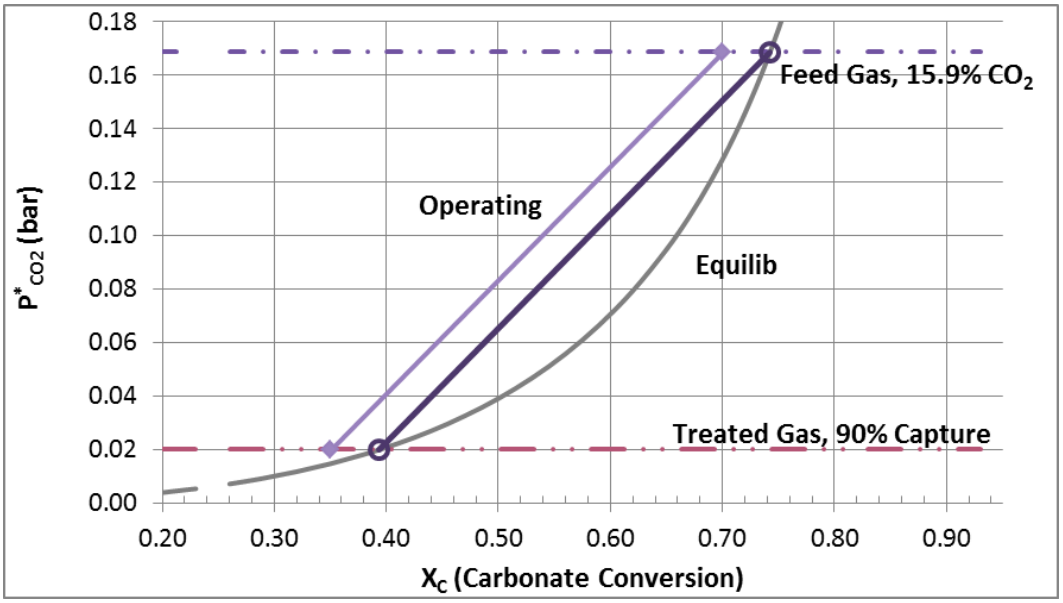

Figure 24: Equilibrium line and operating lines compared in 20% K_2CO_3 at 40°C; after calibrating model with equilibrium data.

Equilibrium Partial Pressure Data, K_2CO_3 System

An accurate prediction of equilibrium partial pressure is needed to assure the most accurate energy balance calculations and to provide accurate guidance for minimum liquid circulation rates based on lean threshold and maximum rich loading. An excellent equilibrium partial pressure data set is available in literature, but mainly developed for higher temperature absorption applications: 70°C to 90°C data in 20%, 30%, and 40% w/w K_2CO_3 by Tosh et alia (1959). [14] The enzymatic process was initially thought to operate in the range of approximately 35 to 45°C. Our analysis revealed the "out of the box" model did not match data very well below 110°C, and so some effort was spent collecting equilibrium data and matching results with Aspen. Akermin collected equilibrium partial pressure data in its own laboratory for this lower end temperature condition in late 2010.

A 20 wt% K_2CO_3 solution was fed at a rate of 145 mL/min to the CLR, which was filled with Sulzer DX Packing (900 m^2/m^3 gauze packing). Soluble enzyme was added to achieve approximately 0.25 g Novozymes CA/Liter solution. Gas was fed a 4 SLPM comprising various mixtures (5%, 8%, 10%, and 15% CO_2) at 7-kPa absorber bottom pressure and saturated at 35°C before feeding to the absorber. The CO_2 capture flux was determined from the gas analysis and reported as the moles of CO_2 captured per m^2 packing per second. A linear projection of the flux data was used to determine the equilibrium partial pressure where CO_2 flux would be zero, see Figure 25. Besides the zero flux intersection, Akermin also observed the CO_2 loading where absorption ceased for each CO_2 feed condition.

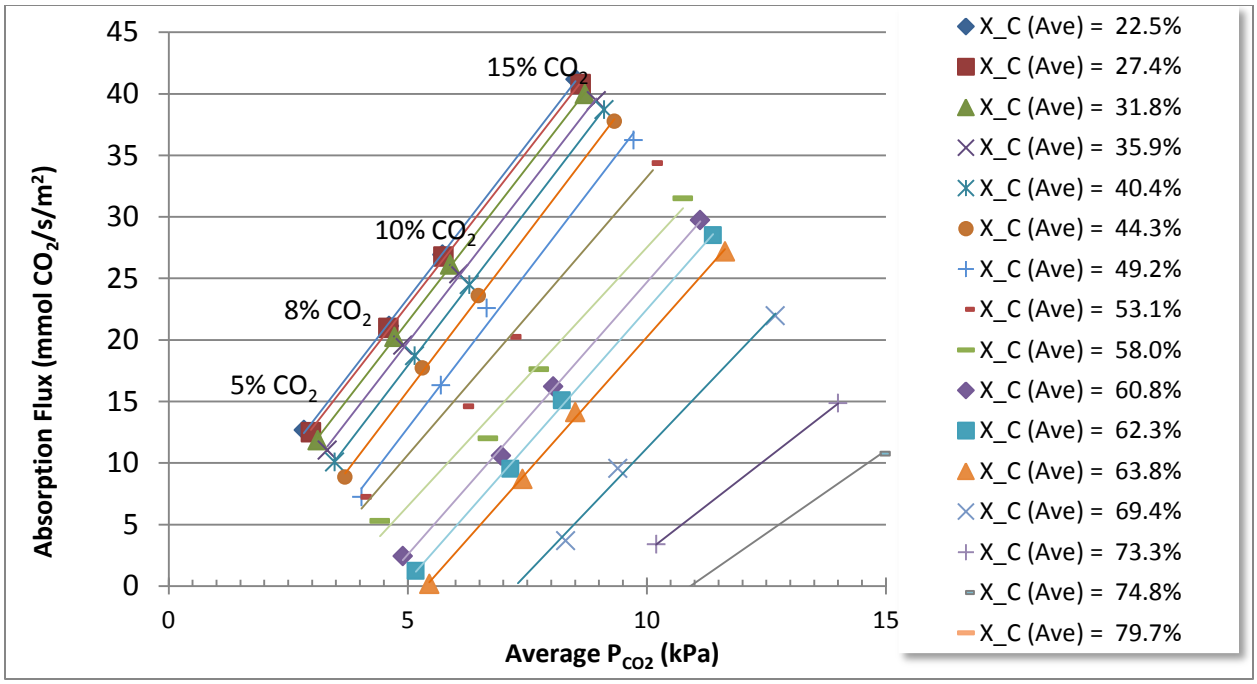

Figure 25: Absorption Flux Measurements in CLR reactor using Sulzer DX packing, 20% K_2CO_3 at 35°C, 0.25 g/L soluble Novozymes CA using varied % CO_2 feeds (dry basis), 4 SLPM gas saturated at 35°C.

Calculation of Equilibrium Constant (K_{CO2}), K_2CO_3 System

For the overall CO_2 hydration reaction in a carbonate base ($CO_3^{=}$) solution there are two bicarbonate ions (HCO_3^-) formed, and so the equilibrium constant can be defined as follows, Equation 13:

$$K_{CO_2} = \frac{[HCO_3^-]^2}{[CO_3^=][H_2O]P_{CO_2}} \tag{13}$$

In Equation 14 below, a simple mole balance was used to write concentrations in terms of the CO_2 loading (X_C) as carbonate conversion to bicarbonate and the mole ratio of carbonate to water, R_{CW}, in the ("as pure") unloaded reference condition:

$$\frac{1}{K_{CO_2}} = \left(\frac{1 - R_{CW}}{4\,R_{CW}}\right)\frac{(1 - X_C)}{(X_c)^2}P_{CO_2} \tag{14}$$

The mole ratio of carbonate to water in the unloaded referenced condition, R_{CW}, is related to the mass fraction of K_2CO_3 in the "as pure" condition (x_0), for example 0.2 g K_2CO_3/g solution, and molecular

weights of water and K_2CO_3, M_W and $M_{K_2CO_3}$, respectively, as observed in Equation 15. The calculation of the equilibrium constant for the data collected in the CLR can be observed in Table 7.

$$R_{CW} = \left(\frac{n_{K_2CO_3}}{n_{H_2O}}\right)_{as\ pure} = n_{K^+}/2n_w = \frac{x_0}{1-x_0}\left(\frac{M_W}{M_{K_2CO_3}}\right) \tag{15}$$

Table 7: Summary of P^*_{CO2} data and corresponding equilibrium constant determined from flux data (Figure 25) in 20% K_2CO_3 at 35°C using DX packing in Akermin's CLR system.

X_C *[% converted to bicarbonate]*	α_K *[mol CO_2/K^+]*	$P^*_{CO_2}$ **[kPa]** *(Dilute Model Analysis)*	**$1/K_{CO2}$** *[kPa]*
22.5%	0.113	0.36	42.9
27.4%	0.137	0.45	34.2
31.8%	0.159	0.72	38.2
35.9%	0.179	1.00	38.9
40.4%	0.202	1.48	42.0
44.3%	0.221	1.90	42.2
49.2%	0.246	2.47	40.5
53.1%	0.265	3.16	41.0
58.0%	0.290	4.10	39.7
60.8%	0.304	4.42	36.3
62.3%	0.312	4.90	36.9
63.8%	0.319	5.38	37.2
69.4%	0.347	7.25	35.8
73.3%	0.366	9.08	35.0
74.8%	0.374	10.92	38.0
79.7%	0.398	16.55	40.9
AVERAGE:			**38.7 kPa**

Equilibrium constants were calculated using Equation 14 with the Tosh (1959) data set, and the average values of ($1/K_{CO2}$) across all CO_2 loading conditions were plotted against the inverse of absolute

temperature in Figure 26 below. The same equilibrium constant calculation was performed with Akermin's equilibrium partial pressure data at 35°C and included on the same Figure 26 below.

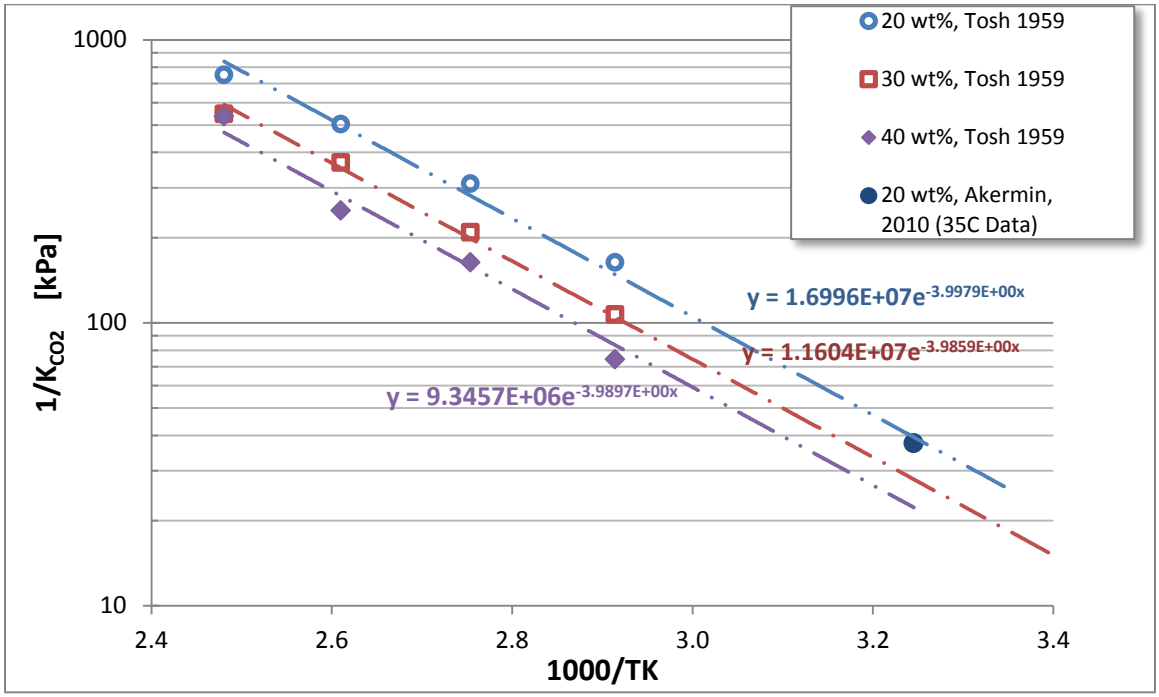

Figure 26: Arrhenius plot of Equilibrium constants for CO_2 absorbed in to K_2CO_3 solutions

A simple regression of the equilibrium constant data is shown in Figure 26. The results can be used for accurate calculation of CO_2 partial pressure (P_{CO2}) at any concentration, CO_2 loading, and temperature in the data range. Figure 27 below presents the calculated equilibrium partial pressures for 20% K_2CO_3 as a curve with CO_2 loading at various temperatures, and all available equilibrium partial pressure data for 20% K_2CO_3 is plotted using data markers.

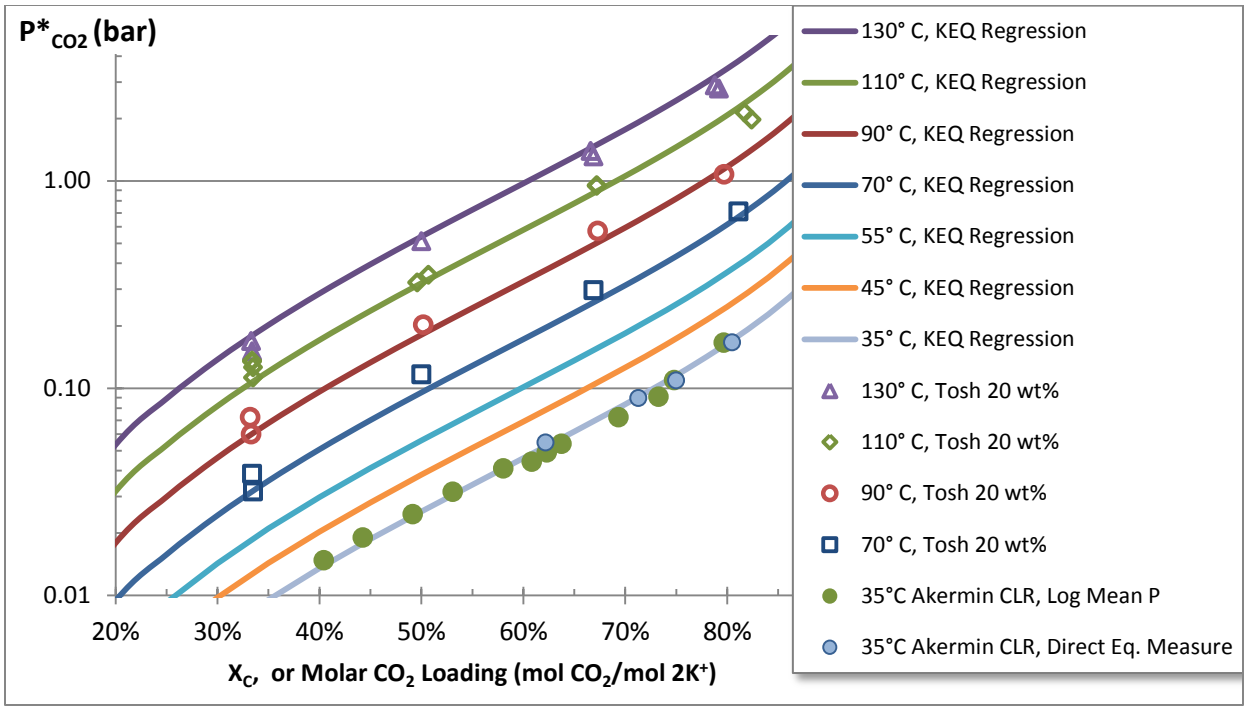

Figure 27: Equilibrium CO_2 partial pressure data points for 20 wt% equivalent K_2CO_3 solutions compared to equilibrium curves derived from correlation presented in Figure 26.

Regressions from the expanded equilibrium partial pressures data set (from 35 to 130°C) were used to tune Aspen parameters for more accurate equilibrium partial pressure predictions in energy balance modeling going forward.

Heat of Reaction Analysis

Heat of reaction as a function of temperature was studied using a Gibbs-Hemholtz analysis of the Tosh data set. A form of the Gibbs-Hemholtz equation, Equation 16, was used to calculate heat of reaction. [15]

$$\Delta h_{rxn} = -RT^2 \left[\frac{\partial \, ln(P^*_{CO2})}{\partial (T)} \right]_{X_C} \tag{16}$$

Tosh (1959) data at constant CO_2 loading was regressed using an exponential relationship, Equation 17.

$$\left(P^*_{CO_2}\right)_{X_C=const} = a \, e^{b \, T}$$

(17)

Taking the derivative and substituting in to Equation 16, yields the following simplification in Equation 18.

$$\Delta h_{rxn} = b\, R\, T^2$$

(18)

The heat of reaction is therefore readily calculated from the exponential coefficient, b, of the exponential regression. The heat of reaction (desorption) determined by Akermin's analysis of the Tosh (1959) data is plotted in Figure 28 along with the heat of reaction at the precipitation limit as reported by Hilliard (2008). [7] When these results were compared with AspenPlus Version 7.3 prediction, it was revealed that the Aspen model was significantly over predicting the heat of reaction. After consulting with Aspen, a patch was provided to this version of AspenPlus.

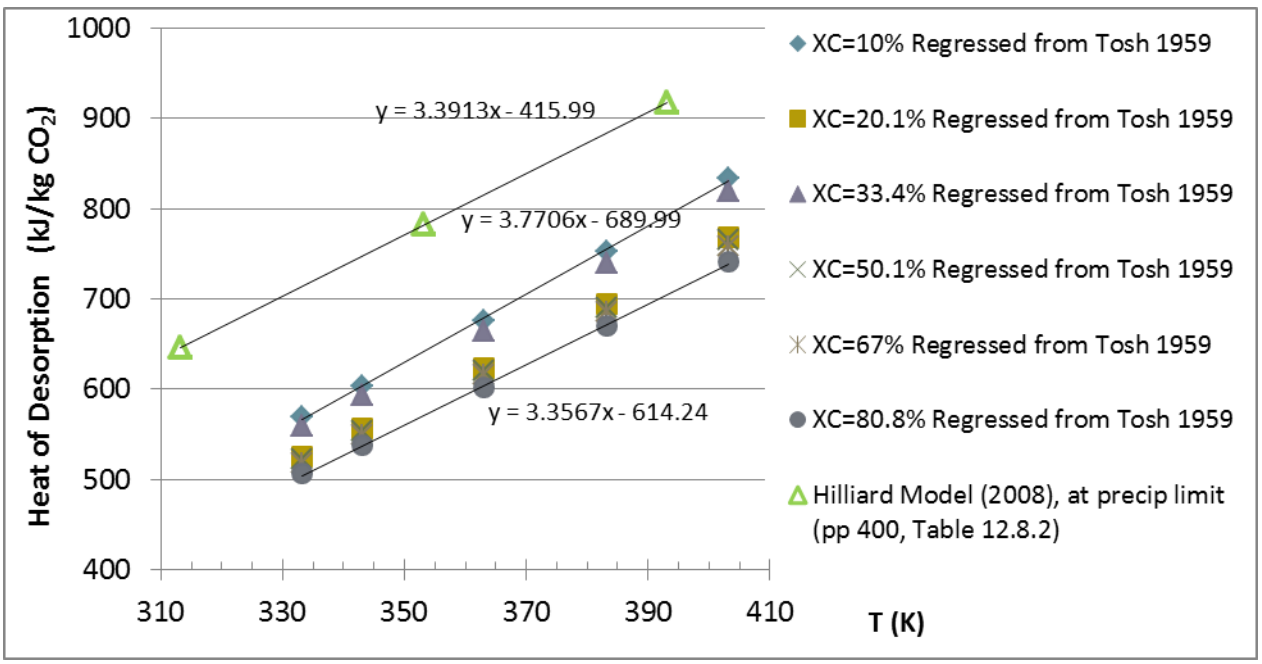

Figure 28: Heat of desorption (kJ/kg CO_2) calculated from equilibrium partial pressure data from Tosh (1959), 20 wt% cases and compared with Hilliard model at precipitation limit. [7]

Precipitation Data (K_2CO_3/$KHCO_3$ System)

As part of the model development, Aspen precipitation estimates were compared against laboratory and literature data. [16] [17] It was determined that the required update to the parameters was most reasonably accomplished via the molality-based solubility product constant, K_{SP}, calculated via Equation 19.

$$K_{SP} = m_{K^+} m_{HCO_3^-} \tag{19}$$

A regression of solubility product constant data yields Equation 20.

$$K_{SP} = 7.2923 + \frac{-2580.7}{T} + 0.6685\ \ln(T)\,, \qquad T\ in\ K \tag{20}$$

This equation was used to update solubility product parameters within the Aspen model for K_2CO_3. A comparison of the new $KHCO_3$ prediction estimate against literature can be found in Figure 29. The Aspen model was updated for accurate prediction of $KHCO_3$ precipitation.

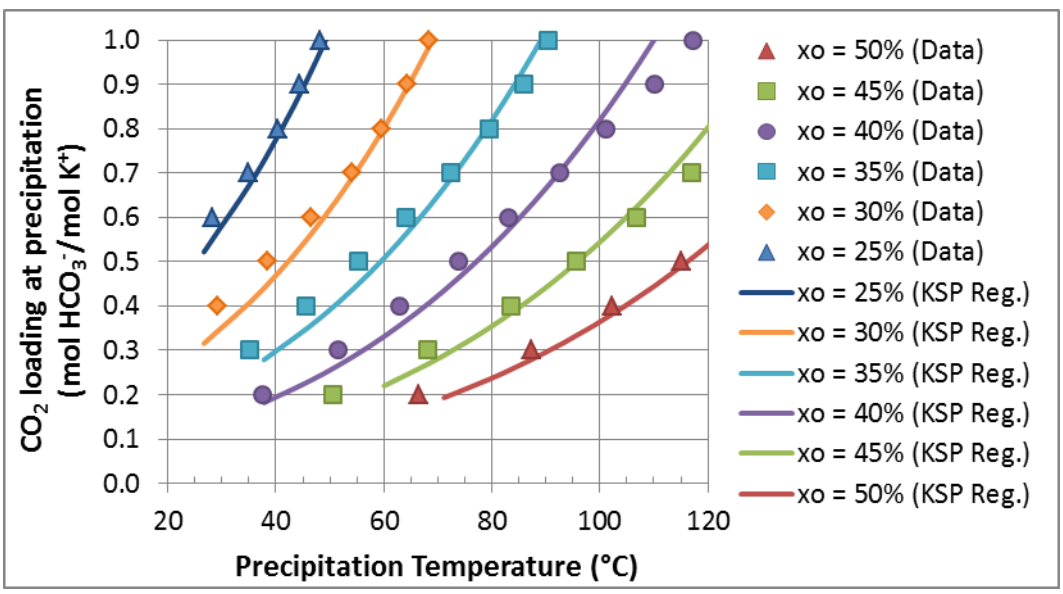

Figure 29: Loading at which $KHCO_3$ precipitation occurs versus temperature, updated Aspen prediction compared to literature data. [17]

Viscosity Data in $K_2CO_3/KHCO_3$ System

Diffusivity has a key role in reaction-enhanced mass transfer theory, specifically in applications where surface renewal theory is applicable [12]. As such, it was important for Akermin to gain a deeper appreciation of the diffusivity of CO_2 in aqueous solutions of K_2CO_3.

The Stokes-Einstein relationship is a special case of kinetic theory that predicts viscosity influences the motion of spherical particles in liquids of low Reynolds number. The Stokes-Einstein relationship states that diffusivity is proportional to temperature, and inversely proportional to viscosity and diffusion diameter. Similarly, Joosten and Danckwerts (1972) [18] found that diffusion of CO_2 (or its non-reactive analogue NO_2) in K_2CO_3-$KHCO_3$ mixtures can be predicted based on diffusion data in water ($D_{CO_2\ (water)}$) and dynamic viscosity (μ.) measurements in carbonate solution using Equation 21.

$$D_{CO_2\ (Carb\ Soln)} = D_{CO_2\ (water)}\left(\mu_{water}/\mu_{(Carb\ Soln)}\right)^{0.818} \tag{21}$$

Akermin measured the viscosity of carbonate solutions using a vibratory viscometer by Cole Parmer EW-98946-10 at room temperature and also at various elevated temperatures.

Figure 30 shows that the viscosity in carbonate solutions at room temperature increases with K_2CO_3 concentration; however, viscosity is independent of CO_2 loading up to the equilibrium limit of interest for the flue gas application (0.4 mol CO_2/mol K^+, or 80% converted).

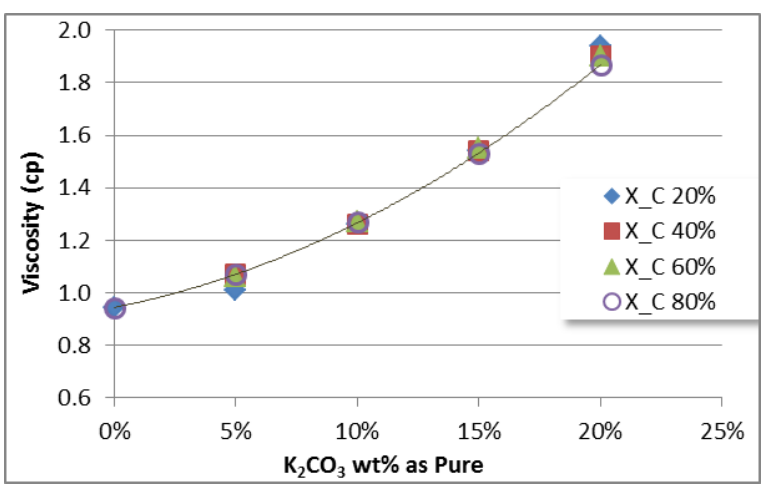

Figure 30 Viscosity of potassium carbonate solutions with varied concentrations and CO_2 loadings (X_C, as carbonate converted to bicarbonate) at room temperature.

Akermin also collected data on viscosity in carbonate solutions as a function of temperature, see Figure 31. It was concluded that accurate viscosity and temperature measurement is one way to estimate the equivalent concentration of K_2CO_3 solutions at any CO_2 loading.

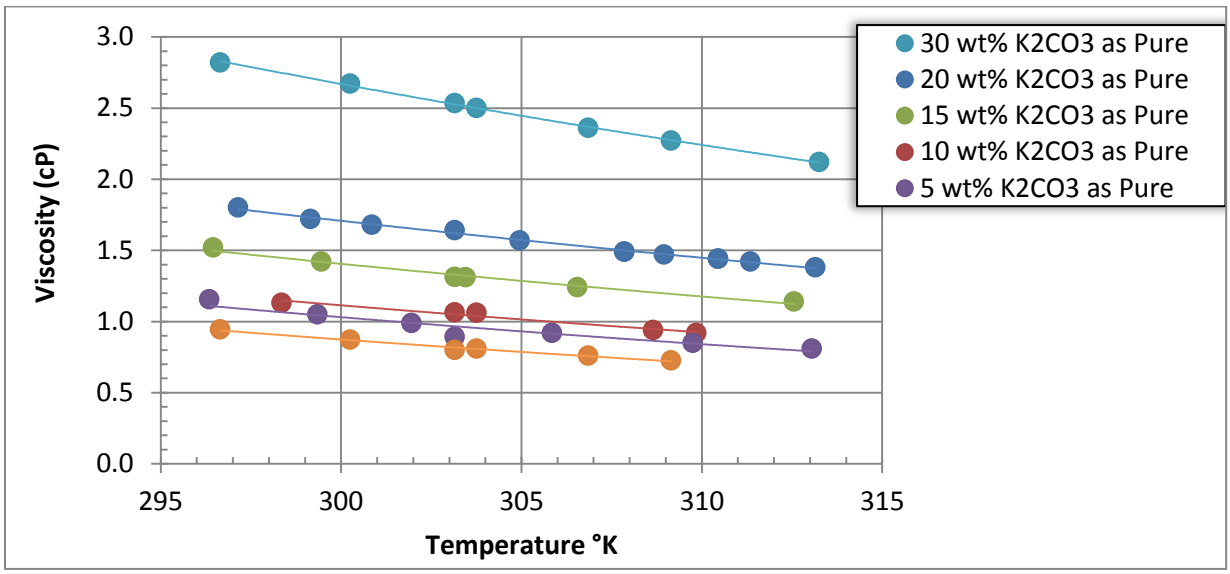

Figure 31: Viscosity of potassium carbonate solutions as a function of temperature

Subtask 6.2 – Perform Wetted Wall Tests, Validate K_2CO_3 Design/Sizing Modules (PNNL)

Wetted wall column testing will be performed at PNNL to measure gas-liquid mass transfer rates and reaction kinetics for potential CO_2 absorption solvents with and without carbonic anhydrase enzyme. The bench-scale, wetted wall system maintains a flowing thin film of solvent in contact with a gas stream within a sealed chamber. The inlet gas composition and flow rate, solvent flow rate, and temperature within the chamber are finely controlled. Gases exiting the chamber are passed through a chilled water condenser to recover volatilized solvents, continuously sampled using a residual gas analyzer equipped with a mass spectrometer, and then vented to the atmosphere. Wetted wall testing of multiple candidate solvents will provide the preliminary performance inputs for Aspen process modeling to support predicted plant-scale performance and economic assessments."

The test duration for the wetted wall column was defined by the time required to attain a stable mass transfer rate. Enzyme durability was assessed on Akermin's test stand.

A comprehensive wetted wall testing series was conducted with K_2CO_3 and MDEA solvents; and MEA was also tested to validate mass transfer coefficient results with comparison to published data.

While PNNL also conducted testing with soluble enzyme, difficulties and system upsets were experienced due to foaming and denaturing of the enzyme, which required frequent system drain and rebuild. The soluble CA enzymes were apparently denaturing rapidly in pumps and liquid orifice plates deployed in the wetted wall column. Attempts were made to quantify the retained soluble protein, but uncertainty remained in the quantification of active CA.

Two enzymes were tested in the WWC: bovine carbonic anhydrase (BCA) from Sigma-Aldrich and Novozymes supplied CA enzymes. Early experience with bovine CA showed rapid enzyme inactivation and major system upsets due to foaming and protein agglomeration. Subsequent testing with Novozymes CA enzyme in K_2CO_3 showed an apparent leveling off of overall mass transfer coefficients, suggesting either a limit in enzyme activity, or diffusional limits that may be specific to the wetted wall arrangement. Nevertheless, the highest observed increases in overall mass transfer coefficients with the K_2CO_3/ Novozymes CA were approximately 3-times that of the no-enzyme K_2CO_3 reference.

The main value of the wetted wall column data is that it provides a baseline mass transfer coefficient data relative to a known surface area. Therefore, the WWC data generated by PNNL were used by Akermin to compare mass transfer coefficient measurements in packed column reactors to develop area efficiency estimates. Table 8 below provides a summary of wetted wall column data by PNNL for K_2CO_3 at 30°C, MDEA at 35°C, and MEA at 40°C.

Table 8: Summary of Wetted Wall Column (WWC) Data generated by PNNL (2011) for un-catalyzed solvents

Solvent Case	CO_2 Loading (mol/mol)	$K_{G,I}$ mmole/[kPa m^2 s]
17% K2CO3, 30°C	0.092	0.089
17% K2CO3, 30°C	0.092	0.101
17% K2CO3, 30°C	0.184	0.093
17% K2CO3, 30°C	0.092	0.060
17% K2CO3, 30°C	0.181	0.055
17% K2CO3, 30°C	0.347	0.051
17% K2CO3, 30°C	0.347	0.068
17% K2CO3, 30°C	0.425	0.051
12% MDEA, 35°C	0.000	0.162
12% MDEA, 35°C	0.097	0.143
12% MDEA, 35°C	0.161	0.137
12% MDEA, 35°C	0.258	0.138
12% MDEA, 35°C	0.375	0.123
30% MEA, 40°C	0.388	0.831
30% MEA, 40°C	0.525	0.360

PNNL wetted wall column data for MEA was previously shown in Figure 18 along with literature data, and showed good correlation with literature data. PNNL wetted wall column data for K_2CO_3 and MDEA was used to calibrate the area efficiencies of Akermin's packed column reaction systems.

Subtask 6.3 – Revised Techno-Economic Analysis, Industrial Scale, Wet Wall Feedback (PNNL)

Update carbon capture modules in Aspen Plus® based on wetted wall test feedback. Update cost and performance estimates for alternative solvent systems based on updated models. PNNL will provide the updated alkaline carbon capture (subsystem) module to Akermin for internal review. Battelle will provide data analysis and reporting support for this task.

A first revision of our techno-economic assessment was performed by PNNL in this task. It was assumed that the absorber would have about 24.4-m of packing (about 80-ft) for this first revision. PNNL

determined that a blank column would be about 396-m tall (about 1300-ft) using M350Y packing. Therefore, a 16-fold reduction in column height would be required. A second key assumption in this analysis was that the stripper column would be modeled as an equilibrium reactor, which is the typical approach. Retrospectively, this equates to assuming there are no kinetic limitations in the stripper. The design assumed a lower temperature stripping column to take advantage of reduced parasitic load with lower pressure steam. In this case, 8.5 psia extraction steam was specified to regenerate K_2CO_3 in this system.

Net power and parasitic power calculations are summarized in Table 9 below for the Akermin case and the NETL reference cases (NETL Case-11, NETL Case-12 version-1):

Table 9 Summary of Net Power Calculation for Economic Analysis Cases and CO_2 emission rates

	No CO_2 Capture (Case-11)	**30% MEA Ref. Case-12, v1 (by PNNL) [3,824 kJ/kg CO_2]**	**Akermin/20% K_2CO_3 (PNNL/Preliminary) [3,128 kJ/kg CO_2]**
Regen. Heat Source	**n/a**	**IP Steam**	**8.5 psia steam extraction**
Gross Power if no CO_2 Capture	851,150	851,150	851,150
Steam Extraction Loss (kW)	-	173,419	62,763
Gross Power Generation (kW)	**851,150**	**677,731**	**788,387**
CO_2 Compression (kW)		50,704	76,747
Absorption Pumps & Fans (kW)		14,897	16,368
Cooling Water Pumps & Fans	21,447	15,518	15,473
Condensate & BFW Pumps (kW)	23,755	23,293	23,741
Constant Coal Auxiliaries (kW)	27,700	27,700	27,700
Transformer Loss (kW)	2,979	2,372	2,759
Total Operating Parasitic (kW)	**75,881**	**134,484**	**162,788**
NET POWER OUTPUT (kW)	**775,269**	**543,247**	**625,599**
% Increased net power over MEA	n/a	0%	15.2%
% Power Loss relative to no cap	0.0%	29.9%	19.3%
CO_2 emission rate (kg CO_2/kWh)	**0.814**	**0.117**	**0.103**
Reduction in CO_2 emission rate relative to Case 11	**0%**	**85.6%**	**87.3%**

Notably, while 90% of fed CO_2 is captured in both cases, the Akermin case results in 12% lower CO_2 emission rate compared to 30% MEA case (NETL Case-12). Likewise, the NETL Case-12 only reduces

the CO_2 emission rate over the Case-11 baseline by approximately 85% due to increased parasitic power requirements. In contrast, a system with increased thermal efficiency (decreased parasitic power) results in greater emission reduction benefit. For example, this preliminary estimate of the Akermin biocatalyst enhanced K_2CO_3 system reduces the overall emission rates by approximately 87%. This begs the question as to if a target equivalent emission rate is the more appropriate performance requirement instead of a 90% capture requirement considering technologies may have variable parasitic power efficiencies.

PNNL estimated the reboiler heat duty to be approximately 3.13 GJ/t CO_2 (3128 kJ/kg CO_2). One of Akermin's critical performance targets for BP2 was to demonstrate an overall regeneration energy of less than 2,100 kJ/kg CO_2 (i.e., <900 Btu/lb CO_2) in the bench unit, which is about 33% lower than preliminary performance estimates by PNNL. This preliminary analysis did not achieve this goal.

Preliminary estimates of LCOE were also prepared for comparison with NETL Case-12, version 1. [19] After the preliminary analysis was complete, it was determined that the 2010 revision, Case-12 version 2 [20] assumptions should be used for the final techno-economic analysis (TEA)—see Subtask 6.4. A summary of the preliminary TEA results are presented in Table 10 below.

Table 10: Preliminary TEA by PNNL (2011), fuel cost calculation, constant coal feed.

Summary of Levelized Costs (¢/kWe-hr)	**No Capture (NETL Case 11)**	**30% MEA Case-12, version 1 (PNNL Est.)**	**20% K2CO3 (16X) (PNNL) 8.5 psia Extraction**
Fuel Cost	1.90	2.72	2.37
Capital Cost	3.46	6.74	6.56
Variable Cost	0.56	1.04	0.83
Fixed Operating Cost	0.39	0.58	0.51
Transportation, Sequesration & Monitoring (TSM)	------	0.40	0.35
Total (cents/kWh)	**6.32**	**11.48**	**10.63**
Increase versus No Capture	**------**	***81.7%***	***68.2%***

The following chart illustrates the progress toward the DOE goal, Figure 32, under the assumptions for this first revision of the TEA.

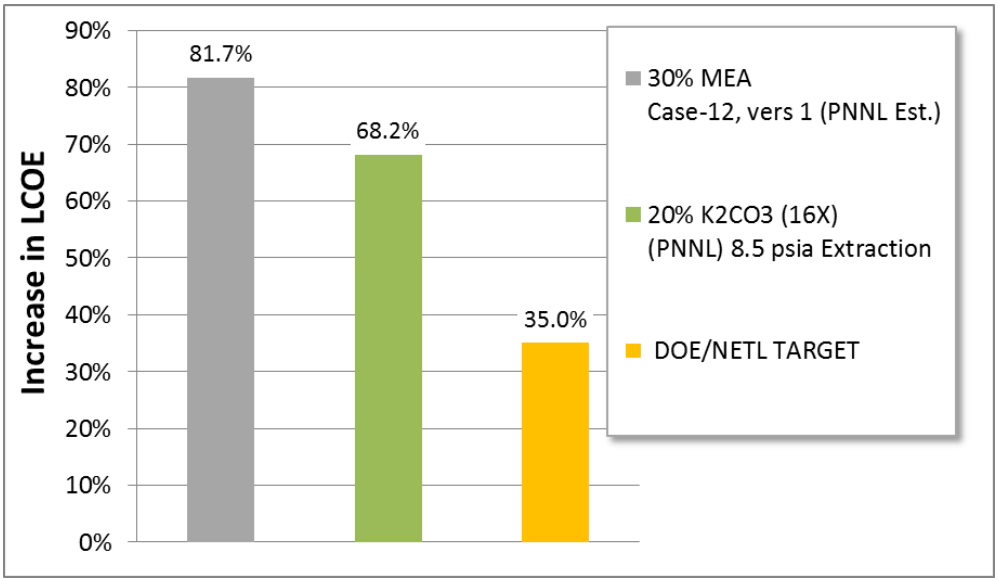

Figure 32: Results of preliminary TEA by PNNL. Assumed NETL Case-12 v1 conditions and also assumed equilibrium achieved in stripper (no kinetic limitations were assumed in the stripper at this juncture)

Prior to plant-level Aspen modeling, a series of validation studies were performed. First, bicarbonate precipitation was predicted in Aspen and compared to literature and Akermin testing data. It was determined that the Aspen physical properties for bicarbonate solubility were justifiably updated to include the fits against the Akermin test data.

Finally, a discrepancy between the expected and Aspen-generated heats of reaction for CO_2 into aqueous K_2CO_3 was identified. This led to direct engagement from Aspen and their updates to associated library physical properties (see heat of reaction analysis under Task 6.1).

Upon validation, PNNL used the Aspen model to estimate full-scale cost performance for catalyzed K_2CO_3 and MDEA gas treatment systems. Each of these solvent options showed a significant energy advantage over the MEA reference [19] that is associated with the opportunity to optimize those systems around vacuum stripping.

The absorber tower costs for the K_2CO_3 system dominated the capital costs. Therefore, the opportunity for further energy cost savings was determined to be in reducing the capital costs. This could be achieved through even better enzyme catalyzing effect, advanced absorber designs, etc. Note that if the capital costs for the K_2CO_3 system was reduced to the equivalent of the MEA system, the corresponding LCOE increase would be approximately 57% compared to the no capture reference case.

The preliminary TEA indicated a notable reduction in the LCOE relative to the 30% MEA (NETL Case-12, version1). Equilibrium modeling of the stripper showed potential to reduce reboiler heat duty to approximately 3.13 GJ/t; however, this assumed no kinetic limitations in the vacuum stripping process.

Nevertheless, optimization of the basic solvent flow sheet with K_2CO_3 does not appear sufficient to meet the original project goal of 2.1 GJ/t CO_2. Even so, potential for cost savings with biocatalyst absorber enhancement and vacuum stripping was shown by this analysis.

Subtask 6.4 – Revised Techno-Economic Analysis, Bench Unit Feedback (PNNL)

If an update is recommended by Battelle (Task 9.4), PNNL will update carbon capture modules in Aspen Plus® based on feedback from the bench-scale tests. Update cost and performance estimates for alternative solvent systems based on updated models. Provide updated alkaline carbon capture (subsystem) module to Akermin.

This task addresses the final revision of the TEA based on bench unit testing feedback. The TEA results described under Task 6.3 were updated based on feedback from the NETL-Akermin Bench Unit testing. The updated analysis also included an update to the MEA baseline case (NETL Case-12, revision 2) compared to Task 6.3. [20] This section seeks to summarize the key observations and conclusions from the final TEA. The final report from PNNL is included in Appendix A.

Akermin specified three K_2CO_3 cases for analysis by PNNL based on previous modeling experience and bench unit performance observations. One of the key feed-back conclusions from the bench unit testing was that the stripper energy performance depends on the kinetics of the stripping process—whereas, the preliminary TEA assumed equilibrium in the stripper.

Each of the Akermin cases assumes biocatalyst coating is deployed in the absorber resulting in either a 6-fold enhancement at operating conditions (current bench unit performance), or a 10-fold enhancement (the longer-term goal, but consistent with recent laboratory data). One final case assumes enzymatic enhancement in both the absorber and the stripping column. A 16-fold absorber column height reduction case was not included in this revised TEA based on available biocatalyst enhancement data at 45°C. Column height reduction assumptions for this revision of the TEA are summarized in Table 11 below:

Table 11: Overall Column Height Reduction Assumptions for PNNL TEA Study

Case	Absorber Flux Relative to Blank	Stripper Flux Relative to Blank
Akermin-3A (6X1)	6	1
Akermin-3A (10X1)	10	1
Akermin-3A (10X5)	10	5

Case 3A (6X1) represents a system with 6-fold reduction in column height relative to blank at operating temperature. This system has coated packing in the absorber with activity comparable to a catalyst formulation demonstrated in the NETL-Akermin bench unit.

Case 3A (10X1) represents a catalyst with a higher activity that results in a 10-fold absorber column height reduction. It should also be noted that increased activity of the catalyst will also result in requiring less overall catalyst, reducing the enzyme variable cost relative to Case 3A (6X1). This catalyst performance assumption is consistent with laboratory data demonstrated with improved biocatalyst formulations—see Table 5

Case 3A (10X5) represents a scenario where catalyst is deployed in both the absorber and the stripper. This case helps to quantify the economic benefit of improving stripper performance. In this case, a 10-fold reduction in height in the absorber and a 5-fold reduction in height in the stripper is assumed. The same catalyst activity is assumed with the same activation energy shift. The corresponding height reductions determined by Aspen are consistent with enzymatic multiplier with temperature data.

PNNL also updated the 30% MEA reference case to be consistent with NETL's most recent baseline (NETL Case 12 version 2). Other process conditions associated with these three K_2CO_3 cases can be found in PNNL Final Report (Appendix A). Table 12 presents the results of PNNL's updated analysis of the LCOE.

Table 12: Summary of Levelized Cost of Electricity (Customer COE) Estimates by PNNL

	No Capture (NETL-11) Supercritical PC Boiler	30% MEA (NETL- 12)	K_2CO_3 Akermin-3A (6X1)	K_2CO_3 Akermin-3A (10X1)	K_2CO_3 Akermin-3A (10X5)
Fuel Cost	14.2	19.6	18.8	18.8	18.8
Capital Cost	31.7	59.6	61.6	59.0	55.2
Variable Cost	5.0	8.7	7.8	7.8	7.8
Enzyme Variable Cost	0.0	0.0	3.2	1.9	2.8
Fixed Operating Cost	8.0	13.0	11.9	11.9	11.9
Transport, Seq. & Monitor (TSM)	--	5.6	5.4	5.4	5.4
COE ($/MWh)	**58.9**	**106.5**	**108.7**	**104.8**	**101.9**
Levelization Factor†	1.269	1.269	1.269	1.269	1.269
LCOE ($/MWh) (customer price)	**74.7**	**135.1**	**137.9**	**133.0**	**129.3**
% Increase in LCOE versus No Capture	**--**	***80.9%***	***84.7%***	***78.1%***	***73.1%***
% Increase in LCOE relative to NETL-12	**--**	**--**	***2.0%***	***-2.1%***	***-4.4%***

†Levelization factor converts the cost of generating electricity (i.e., the COE) to an estimated delivered price of electricity at the point connection to a load, termed levelized cost of energy (LCOE).

Figure 33 presents stacked bar chart of the various contributions to the increased cost of electricity, which helps to illustrate the major contributors to cost.

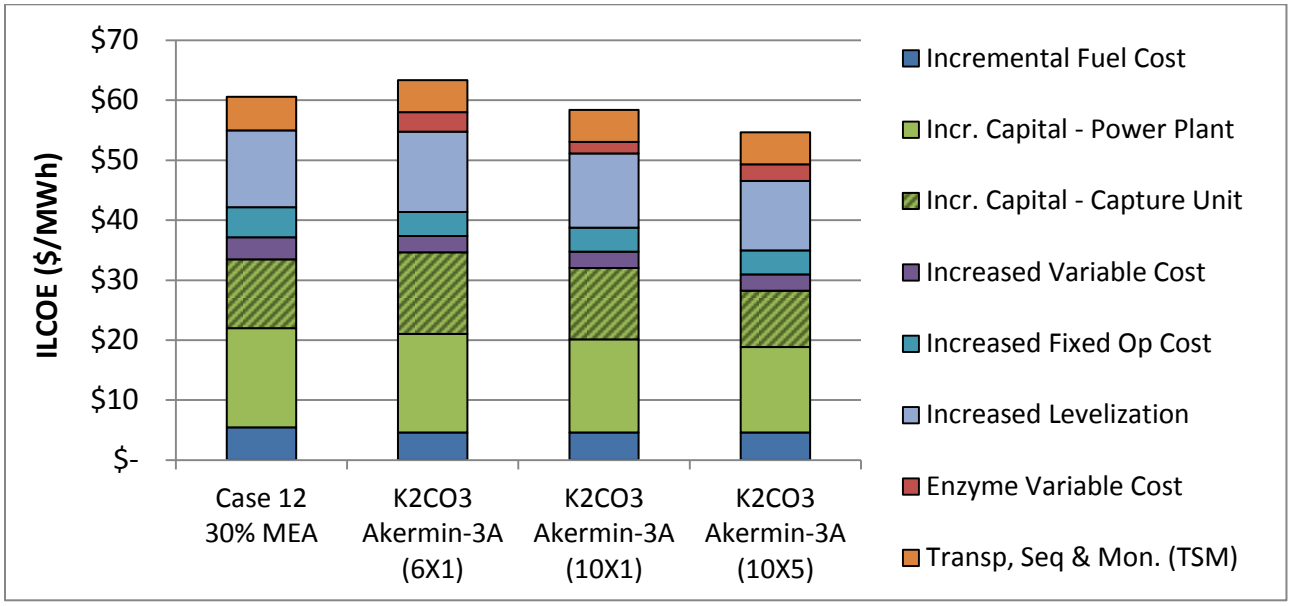

Figure 33: Components of the increase in cost of electricity, including incremental levelization costs.

Components of the increased cost of electricity:

- **Incremental fuel costs:** coal consumption needed to offset increased parasitic loads
- **Incremental capital cost, power plant:** incremental amortized cost of larger power island
- **Incremental capital costs, CO_2 capture unit:** amortized cost of CO_2 capture system, including compression
- **Increased variable costs:** incremental costs for water use, water treatment, maintenance materials, limestone, ammonia, SCR catalyst, ash disposal, caustic, and solvent replacement
- **Increased fixed operating costs:** increased operating labor, maintenance labor, administrative and support, property taxes and insurance
- **Increased levelization:** incremental cost adder (26.9% of all other costs) for delivered electricity
- **Enzyme variable cost:** addresses enzyme replacement cost which includes coating cost as well as removal, recycle, and reinstall and assumes target 3-year replacement cycle for example below.
- **Transportation, Sequestration and Monitoring:** CO_2 transport, storage, monitoring.

Figure 33 illustrates that capital cost has a dominant role in the incremental cost of electricity (and cost of CO_2 capture). A further review shows that the incremental power plant costs are the largest contributor to increased capital costs, comprising about 60% of the total capital charge. The increased capital costs for the power plant resulted because a larger power island is needed to maintain the 550 MWe net power

output. The increase parasitic loads that result from CO_2 capture drive the incremental power plant capital costs. The increased parasitic loads are directly attributable to equivalent work of CO_2 capture and compression that must be supplied by steam and electricity from the power plant. Therefore, optimizing the energy performance of the CO_2 capture system is critical.

The equivalent work of the updated reference case (NETL Case-12, v2, 30% MEA) and the Akermin 3A cases (20% K_2CO_3 enhanced with biocatalyst) is presented in Figure 34. The equivalent work is reduced by about 16% with the biocatalyst-enhanced K_2CO_3 in a basic solvent flow sheet. The contributions to equivalent work for all major process operations is shown, including parasitic impact of solvent regeneration, CO_2 compression, liquid circulation, vacuum blower power, and flue gas fan. The largest component is reboiler equivalent work, or the parasitic impact of steam extraction for solvent regeneration. The equivalent work is the same for all of the Akermin 3A cases because the reboiler temperature is the same and reboiler heat duty is the same. The only difference between the 3A subcases is the capital cost of the absorber and stripper columns.

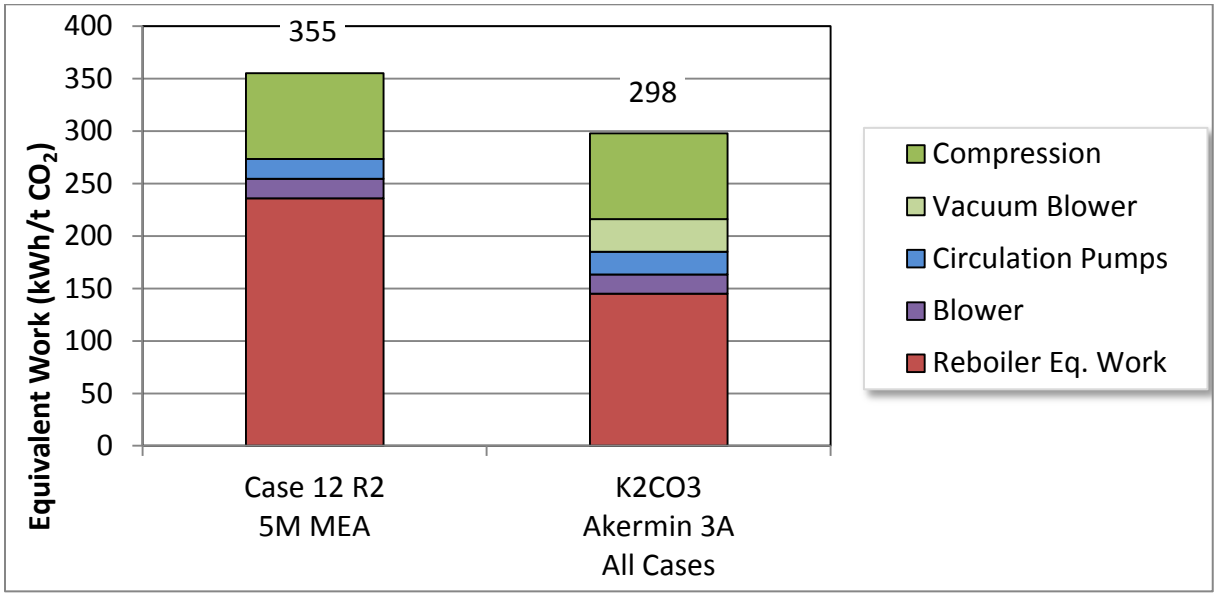

Figure 34: Equivalent Work (kWh/t CO_2) for Case 12 and Akermin 3A Cases

The equivalent work for 20% K_2CO_3 in the Akermin 3A case is about 16% lower than the updated 30% MEA reference case, NETL-12, v2. However, the reboiler heat duty for 3A case and 30% MEA reference case are 3.8 and 3.6 GJ/t CO_2, respectively. The reduction in equivalent work is the direct result of utilization of lower-grade steam in the Akermin 3A case. Obviously, reboiler heat duty is only part of the parasitic power equation. The extraction steam temperature (or its potential to produce power) is also

an important consideration. Minimizing equivalent work reduces parasitic load on the power plant, so lower equivalent work translates into reduced power plant capital costs and reduced cost of capture.

While regeneration at lower pressure (i.e., lower temperature) minimizes the power loss impact of extracting steam from the turbine, it also slows the rate of bicarbonate dehydration and can result in kinetic limitations in the stripping column. To address the kinetic limitations, a significantly larger stripper column was assumed in this TEA update to minimize the reboiler heat duty. Even so, the reboiler heat duty that resulted was about 21% higher than previous estimates (3.8 GJ/t CO_2 compared to 3.13 GJ/t CO_2, see Subtask 6.3). To address the issue of stripper size and cost, Akermin also explored the economics of adding a catalyst to the stripper to reduce its size while maintaining the same reboiler heat duty. Subcase (10x5) assumes a biocatalyst is deployed in both the absorber and the stripper with the same catalyst replacement cycle; a 10-fold reduction of absorber height at 40 to 45°C is achieved, with a 5-fold reduction in stripper height achieved at 80 to 85°C. A broader study to understand the economic merits of varied stripper sizing with catalyst and lower temperature operation has not been fully explored at this juncture. The estimated capital cost of major pieces of equipment can be found in Figure 35.

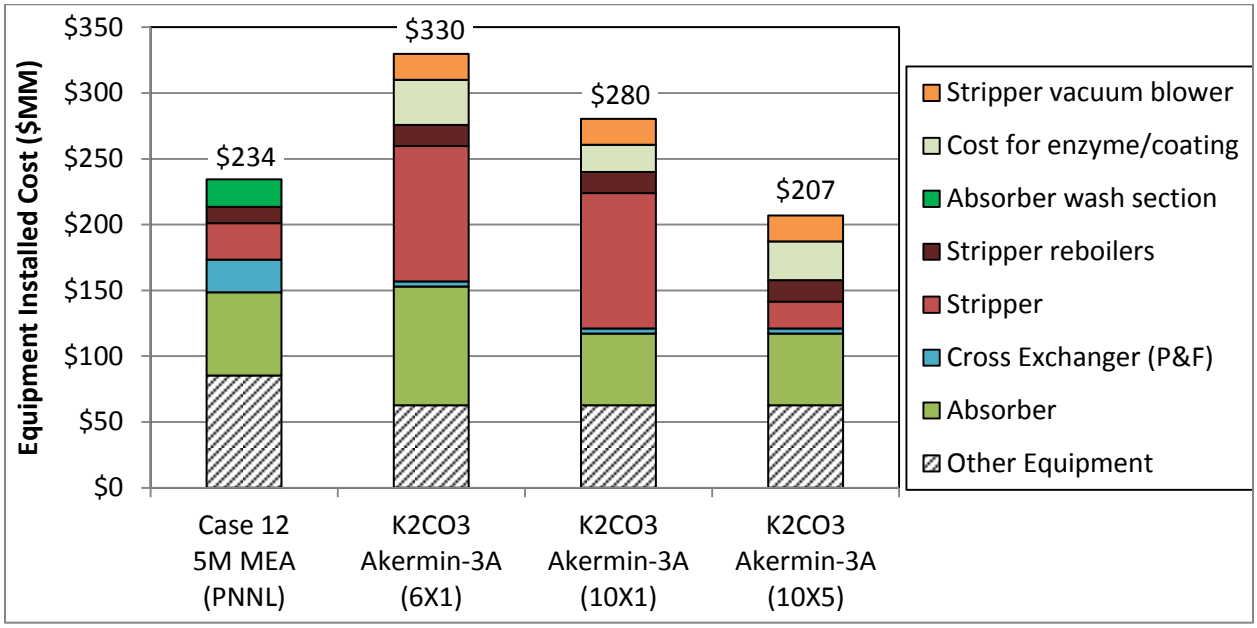

Figure 35: Estimated Equipment Installed Cost for the Full-Scale CO_2 Capture Unit (550 MW Net)

The current demonstration validates the feasibility of a biocatalyst-coated packing system to enable an environmentally-benign (non-toxic, non-hazardous) K_2CO_3 salt solution for CO_2 capture that achieves an essentially pure CO_2 product and produces zero toxic air emissions. All of these benefits were demonstrated while achieving a competitive cost relative to the baseline. Meanwhile, there remain several options that are worth considering for improving overall energy and cost performance in future work.

First, increasing the concentration of K_2CO_3 would seem to be an obvious path to reducing reboiler heat duty, but this approach is confined to a maximum of about 24% K_2CO_3 due to bicarbonate product solubility at 40°C. From an operations perspective, this might equate to holding 22% w/w ± 2% to avoid unintended potassium bicarbonate precipitation, which may result in 10% improvement in specific reboiler duty. Allowing precipitation is another possibility. Precipitation concentration to enhance energy performance has been discussed in the literature, but the resulting system is operationally complex with uncertain capital cost. [21] Alternatively, higher temperature absorption enables higher concentrations, but a less favorable equilibrium performance hinders energy benefits. Conversely, lower concentrations may improve the equilibrium rich loading, but at the cost of increased sensible duty. In the optimization studies, 20% seemed to be a reasonable compromise. Instead, other solvents with higher solubility for bicarbonate might also be considered to improve regeneration energy requirements.

Secondly, novel schemes for solvent regeneration should be explored. Reducing the lean loading requires more heat input per mole of CO_2 released in the stripper. While reducing lean loading improves operational capacity and thus reduces the sensible duty, Akermin's analysis showed that the minimum reboiler heat duty is achieved at the lean threshold—reducing lean loading below this threshold increases rather than decreases the reboiler heat duty in the K_2CO_3 system. This effect has been described in the literature as lean pinch. [22] Alternative stripper designs that minimize lean pinch in the K_2CO_3 system should be explored in future work. Thirdly, alternative flow sheets that maximize potential benefits of a lower temperature stripping process should be explored in future work—including configurations that facilitate or enable deployment of enzyme in the stripper.

Finally, combinations of solvent, flow sheet, and novel stripper designs are expected to provide major benefits to reducing CO_2 capture costs with biocatalyst enhanced solvents.

Subtask 6.5 – Commercial Review of TEA (WorleyParsons)

Review capital cost, operating cost, avoided cost of CO_2 capture, and avoided cost of electricity estimates prepared by PNNL. Provide report to Akermin with the evaluation of a commercial perspective of the proposed approach.

A draft of the PNNL TEA was reviewed by WorleyParsons, who provided a list of questions and preliminary feedback in a conference call. Akermin and PNNL reviewed the WorleyParsons preliminary comments and updated the PNNL report on the final TEA. WorleyParsons reviewed the cost of electricity calculations and also calculated the avoided cost of CO_2 capture based on the TEA results by PNNL.

A comparison of the Akermin and WP COEs are provided in the following (Table 13). The WP calculations validate the COE values from the PNNL report. The differences in the last significant figure are assumed to be related to the rounding of the numbers. This table also includs the avoided cost of CO_2 captured. These values can be compared to the \$68.95/tonne CO_2 for the supercritical capture case in the DOE/NETL Baseline report. [23]

Table 13: WorleyParsons calculation of cost of electricity compared with PNNL-Akermin estimates and cost of avoided CO_2 for each of the Akermin 3A subcases.

	Akermin-3A 6x1		Akermin-3A 10x1		Akermin-3A 10x5	
Total Plant Costs ($/kW)	2,997		2,869		2,685	
Total Overnight Cost (2007$/kw)	3,690		3,534		3,308	
Total Overnight Cost (2007$x1,000)	2,028,542		1,942,782		1,818,541	
Total As Spent Capital (2007$)	4207		4029		3771	
Annual Fixed Operating Costs ($/yr)	48,944,654		48,944,654		48,944,654	
Variable Operating Costs ($/MWh)	11.01		9.70		10.53	
COE($/MWh, 2007$)	PNNL	W-P	PNNL	W-P	PNNL	W-P
CO2 TS&M Costs	5.4	5.4	5.4	5.4	5.4	5.4
Fuel Costs	18.8	18.8	18.8	18.8	18.8	18.8
Variable Costs	11.0	11.0	9.7	9.7	10.6	10.5
Fixed Costs	11.9	12.0	11.9	12.0	11.9	12.0
Capital Costs	61.6	61.6	59.0	59.0	55.2	55.2
COE($/MWh, 2007$)	**108.7**	**108.7**	**104.8**	**104.8**	**101.9**	**101.9**
Cost of CO_2 Avoided ($/t CO_2 avoided)	71.64		66.03		61.80	
Cost of CO_2 Capture ($/t CO_2 cap.)	**52.25**		**48.16**		**45.08**	

The cost of CO_2 captured and the cost of avoided CO_2 can be compared the DOE/NETL Baseline report, revision 2 results: $47.84/tonne CO_2 captured and $68.95/tonne CO_2 avoided. Based on the above results, the cost of capture for Akermin Case 3A (10x1), where biocatalyst is deployed only in the absorber, is approximately equal to that of NETL Case 12, Rev 2. However, the cost of capture is projected to be reduced by about 6% in the case where biocatalyst is deployed in both the absorber and stripper. Likewise, the cost of avoided CO_2 is anticipated to be reduced by 10.4% for the best case.

WorleyParsons' Conclusions:

In general, the PNNL report meets the specified objectives, provided that the WorleyParsons comments are resolved to Akermin's satisfaction. The independent calculation of the COE performed by

WorleyParsons validated the PNNL results. It should be noted that the WorleyParsons calculation was based the capital and operating costs estimated by PNNL. [23]

Below are WorleyParson's recommendations with the Akermin response:

- Include the rationale for the expected absorber reaction rate improvement from 6X to 10X, and a description of the design features (improvements to the pilot design) that could enable such improvement
    - Akermin considers the assumption of a 10-fold enhancement in the absorber reasonable based on the data provided in this report. Specifically, a more recent biocatalyst coated packing formulation (CSP-3 in Table 5, and LW-A145-60C in Figure 20) was tested in the laboratory closed loop reactor system yielded a 12.5-fold enhancement in mass transfer coefficient at 45°C. The estimated multiplier of this sample using a room temperature reference is about 17x.

- Include the rationale for the enzyme performance under the elevated temperature conditions in the stripper column [23]
    - There are numerous literature examples of enzymes operating at elevated temperature. For example, some industrial starch-converting enzymatic processes operate at temperatures as high as 105°C. Moreover, it was already demonstrated that a genetically-engineered CA could effectively operate in a stripper at 87°C. [24] Hence, the use of CA in the stripper appears to be a reasonable proposition.

Task 7 – Engineering of Bench Scale Carbon Capture System

<u>Subtask 7.1 – Prepare Process Flow Diagram and Process Design Specifications</u>

Akermin will prepare a process flow diagram (PFD) for the bench-scale system that will have been reviewed by Battelle, PNNL and NETL. Akermin, in consultation with PNNL and Battelle, will prepare a process design specification that will be submitted to Battelle for review; for example, considering column packing specifics, enzyme loading, flue gas flow and composition, incoming flue gas temperature, humidity, solvent ionic strength, solvent lean capacity (or pH or bicarbonate/carbonate ratios), absorber feed temperature, and reboiler pressure condition. After review by Battelle, the PFD and process design specification will be submitted to PNNL for absorber and desorber column sizing, optimization, and mass and energy estimation.

A bench-scale test unit was designed with the goal of removing 90% of the CO_2 from 500 SLPM (30 Nm^3/hr) (dry basis) of coal-derived flue gas. The unit was constructed in Saint Louis, MO and transported to Wilsonville, AL upon completion of factory acceptance testing (FAT) for commissioning at the National Carbon Capture Center (NCCC).

A PFD for the unit was drafted June 10, 2011 (Rev A) and submitted to Battelle for review in BP1. Based on recommendations from their review, the PFD was updated June 28, 2011 (Rev B), and later on March 16, 2012 (Rev C). Revisions were released as needed including the prebuild release on September 11, 2012 (Rev E), and the as-built released on May 6, 2013 (Rev F). The most current revision is attached in the Appendix B as a final deliverable for the project.

A process design specification was originally drafted September 9, 2011 to solicit budgetary quotes for fabrication of the NETL-Akermin bench unit. Battelle gave inputs to the preliminary process design specification which was used in the bidding process.

Akermin selected EPIC Systems for the final engineering, fabrication and programming for the NETL-Akermin bench unit in December 2011. The NCCC agreed to be the host site for testing, and completed a technical collaboration agreement on May 17, 2012.

As the project evolved, additional releases of the specification and piping and instrumentation diagram (P&ID) were made as needed, the final version being released on May 21, 2012 (Rev E). The specification and P&ID were reviewed on June 27, 2012 by ABS Consulting at the process hazards analysis. Feedback was incorporated into the Controls Process Narrative (Task 7.6).

Subtask 7.2 – Review Bench Unit PFD and Process Design Specification (Battelle)

Battelle will review and comment on the PFD and process specifications by Akermin that shall become the design basis for the bench-scale continuous flow system.

Battelle assisted Akermin in preparation of an outline process specification. Akermin utilized the outline and developed a preliminary process design specification that was reviewed by Battelle.

Subtask 7.3 – Specify Column Sizes, Mass and Energy Balance Estimates, Bench-Unit

PNNL will provide inputs to Akermin's process design specification prior to review by Battelle. PNNL will employ Aspen Plus® and other column performance/design modules, as updated per results of wetted wall testing, to size the CO_2 absorber and desorber columns according to the process design specification. The absorber column shall be designed to remove up to 90% of the fed CO_2 in the simulated flue gas at the nominal design gas flow with enzyme-enhanced column packing. The desorber column design shall use best efforts to minimize reboiler heat requirements. PNNL shall provide mass and energy balance estimates for the bench-scale unit under baseline and enzyme-enhanced conditions.

PNNL used AspenPlus Version 7.3 with rate-based distillation to estimate column sizes assuming 10-fold overall multiplier in mass transfer coefficient and 90% capture of CO_2 from flue gas at near ambient pressures.

The preliminary design at the time of the Battelle review was two absorber columns each with 280-L of M350Y packing (about 98 m^2 surface area) in a column with 15.3 cm packing diameter x 15.3 meter packing height (6.3 inch diameter x 50.2 ft packing). The liquid load with this packing diameter was about 15 m^3/m^2-hr, and the gas superficial velocity was about 0.5 m/s.

Cost, installation and shipping concerns were raised regarding the height of the column with 15.3-m packing since it would have resulted in total column height over 24-m tall (about80-ft) with multiple liquid distribution stages. A two column option was deemed too complex, but the tall column would require more expensive structure and may have siting challenges (siting at NCCC was being discussed, but not finalized). Another concern raised by a third-party was the potential for large edge effects in the smaller diameter with orthogonal cut sheets of corrugated packing. Therefore, to address these concerns, Akermin made a design change that increased the diameter of the column while using approximately the same internal volume (260-L), but also increased the total surface area by 30% in absorber and stripper columns by increasing the specific area of the packing to 500 m^2/m^3 using M500X, or about 130 m^2 packing.

The final absorber design, see Table 14, was frozen at 20.3 cm packing diameter (21.1 cm inside column diameter) x 8-m tall with Sulzer M500X. The liquid load in the revised design was 8.5 m^3/m^2-hr and the gas superficial velocity was about 0.28 m/s. The area efficiency was assumed to be 30% based on literature review. [25] The increased specific surface area was intended to offset the potential loss in effective area with reduced liquid load and gas velocity.

Table 14: Final Absorber and Stripper Column Sizes

Equipment Label	Packing	SA/V (m^2/m^3 pack)	Inside Column Diameter (cm, nominal)	Packing Height (m)	Pressure (barg)	Gas and Liquid Feed Temperatures (°C)
ABS-1	M500X	500	21.1	8 m	0.07	20 to 60°
STR-1	M500X	500	34.3	8 m	-0.7 to 2	65 to 140°

Subtask 7.4 – Prepare Engineering Package for Bench-Scale Unit

Akermin will work closely with vendors to prepare the engineering and design specification for the bench-scale unit including piping and instrumentation diagram. Akermin will work with vendors to produce equipment drawings and general arrangement drawings. Akermin will produce column design drawings (with vendors) and packing specifications in consultation with collaborators (PNNL and Battelle).

An engineering process specification was prepared in the fourth quarter of 2011. This document was the basis for a fixed price estimate in preparation by a selected vendor for the bench unit. The piping and instrumentation diagrams were finalized January 2012 (see Appendix C – Bench Unit Piping & Instrumentation Diagram (P&ID)), equipment drawings, including columns, and general arrangement drawings (see Appendix D – General Arrangement).

Subtask 7.5 – Consult and Review Final Column Design (Battelle)

Battelle will consult with Akermin and provide assistance as needed for development and review of preliminary column design for bench-unit.

Battelle provided a review of the Akermin PFD, mass and energy balance, and absorber sizing. The preliminary design at the time of the Battelle review was based on assumed 10-fold biocatalyst enhancement that would incorporate (2) columns with 280-L of M350Y packing (about 98 m^2 surface area): 15.3 cm packing diameter x 15.3 meter tall (6.3 inch diameter x 50.2 ft packing).

Battelle's report is attached. Conclusions from the Battelle report are based on the preliminary design.

The material and energy balances from the Aspen simulations converged correctly and the calculations are sound in both models. However, heat loss was not included in the Aspen simulation. It is recommended that a 10% heat loss be included in the Aspen model before the design is finalized.

The column design appears sound as the liquid load of the column is sufficient. However, the operating point of the column is at the low end of the F factor vendor data, which may limit the turndown ability of the column. It appears the 6" diameter was selected as a reasonable trade-off between performance and physical practicality (length-to-diameter ratio). Akermin may consider further investigation of additional column diameters. A smaller diameter will increase the F factor and pressure drop, but will increase the ability to turn-down the absorption column. A larger diameter will decrease an already small F factor and pressure drop, and will decrease the ability to turn-down the column. If different diameters are considered, the column liquid load and flooding should be verified with Sulzer to make sure they are good.

The pressure drop in the Aspen model may be low. There may be additional pressure drop due to flow distributers and mist eliminators. It is recommended that Akermin consider verifying with Sulzer what equipment is needed for the two absorption columns and what pressure drop is expected in the design then to add that pressure drop to the Aspen model. The fan then can be designed from that data.

Equipment sizing and selection should include some safety factor (5 to 10%) to allow for operational adjustments and inefficiencies. [26]

Subtask 7.6 – Controls and Process Narrative

Akermin will prepare a minimum functional controls document, loop diagrams, and process narrative to specify control system for programming and integration by others.

A controls and process narrative was drafted June 25, 2012. Recommendations from a process hazards analysis conducted June 27, 2012 were incorporated into a redraft of the narrative. Akermin also prepared a standard operating procedure (SOP) for the unit that was provided to NCCC operators.

Task 8 – Procure, Install and Startup Bench-Scale Unit (Lead Organization: Akermin)

Subtask 8.1 – Procure Bench-Scale Unit

Akermin shall procure the bench-scale unit. Akermin will work closely with the chosen supplier through a series of design reviews to insure that the system meets all process and design specifications.

Subtask 8.1 included engineering review efforts and engineering revisions that were tracked through fabrication and factory acceptance testing of the bench unit control system. A purchase order for the bench unit skid was issued on March 13, 2012 to EPIC Systems Inc., and a site meeting at the NCCC was held on August 28, 2012 to plan for design integration, installation and commissioning of the bench unit. Factory acceptance testing was completed at EPIC Systems in Saint Louis, MO on November 27, 2012 that indicated acceptable completion of fabrication and control system integration suitable for shipment to the NCCC host site in Wilsonville, AL.

Subtask 8.2 –Install and Commission Bench-Scale Unit

Akermin shall coordinate delivery, installation and commissioning of the bench-scale unit. Akermin shall implement and test a data acquisition system for the bench unit. Akermin will commission the bench unit operations using specified carbonate solvent with baseline packing materials (no enzyme).

The NETL-Akermin Bench Unit was delivered at the NCCC on November 28, 2012 and installation occurred on December 5, 2012. Power, flue gas and ultimately steam were operating on the skid by December 12, 2012. A power plant outage occurred on December 17, 2012, resulting in a foreshortened commissioning window. As a result, the final commissioning and baseline (blank) testing efforts were pushed into middle of January 2013 and completed by the end of February 2013.

Task 9 – Demonstrate CO_2 Capture in Enzyme Catalyzed Bench-Scale Unit (Lead: Akermin)

Subtask 9.1 – Procure Scaled-Up Enzyme

Akermin will work with enzyme suppliers to procure sufficient quantities of specified enzyme at specified purity as needed to manufacture the bench-scale unit column packing materials.

Akermin selected Novozymes A/S of Denmark as the enzyme supplier to support developmental needs. All the work described in this report was performed with CA designated as NS81239 generously provided by Novozymes.

Subtask 9.2 – Scale-up Immobilized Enzyme Column Packing

Akermin will investigate commercial coating methodologies for integration of its silica-based enzyme immobilization chemistry onto absorption column packing material. Akermin will scale-up the immobilized enzyme coating process by working with Sulzer ChemTech, a commercial supplier of coated packing material. Conceptually, the immobilization matrix would be deposited onto packing material via industrial spray coating techniques, but scale-up development is needed to adapt Akermin's laboratory process efforts to the next scale. Akermin will scale-up to produce approximately 200 to 400 L of immobilized enzyme on column packing for bench-scale testing. Several smaller-scale structured packing samples will be prepared and tested for activity as the process is developed and scaled-up.

As described in Subtask 5.2, Akermin developed a technique for spray-coating a CA-containing porous silica coating onto stainless steel structured packing for lab-scale testing. After coating and thermal curing, the coated structured packing samples were equilibrated in carbonate buffer for 24 – 72 h. The resulting assembled packing sample was then tested in Akermin's CLR at 45°C. During the optimization process, Akermin identified a coating formulation that successfully resulted in highly-repeatable overall mass transfer coefficient enhancements between 8-fold and 11-fold with greater the 90% retention of initial mass transfer performance after more than ten days in the CLR.

The first scaled-up coating campaign was undertaken in January 2013. The aforementioned porous silica CA encapsulation and coating process was scaled-up with the assistance of a local coatings specialty shop, Custom Fabrications and Coatings (CFC). The effort included spray-coating and curing of 36 elements of 8-inch diameter Sulzer packing along with two elements of 4-inch packing. The latter 4-inch elements serve as a production run sample for laboratory quality assurance testing.

This 275-liter production run (about 130 m^2 packing) represents greater than 500-fold scale-up of the typical 0.5-liter (2-inch diameter) packing element that is produced and tested in the laboratory. The deposition of all the coating layers was completed by the third week of January, at which time the coated packing was transferred into the industrial oven at CFC. The packing elements were then assembled by Akermin into complete structured packing units and hydrated in a solution of approximately 20% K_2CO_3. Figure 36 shows images of various steps of the scaled-up production run at CFC: A) single rack

containing sheets from an 8-inch diameter structured packing element after coating; B) an 8-inch diameter section of packing during the assembly process; and C) an assembled section of 8-inch packing placed in bucket for hydration stage in carbonate buffer prior to shipping.

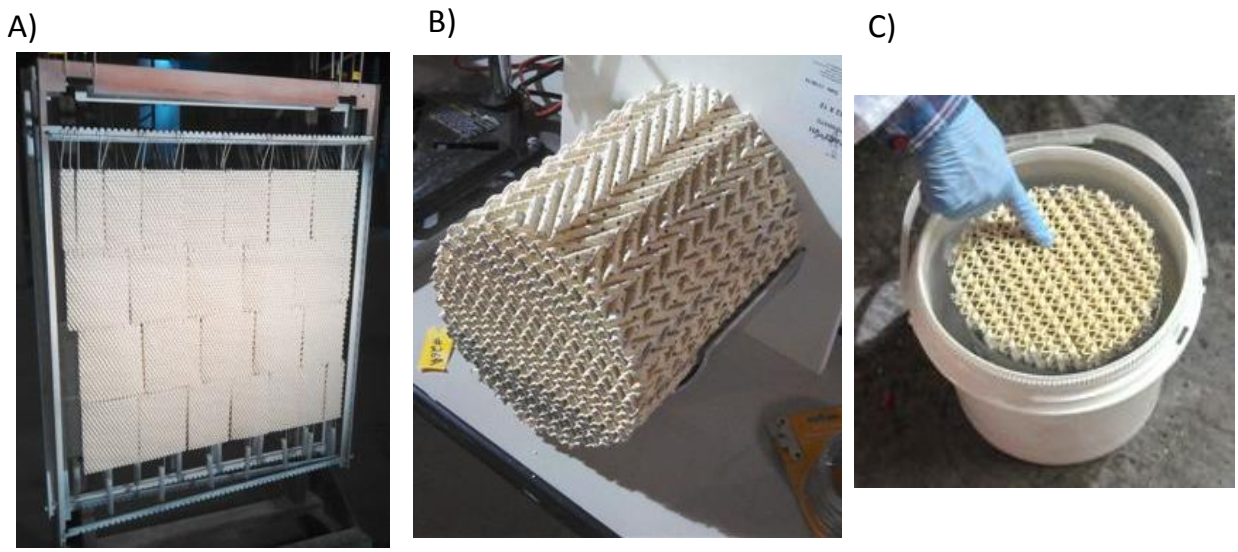

Figure 36 Photographs from 8-inch diameter Sulzer packing coating production run at CFC

The first production run had an apparent process upset which resulted in poor enzyme retention and poor activity, resulting in only 4-fold enhancement over the blank. A detailed review of critical process parameters attributed the process upset to uneven temperature gradients in the gas-fired furnace that was used to cure the coating. After detailed review, the recommended action was to improve temperature control in the curing process, which was afforded with smaller electrically heated ovens.

A second coating campaign was initiated in early April and completed by the beginning of May 2013. Thirty six units of 8-inch diameter coated/hydrated Sulzer M500X packing were transported to the NCCC in Wilsonville Alabama and loaded into the NETL-Akermin bench unit absorber on Tuesday May 7, 2013. The assessment of enzyme-catalyzed CO_2 capture began at 11 PM on May 7, 2013.

Subtask 9.3 – Operate Bench-scale Unit

Akermin will operate the 500 SLPM bench-scale continuous flow reactor for approximately 5 months at the NCCC, with the goal to demonstrate 90% removal of CO_2 from coal-derived flue gas and explore energy performance under various conditions. For approximately 45 days of this testing period the unit will be operated on flue gas containing approximately 4% CO_2 representative of a natural gas fired boiler. For the remainder of the period the unit will be operated on flue gas containing approximately 12% CO_2. Akermin's on-site presence on an as-

needed basis will have an anticipated duration of eight-to-nine months. The duration is based on time for install and interconnections, first run commissioning, baseline testing (without enzyme catalysis), approximately five months testing with immobilized enzyme to demonstrate enzyme performance and longevity, and de-commissioning from the NCCC test slot. The NCCC will provide flue gas and support utilities for testing. While the system will be fully-automated, it is anticipated that Akermin will provide all on-site operational labor as needed.

Steady-State CO_2 capture performance

The biocatalyst-coated packing was installed and began operations on May 7, 2013. The total operational time on flue gas was approximately 2750 hours at the official end of project (midnight on October 1, 2013), but data is presented through 2800 hours on-stream. Various parametric tests were performed during the May-to-June timeframe, and those brief periods are annotated in Figure 37.

Figure 37 shows the steady state capture data for the total time on flue gas. This endurance test was conducted at the design gas and liquid flow conditions: 30 Nm^3/hr (dry basis), 7 kPa absorber bottom pressure, 275 LPH liquid flow, 20% K_2CO_3 and lean loading of approximately 25% carbonate conversion to bicarbonate. The local ambient pressure at the NCCC is about 1.0 bar (absolute). There were a few periods of parametric testing in the first 100-hrs and also as noted on the figure. Flue gas temperature was variable with time of day and weather since supply lines were un-insulated. While flue gas composition had some diurnal variation, it was generally about 12% CO_2 for the first 1300 hrs on-stream, and 4% CO_2 for the remainder of the time (except where noted).

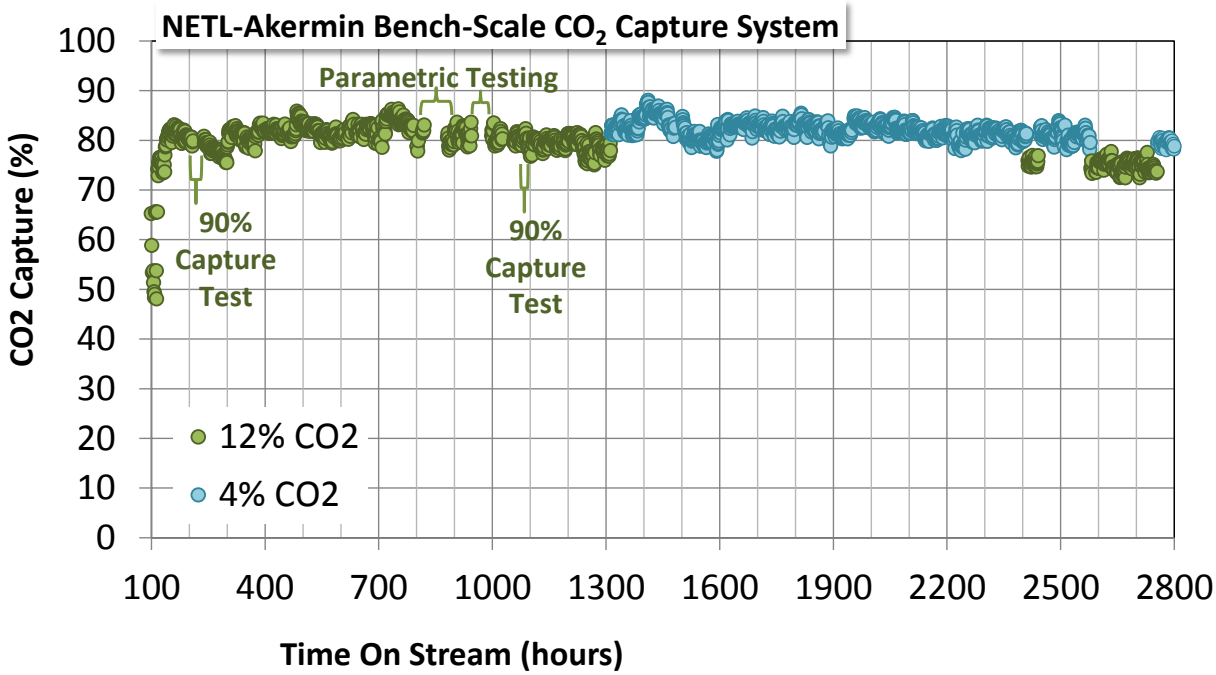

Figure 37: CO_2 capture performance of NETL-Akermin bench unit (based on time on flue gas).

CO_2 capture performance based on hours since startup is presented in Figure 38 with annotations indicating short periods where flue gas was not supplied to the bench unit system.

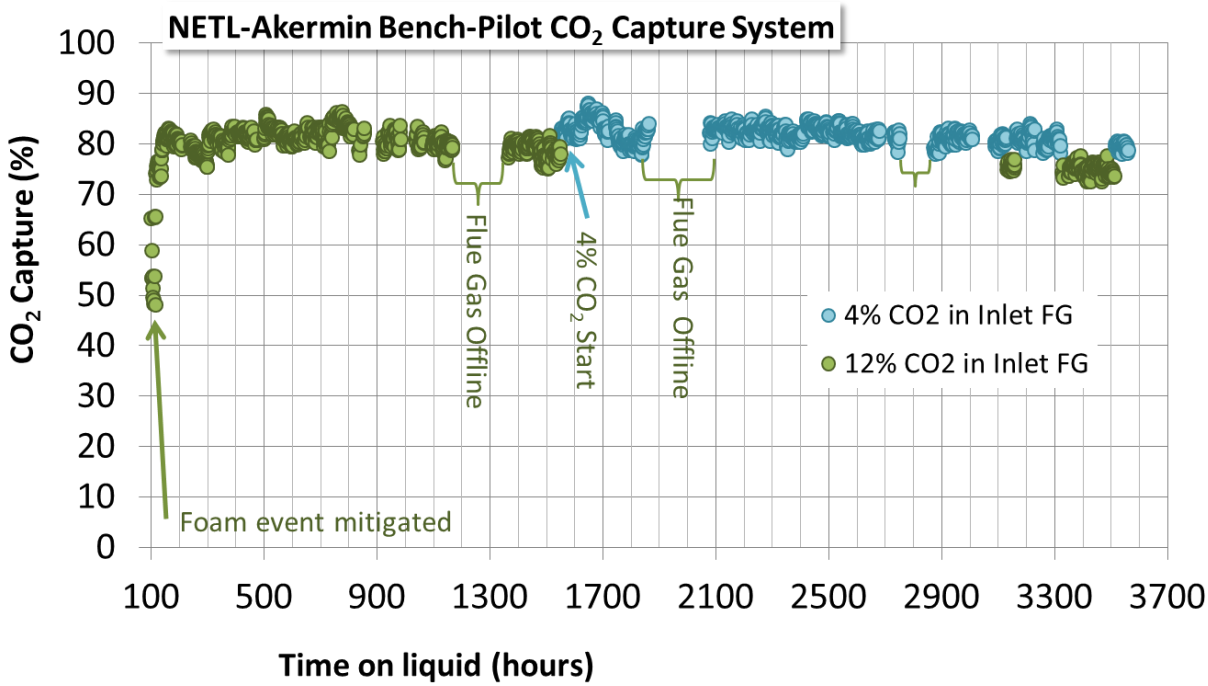

Figure 38: CO_2 Capture performance of NETL-Akermin bench unit (based on time on liquid).

Of the total 3560 hours since startup, the flue gas was supplied approximately 79% of the time. Of the available flue gas supply, the NETL-Akermin bench unit was online 2800 hrs, or about 99% of the time flue gas was available. Maintenance actions required while the system was in operation included modification of the gas analyzer cabinet around 800 hours after start-up and condensate pump (P-3) maintenance at around 2420 hours after start-up and 3270 hours after start-up. The NETL-Akermin bench unit proved to be robust and the enzyme catalyst responded well to the various process shutdowns. Generally, liquid continued to circulate during flue gas outages where possible, except when instrument air was not available at the plant.

Figure 37 shows gaps where the system was online with flue gas, but operating at conditions other than the design gas and liquid flow rates. One of these gaps was the "90% Capture Test" performed between 215 and 225 hrs on-stream. In this case, the flue gas flow was adjusted to equivalent of 19 Nm^3/hr dry basis; the liquid-to-gas (L/G) ratio was held at the design ratio (9.17 L/Nm^3 dry) with lean loading in liquid equal to 0.25 X_{CL}. The 90% capture test was repeated between on-stream hours 1080 and 1090

using 19.5 Nm^3/hr (dry) at the design L/G and 0.25 X_{CL}. Several other tests were performed prior to the first 100 hours on stream to explore impact of varied gas flows at constant lean loading at the design liquid-to-gas (L/G) ratio.

Foaming was discovered in the first 100 hours of operation. This foaming event was attributed to initial transient enzyme leaching, but was easily mitigated with approximately 300 ppm initial antifoam addition. Afterward, approximately 100 ppm antifoam was dosed into the condensate tank about once per week to supplement any possible degradation or loss of antifoam over time; however, it is uncertain if any further benefit was gained after the first few additions. Therefore, the antifoam selection and make-up rate require further investigation.

Parametric energy studies were also performed to understand the impact of rich loading (820 and 890 hours) at constant reboiler pressure, and varied reboiler pressure (i.e., varied reboiler temperature) with approximately constant rich loading as fed to the stripping column (during 940 to 1000 hrs on stream). Results from these parametric energy studies are discussed later in this subsection.

Biocatalyst-coated packing demonstrated an on-going stable performance with an average of about 80% CO_2 capture using 8-m tall packing. This demonstrates a significant and consistent enhancement to the mass transfer rates in K_2CO_3.

Enzyme Replacement Cycle Estimates

While the percentage of CO_2 capture was fairly stable over the course of the endurance run, a detailed data analysis was undertaken to attempt to quantify the decline of catalyst performance with time. This "activity" measurement is best quantified via calculation of the volume average mass transfer coefficient, k_1 (using Eq. 4 previously presented), which has units of inverse time (s^{-1}, or min^{-1}):

$$k_1 = \ln\left[\frac{X^*_{CO_2} - X_{CO_2}}{X^*_{CO_2}}\right]/\tau \tag{4}$$

Where $X^*_{CO_2}$ is the CO_2 capture fraction at equilibrium with lean solution, X_{CO_2} is the measured CO_2 capture, and τ is the gas space time based on the ratio of packed volume by actual volume flow of gas fed to the absorber—a value that should be approximately constant for the endurance test.

The lean loading varies during operation within a small band, but to ensure the analyzed data did not deviate too far from the typical operating condition, only data that were within ±0.5% of the median equilibrium capture condition were used to estimate the decline in mass transfer. Figure 39 shows the trend of normalized mass transfer coefficient versus run time for all flue gas conditions (12% CO_2, and 4% CO_2 feed conditions).

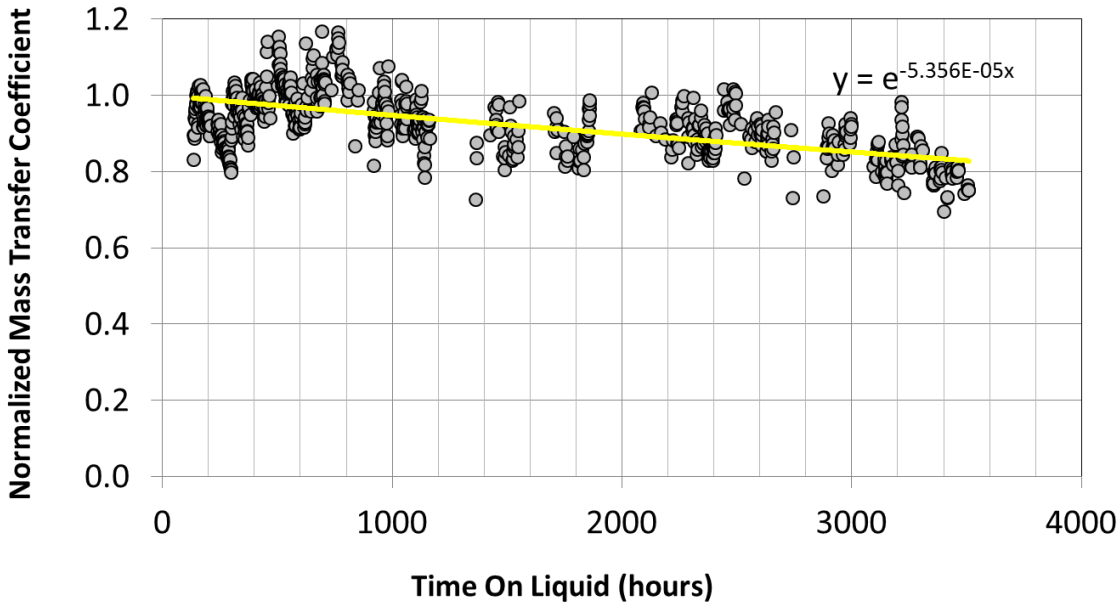

Figure 39: Normalized mass transfer coefficient with time; characteristic decay rate estimated.

Even though stable performance of around 80% CO_2 capture was observed (Figure 37), a thorough data analysis revealed some decline in catalyst activity (Figure 39). Table 15 provides the characteristic time and half-life of the overall mass transfer performance assuming an exponential decay with time on stream. Considering the relatively short test period compared to the characteristic time, a longer test period is recommended in future work to achieve best accuracy.

Table 15: Preliminary catalyst replacement cycle estimates based on current demonstration with 20% K_2CO_3

	Exponent (hrs^{-1})	Time Constant (days)	Half Life (days)
Regression Results:	5.356 E-05	778	539

The catalyst might be expected to retain 50% of its initial mass transfer performance after one year when operated at a power plant with flue gas similar to that received from the NCCC. Enzyme development to improve thermal stability along with improved biocatalyst coating formulation to increase coating durability and adherence to the structured packing support are expected to further improve the long-term endurance performance. It seems realistic that a two-year replacement cycle or better can be achieved with some additional development. Akermin is targeting a three-year replacement cycle as a goal for commercialization, and this goal was implemented into the updated TEA in Subtask 6.4.

Parametric Absorption Rate Studies

Figure 40 presents CO_2 capture data collected at constant lean loading (0.25 X_{CL}), constant liquid-to-gas (L/G) ratio (the design ratio), and constant 40°C lean feed temperature to compare biocatalyst performance to that of the blank (uncatalyzed) packing. Data is also presented in a first-order rate plot in Figure 40(b) to linearize CO_2 capture data, which enables more confident extrapolation to 90% capture for the blank (non-catalyzed packing).

All cases use 36 layers of 8-inch diameter x 8.75-inch tall M500X packing in 8.33-inch inside diameter column. Blank data indicates an improvement in effective area with a higher drip-tube density liquid distributor. The same high drip-tube density distributor was used for biocatalyst-coated packing experiments as well as for comparative blank testing.

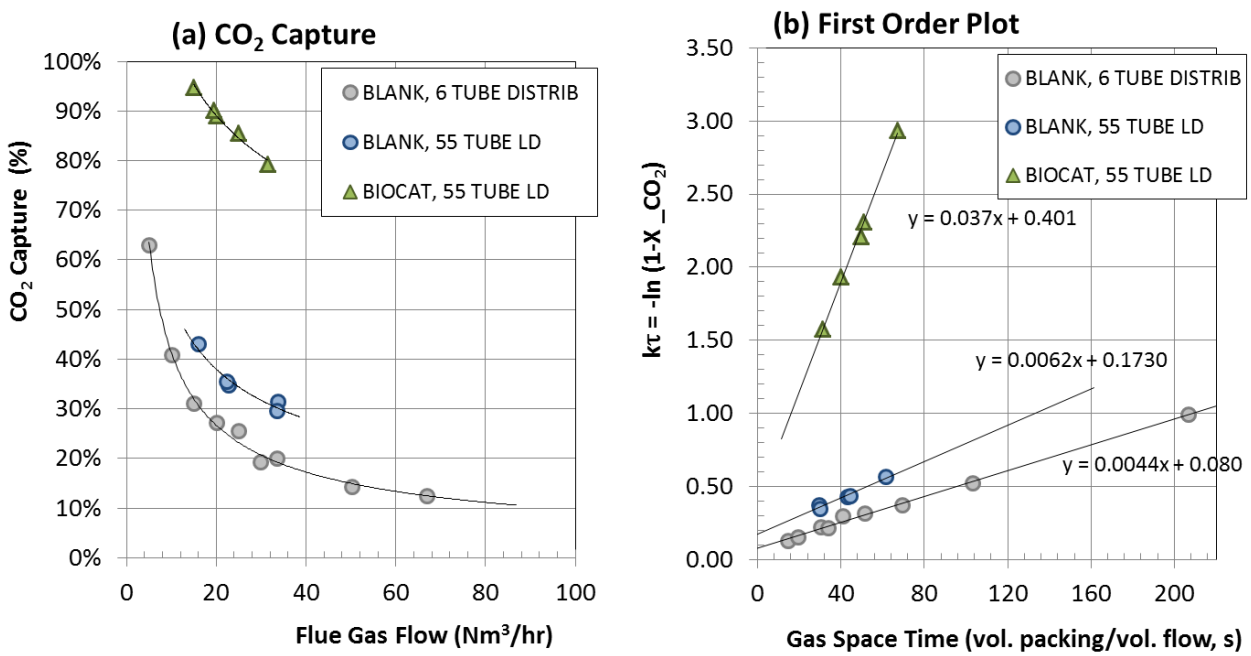

Figure 40: CO_2 capture as a function of gas flow (or space time) for various distributor designs

Investigations demonstrated 90% capture at approximately 20.1 Nm^3/hr gas flow rate (19.5 Nm^3/hr dry basis) with biocatalyst-coated packing. For packing without catalyst, data trends indicate that 90% capture would be achieved at approximately 2.8 Nm^3/hr gas flow (about 2.7 Nm^3/hr dry) with the same liquid-to-gas (L/G) ratio. In contrast, the same volume of biocatalyst coated packing demonstrated 90% capture with in the same column with the same L/G ratio. In other words, a 7-fold increase in gas flow rate can be treated to 90% capture in the current column due to the presence of the biocatalyst.

Figure 41 was used to estimate the area efficiency of the bench unit at the design condition as well as to quantify key enzyme performance parameters needed for process modeling.

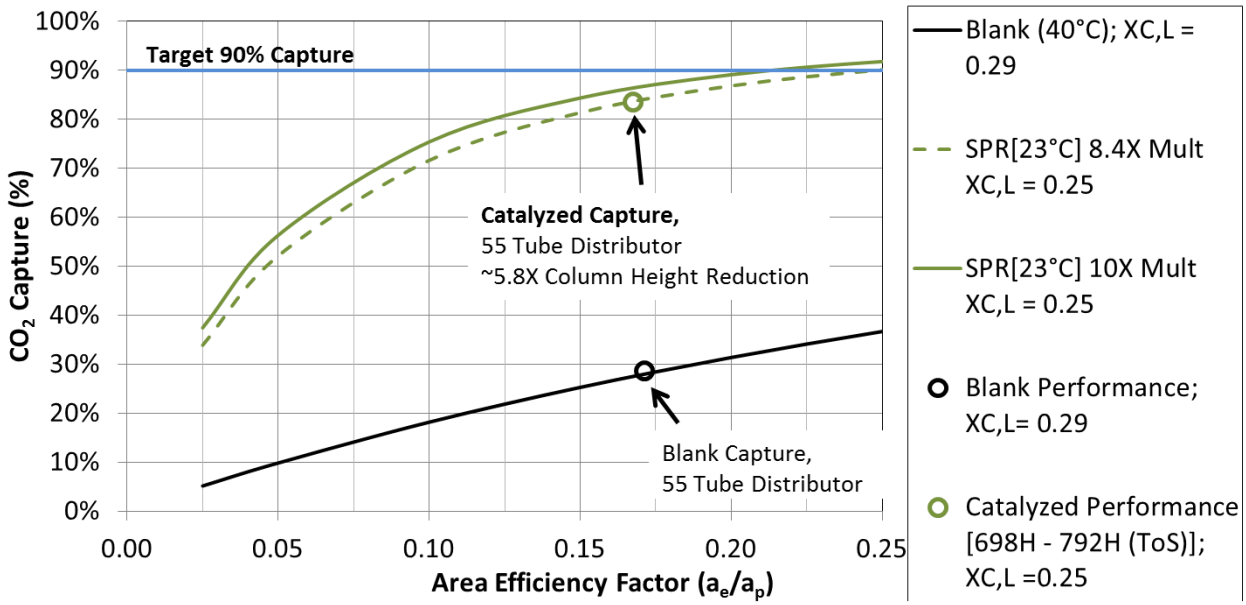

Figure 41: Aspen predictions of CO_2 capture in the NETL-Akermin bench unit with blank packing and biocatalyst coated packing as a function of area efficiency factor.

An Aspen prediction of "blank" CO_2 capture in the bench unit was generated as a function of varied area efficiency factor ($\eta_e = a_e/a_p$). Modeling results (plotted as trend line) were compared with the corresponding CO_2 capture data for bench-unit absorber column operating under similar conditions. The area efficiency was determined to be about 17% at the design gas and liquid flow conditions. Curves for biocatalyst indicate a room temperature lean multiplier of approximately 8.4-fold relative to 23°C blank and equates to about a 6-fold column height reduction. The difference between the 6-fold column height reduction estimate based on modeling for the same gas flow rate, and the 7-fold increase in gas flow at 90% capture for the same liquid-to-gas (L/G) ratio is attributed to wetted area differences with varied gas velocity.

In summary, 90% CO_2 removal in the current column can be achieved with 7-fold higher gas flow with biocatalyst than can be achieved with the blank (un-coated packing). Area efficiencies realized at this scale can be improved with scale-up.

Heat Stable Salt Accumulation

Liquid samples were collected by NCCC and analyzed by Southern Research Institute (SRI) to detect sulfates, nitrites, and nitrates using quantitative analysis by ion chromatography (IC). Figure 42 presents heat stable salt (HSS) accumulation data during the entire biocatalyst operating period from May 7, 2013 through the beginning of October 2013. HSS are compounds that do not decompose under stripping

conditions and therefore represent an irreversible loss in the absorption capacity. Nitrates (NO_3^-) were shown to be below the detection limit in SRI's present method. However, previous analysis from the Akermin system and analyzed in detail by SRI indicated nitrate concentrations are about 20% of the nitrite concentration. This assumption is used for the plot below and data analysis that follows.

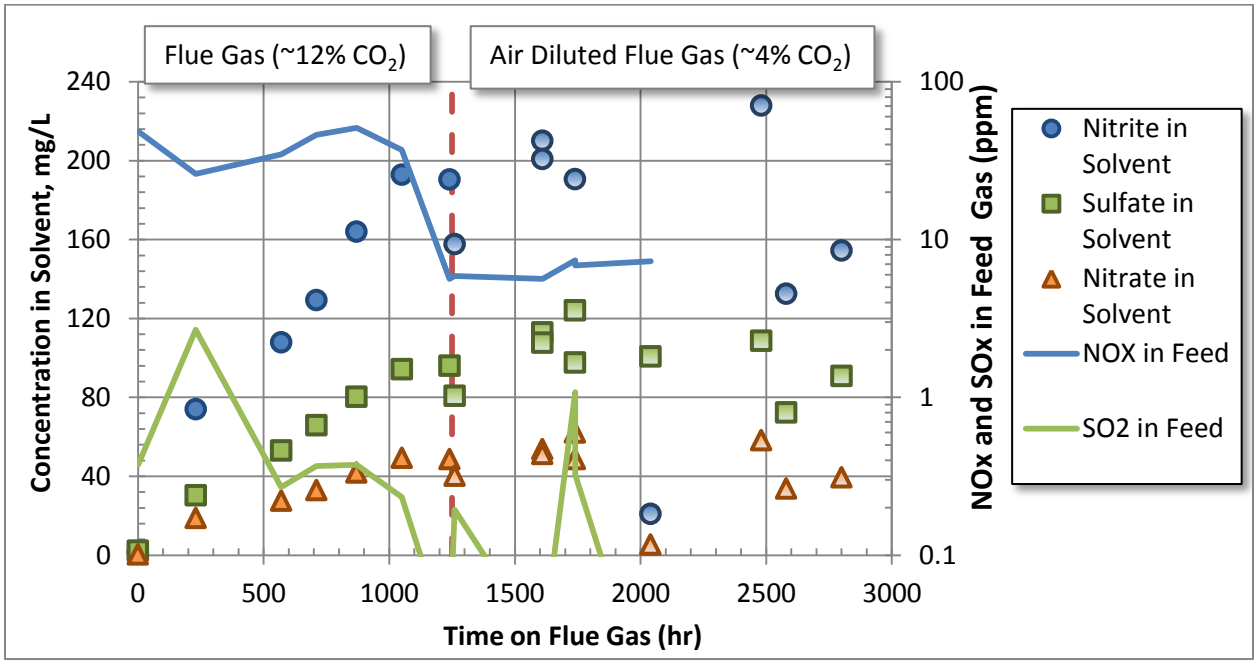

Figure 42: Quantitative analysis of sulfate and nitrite build up with time.

Table 16 presents HSS concentrations that accumulated after 1260 hours on 12% CO_2 coal flue gas from the NCCC. The accumulation of HSS correlated with the concentrations of SO_2 and NO_2 contaminants fed to the system (0 to 3 ppm SO_2, and 26 to 52 ppm NO/NO_2). Loss in solvent capacity is calculated from the HSS accumulation rate. Minor additions of solvent were required to make-up for liquid sampling (about 0.6 L/100 hrs). Capacity losses are corrected for solvent additions in the last column.

Table 16: Heat stable salts and estimated loss in annual solvent capacity based on undiluted coal flue gas.

Standard Test Conditions [12% CO_2 Feed, 5/7/2013 to 7/8/2013, 1260-hrs on flue gas]	HSS (mg/L) after 1260 hrs	Annual Loss of Solvent Capacity	Corrected Annual Loss of Solvent Capacity
Nitrite (NO_2^-)	191	0.80%	0.95%
Nitrate (NO_3^-)	*96*	*0.15%*	*0.16%*
Sulfate (SO_4^{2-})	40	0.39%	0.42%
Total	327	1.34%	1.54%

Table 17 presents incremental HSS accumulated during the air-diluted flue gas test period between 1260 and 2820 hours on-stream. Results suggest there is no quantifiable accumulation of HSS during the test period with air-diluted flue gas.

Table 17: Heat stable salts and estimated loss in annual solvent capacity based on air diluted flue gas feed.

Air Diluted Testing [4% CO_2 Feed, 7/8/2013 to 10/3/2013, 1560-hrs diluted gas]	Increase in HSS (Δ mg/L) 1260 to 2820 hrs	Annual Loss of Solvent Capacity	Corrected Annual Loss of Solvent Capacity
Nitrite (NO_2^-)	-3	-0.11%	-0.05%
Nitrate (NO_3^-)	*-0.8*	*-0.02%*	*-0.01%*
Sulfate (SO_4^{2-})	-10	-0.05%	-0.01%
Total	-13.8	-0.18%	-0.07%

HSS accumulation amounts to approximately 1.53% /year loss in K_2CO_3 capacity with the NCCC's supplied coal flue gas. Under the dilute air condition, there is no quantifiable build-up of HSS.

Corrosion Product Analysis

Liquid samples were collected by NCCC and analyzed by SRI for typical stainless steel corrosion products using inductively-coupled plasma mass spectrometry [ICP/MS]), see data presentation in Figure 43. Typical composition for 304 Stainless Steel*: Fe 71%, Cr 18%, 8% Ni, 2% Mn, Others <1%*. Using the slope of the nickel accumulation data, it was concluded that the corrosion rate is equal to about <0.1 microns per year, given approximately 32 m^2 internal surface area (excluding packing).

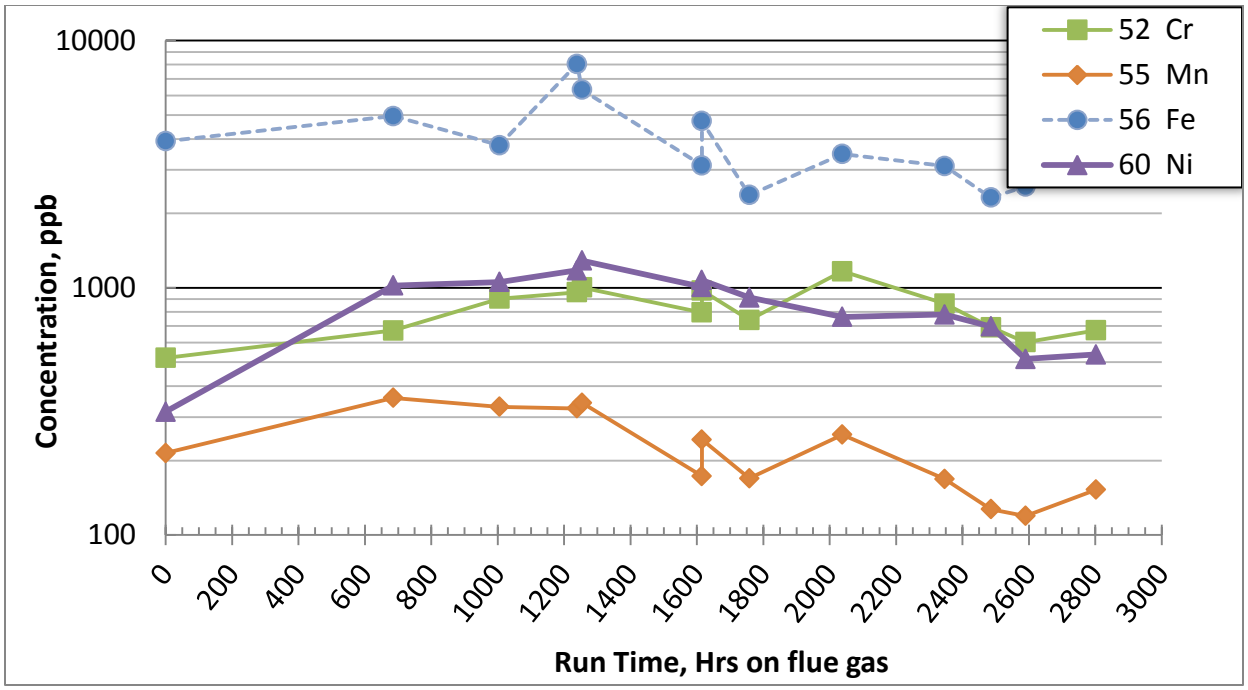

Figure 43: Results for corrosion product accumulation.

Corrosion of stainless steel in the presence of K_2CO_3 is negligible in the post-combustion flue gas application studied.

Trace Heavy Metal Accumulation

Liquid analytical results for other trace contaminants are presented in Figure 44. Liquid samples were collected by NCCC and analyzed by SRI as previously described. The known inhibitors of CA, mercury, copper, and silver (Hg, Cu, Ag), were near or below the lower detection limit, and lead (Pb) was three orders-of-magnitude lower than the expected IC50 (50% inhibition concentration for CA in standard buffer).

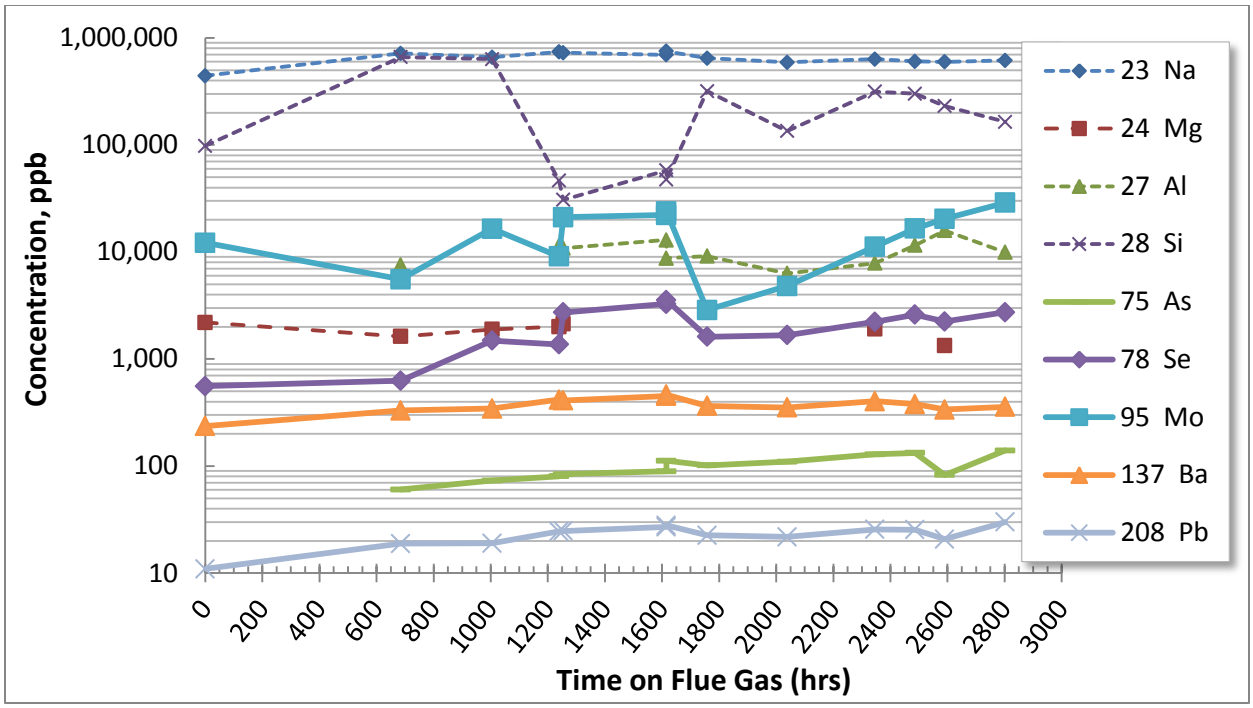

Figure 44: Liquid sample analytical results for various metals.

Conclusion: build-up of heavy metals was insignificant using the NCCC supplied flue gas, and concentrations were well below estimated inhibitory thresholds.

CO_2 Product Purity

Table 18 presents an analysis of trace oxygen and nitrogen in the CO_2 product gas captured by the bench unit. Samples of the CO_2 product were collected and analyzed by NCCC using Gas Chromatography (GC) with a thermal conductivity detector. A separate oxygen peak was not detectible with the current GC setup, but the combined oxygen and argon concentrations were less than approximately 100 ppmv. Results indicated greater than 99.9% purity in the dry product.

Table 18: Results of CO_2 product sampling and (dry basis) analysis by Gas Chromatography

Component	Sample #1	Sample #2
O_2	ND	ND
Ar + O_2	0.01%	0.01%
N_2	0.01%	0.01%
Net CO_2 Purity (dry basis)	99.98%	99.98%

Heat Loss Analysis

Figure 45 indicates that there are five key areas of heat losses in the NETL-Akermin bench unit. It is important to accurately predict the system energy performance under nearly adiabatic conditions at larger scale, and so it is important to quantify and account for the effects of heat losses on the bench scale test unit. Liquid temperatures measured in the bench unit are indicated for one of the typical operating conditions.

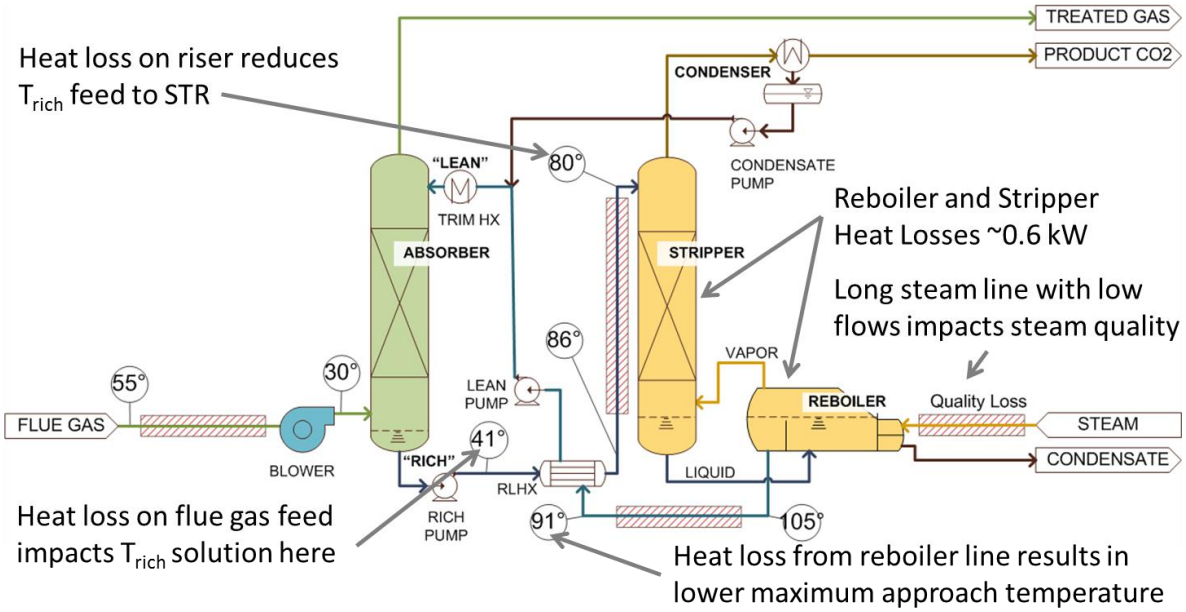

Figure 45: Key areas of heat loss. The impact of heat loss on liquid temperatures is indicated for an atmospheric pressure regeneration condition.

Reduced liquid temperatures as fed to the regeneration column can be accounted for directly in the model, but it is also important to quantify the general heat loss from the reboiler and stripping column. Figure 46 provides a heat loss estimate for the reboiler and stripping column as a function of internal surface temperature based on column dimensions, insulation specifications, and assuming 25°C ambient.

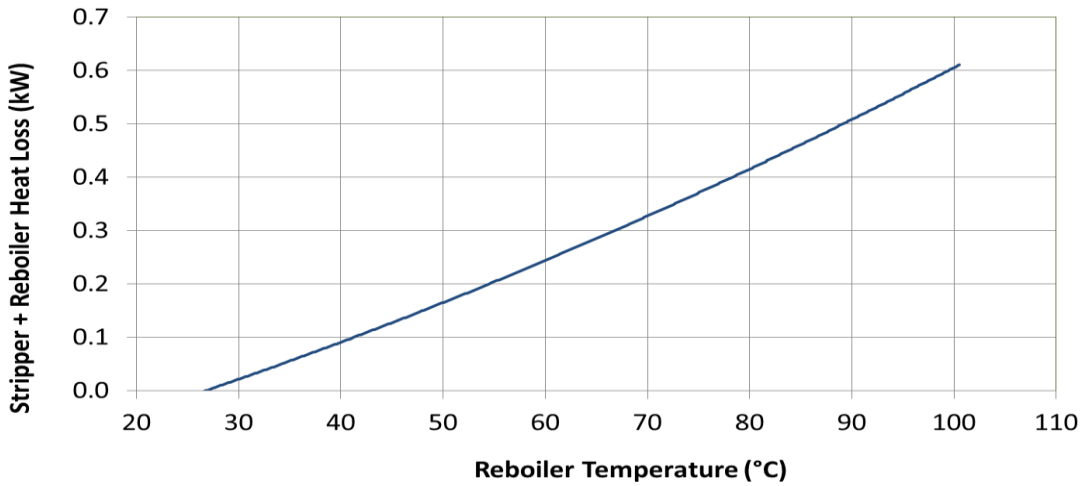

Figure 46: Heat loss estimates for the reboiler and stripper column.

Reboiler heat duty parametric studies

Akermin performed a series of parametric tests to quantify the reboiler heat duty under varied rich loading conditions (by varying the liquid-to-gas (L/G) ratio) and also varied reboiler pressures (using vacuum blower to achieve a lower boiling point temperature). Field data showed that the lowest regeneration energy for a given reboiler temperature is achieved at the maximum rich loading, which agrees with Aspen modeling. The maximum rich loading is an equilibrium limit of the solution for a given feed gas CO_2 partial pressure, solvent concentration, and rich solution temperature.

Table 19 presents the key process parameters explored in the reboiler pressure study, including temperatures and lean loading (measured). Rich loadings were estimated based on mole balance for each case considering the circulation rate. The liquid was 20% K_2CO_3 and the circulation rate was 215 LPH.

Table 19: Reboiler data for the parametric study with varied reboiler pressure

Reboiler Pressure (bara)	Reboiler Temperature (°C)	Rich Liquid Temperature (°C)	ΔT Hot Approach (°C)	Lean Loading† mol/mol K_2CO_3	Rich Loading† mol/mol K_2CO_3
1.030	101.3	80.8	20.6	0.291	0.645
0.860	96.2	75.8	20.4	0.319	0.645
0.631	87.8	70.4	17.4	0.324	0.650
0.470	80.2	66.0	14.3	0.349	0.673
0.308	69.6	58.5	11.1	0.386	0.697

†20% K_2CO_3 circulated at 215 LPH.

Figure 47 compares measured reboiler heat duties (bench unit tested at NCCC) with Aspen predictions for various reboiler pressures using the measured stripper operating conditions provided in Table 19 and heat loss curve presented in Figure 46. Data confirm that regeneration energy at various test conditions is in close agreement with the Aspen predictions, within about 2.5% of the measured values.

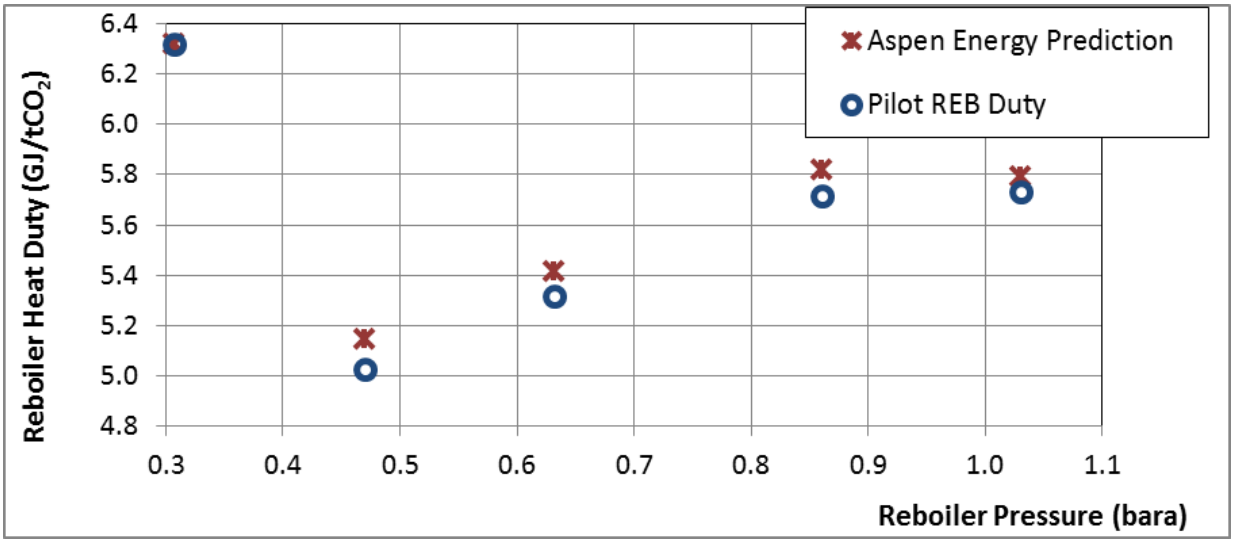

Figure 47: Reboiler heat duties for bench-scale test unit compared to Aspen predictions.

While there was some variability in the rich loadings for this experiment, data indicate that a minimum reboiler heat duty is achieved when the reboiler pressure is in the range of 0.4 to 0.5 bara (absolute) for the current stripping column at the specified liquid circulation rates. The general trend is that reboiler heat duty decreases with decreasing reboiler pressure (temperature). However, at the lowest reboiler pressure (i.e., lowest stripper temperature), the reboiler heat duty starts increasing again when the kinetics of the bicarbonate dehydration reaction ($HCO_3^- \rightarrow H_2O + CO_2$) begins to dominate the stripping process.

Having confirmed the validity of Aspen predictions, Aspen modeling was used to estimate the reboiler heat duty under various lean loadings (X_{CL}) and various reboiler temperatures under adiabatic system conditions. The results can be observed in Figure 48.

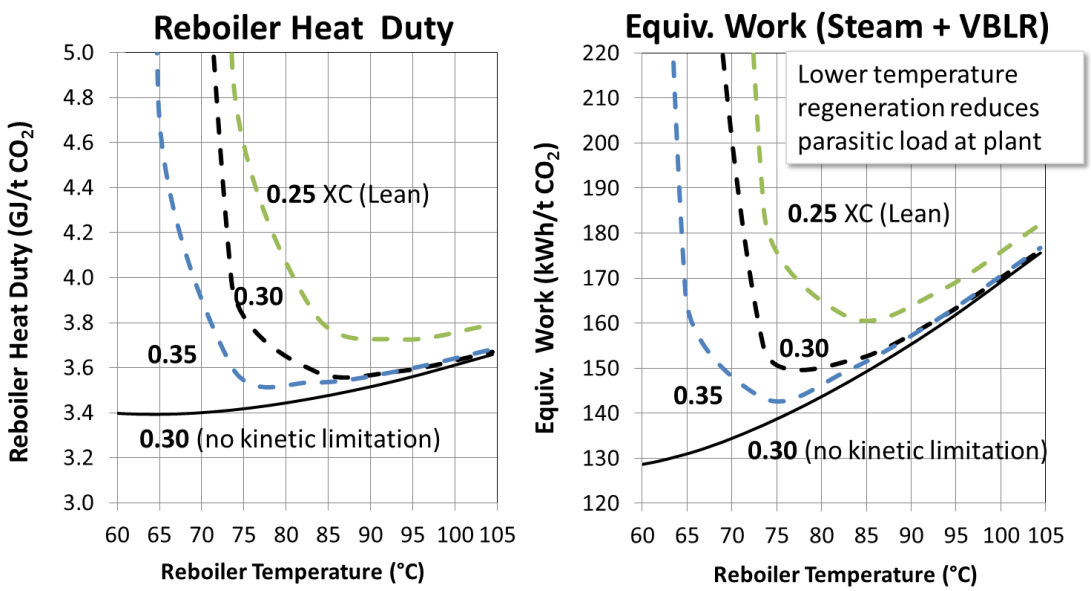

Figure 48: Aspen predictions of reboiler heat duty and equivalent work of steam plus vacuum blower.

Equation 22 was used to calculate the equivalent work of steam regeneration. Since the vacuum blower comprises an additional parasitic demand, the work of compression from vacuum to 1.6 bara was added to the steam regeneration work, assuming multi-stage vacuum compressor with 75% isentropic efficiency per stage.

$$W_{Steam} = 0.9Q_{Reb}\left[1 - \frac{40 + 273.15}{T_{Steam}}\right] \tag{22}$$

Results indicate that the reboiler heat duty of a large-scale adiabatic system using K_2CO_3 in a simple solvent flow sheet (SFS) can achieve reboiler heat duty of approximately 3.5 GJ/t CO_2 and equivalent work for steam regeneration of approximately 150 kWh/t CO_2 (including vacuum compressor work to produce 1.6 bar CO_2 product) if the stripper is sized similar to the bench unit system. This result compares quite favorably with approximately 236 kWh/t CO_2 for work of steam regeneration in 30% MEA in NETL Case 12, Rev 2.

Figure 49 compares the total equivalent work of CO_2 capture (excluding incremental power plant loads) for 30% MEA in NETL Case 12, Rev 2 and K_2CO_3 in a conventional solvent flow sheet (SFS) except that 0.5 bara regeneration pressure is used along with 0.30 mol/mol K_2CO_3 lean loading. This total equivalent work includes all liquid pumps, flue gas blowers, and CO_2 compression to 150 bara.

The stripper of the NETL bench unit is about 2.6-fold larger than the absorber. It was desirable for research purposes to assure the stripper was sufficiently-sized to demonstrate best energy performance. Based on performance data, Aspen modeling was also used to explore performance with reduced stripper sizing.

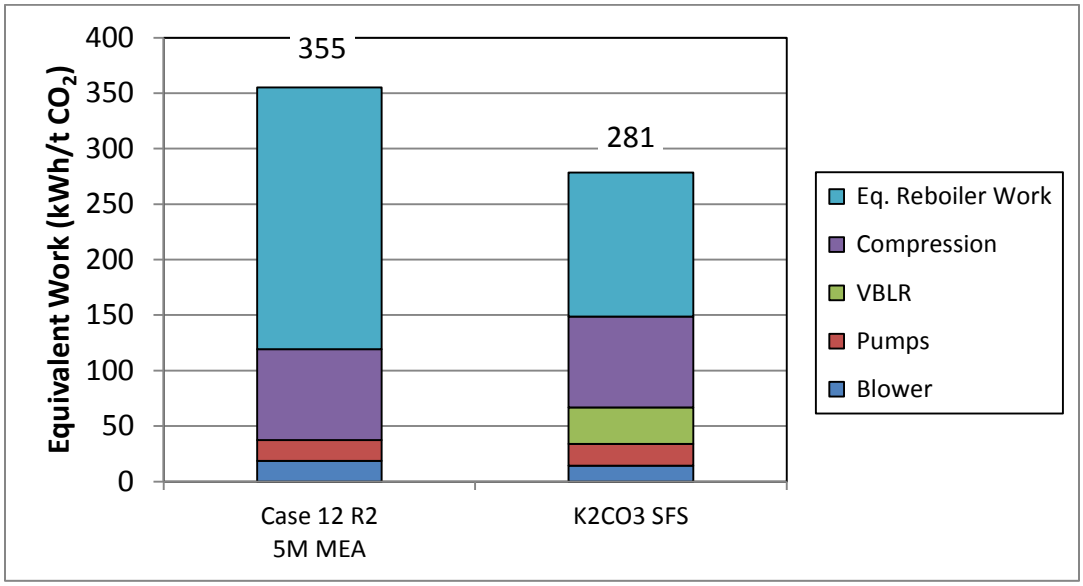

Figure 49: Contributions to equivalent work for an example K_2CO_3 system regenerated at 85°C in a simple solvent flow sheet with stripper sizing on par with bench unit, compared to NETL Case-12 (v2).

The achievable reboiler heat duty with 20% potassium carbonate solution is about 3.5 GJ/t CO_2. The total equivalent work is about 281 kWh/t CO_2 due to lower temperature steam extraction, which compares favorably against the total equivalent work reported for 30% MEA in NETL Case 12, Rev 2.

It is worth mentioning that only a conventional solvent flow sheet (SFS) was considered at this stage of development. However, advanced flow sheets are expected to provide new opportunities to further optimize regeneration energy and reduce equivalent work.

Recommendations for future work:

- Develop advanced stripper designs to minimize lean pinch effects;
- Add catalytic enhancement where feasible to overcome kinetic limitations in the stripper;
- Regenerate at lower temperatures with catalyst to reduce equivalent work;
- Alternative flow sheets that can provide lower energy, lower equivalent work, and further capital cost reduction; and
- Deploy/develop non-toxic non-volatile solvents with increased CO_2 loading capacity.

Summary of Bench Unit Testing Results:

- Demonstrated seven-fold (7x) reduction in space time at 90% capture with biocatalyst-coated packing compared to blank
- Achieved 90% capture using K_2CO_3 solution at approximately 20 Nm^3/hr gas flow rate
- Demonstrated 2800 hours online with an estimated half-life in the range of 500 days
- Verified negligible heat stable salts accumulation (< 1.6% loss of capacity per year)
- Demonstrated high-purity CO_2 product (>99.9% pure CO_2, dry basis)
- Confirmed near zero aerosol formation (NCCC measurements using isokinetic sampling showed salt carry over was below 0.8 ppm lower detection limit)
- Estimated 30% reduction in equivalent work of steam regeneration including additional work for vacuum blower and compared to NETL Case 12 Rev 2
- Estimated 20% reduction in total equivalent work based on bench unit stripper size and performance with ~85°C reboiler temperature
- Established that kinetic limits observed in stripper below 85°C depend on stripper sizing and lean loading

<u>Subtask 9.4 – Data Reporting and Analysis, Bench Unit Feedback</u>

Battelle will collaborate with Akermin on testing and review of bench-scale unit test data. Battelle will compare outputs of the PNNL column size models and pre-build mass and energy performance estimates. Battelle will provide a report that compares detailed column performance (sizing) model predictions relative to the bench-scale unit operational test data. Considering the bench unit operational data, Battelle will determine if a revision is recommended for the revised techno-economic analysis (previously revised based on wetted wall feedback).

Based on observations from the NETL Bench Unit regarding the potential limiting stripping kinetics of K_2CO_3 and an update of Case 12 to Revision 2, it was recommended to reassess the full-scale TEA conducted previously by PNNL. As a result, the TEA was updated by PNNL under Subtask 6.4. It was determined that a specific emphasis should be placed on exploring the impact of CO_2 capture enhancement in absorber and stripping column size to understand impact on energy, capital costing, and levelized cost of electricity (LCOE).

3.0 Schedule & Milestone Status

The project is comprised of two budget periods. The blue vertical lines of the Gantt section denote the fiscal year breaks. As part of the revised contract, the schedule now includes five quarters in the first budget period (now complete), and seven quarters in the second budget period.

Table 20 Milestone Gantt and Status Table

Task(s)	MS ID #	Project Milestone Description	10/1/10 – 12/31/11					01/1/12 – 09/30/2013							Plan End Date	Act. End Date	Comments (notes, explanation of deviation from plan)
			Budget Period 1					Budget Period 2									
				CY2011				CY2012				CY2013					
			Q 1	Q 2	Q 3	Q 4	Q 5	Q 6	Q 7	Q 8	Q 9	Q 10	Q 11	Q 12			
Task-3	A1	Greater than 80% physical retention demonstrated in flow system													12/31 2010	12/31 2010	Completed on schedule
Task-6	P1	Wetted wall kinetic testing complete for K_2CO_3 solvents													03/17 2011	03/17 2011	Completed on schedule
Task-4	A2	Define preferred conditions for low energy operation													03/18 2011	3/18 2011	Completed on schedule
Task-5	A3	Lab-scale CLR demonstrates 10X absorption rate													04/21 2011	10/27 2011	Completed in Q5
Task-6	P2	Complete initial techno-economic analysis													05/12 2011	12/12 2011	M&E Bal on schedule: 5/12/11 Draft LCOE by PNNL on 9/28/11 Presented to DOE 12/12/2011
Task-7	B1	Complete review of Akermin's PFD and process specifications													06/02 2011	10/28 2011	Initial PFD complete 6/2011 and reviewed; Specification completed Q4, reviewed by

																	Battelle 10/28/11.
Task-7	P3	Finalize bench-unit column design and M&E balance													08/22 2011	09/28 2011	Completed by end of Q4. Akermin is exploring alt. diameter options to lower height for cost
Task-7	B2	Review of PNNL's M&E balance and column sizing													08/22 2011	12/15 2011	Completed end of Q5.
Task-7	A4	Bench-unit engineering package released for bid													08/25 2011	09/09 2011	Completed end of Q5
Task-5	A5	Lab-scale CLR tested with trace contaminants													5/31/ 2012	5/24/ 2012	Completed on schedule.
Task-3	A6	Two hundred day lifetime demonstrated, immobilized enzyme													8/31/ 2012	9/10/ 2012	Completed 200-days on 9/10/2012
Task-3 Task-9	A7	Scaled-up Immobilized enzyme packing meets spec, ready for install													11/12/ 2012	5/7/ 2013	Complete
Task-9	A8	Bench-unit interim operational report													3/31/ 2013	07/31 /2013	Completed with QR11
All	A9	Draft Final Report													10/31/ 2013	11/11 /2013	1 month after end of project
Task-1	A10	Submit Executed Site Agreement and NEPA doc.													5/31/ 2012	5/17/ 2012	Site agreement fully executed on 5/17/12. NEPA doc revised on 8/22/12.
Task-7	A11	Process Hazard Analysis													6/30/ 2012	6/27/ 2012	Completed on schedule.
Task-8	A12	Factory Acceptance Test													11/30/ 2012	11/27 2012	Completed on schedule.
Task-6	P4	Techno-economic analysis, bench-unit feedback													9/20/ 2013	10/30 /2013	Draft TEA received on schedule, updated with inputs from WP.
Task-6 Task-9	B3	Final Report on Techno-Economic Analysis													9/27/ 2013	11/7/ 2013	Received 11/7/2013, attached to this final report.

4.0 Success Criteria

Table 21: Project Success Criteria and Completion Notes

Decision Point	Basis for Decision/Success Criteria	Completion notes
Completion of Budget Period 1	Successful completion of all work proposed in Budget Period 1.	Akermin, PNNL, and Battelle have completed all work proposed for budget period, any deviations from task descriptions are described in this report.
	Demonstrate greater than 80% physical retention of the enzyme with flow.	Akermin has demonstrated >87% enzyme retention with the silica based sol-gel immobilization technology after 100 hours on stream as described in fifth quarterly report (Feb 2, 2011), and the same sample batch showed >10X multiplier in overall mass transfer coefficient in CLR testing.
	Demonstrate 10X absorption rate increase in the lab-scale CLR.	Akermin met this milestone on 10/27/2011 with silica based sample (DP 6-69) with approximately 24 hours on-stream.
	Submission of an initial Aspen model of the Akermin technology in a 550 MW PC power plant.	PNNL provided Aspen results and stream tables presented in the content and appendix to the third quarterly report (7/2011, p. 39-56).
	Submission of an initial techno-economic analysis of the Akermin technology.	Akermin received preliminary techno-economic analysis results from PNNL at the end of Q4 for review by Akermin as noted in the fourth and fifth quarterly reports (10/2011, p. 30; and 12/2011, p. 30).
	Submission of the engineering bid package for the bench-scale test unit that includes a detailed PFD, equipment sizing, and complee mass and energy balances.	Akermin prepared a bid package that was released as a budgetary request to four potential bench unit engineering/fabricators in Sept 2011—the median cost estimate was $987,500 with shipping compared to the budget of $509,300 including all instrumentation and shipping. Akermin submitted this preliminary bid package as an attachment to the fourth quarterly report (10/2011, p. 43)

	Submission and approval of a Continuation Application in accordance with the terms and conditions of the award. The Continuation Application should include a detailed budget and budget justification for budget revisions or budget items not previously justified including quotes and budget justification for service contractors and major equipment items	Akermin submitted a preliminary continuation application (CA) on 12/2011. A final CA was submitted on 3/12/2012, and approval was received on September 12, 2012
Completion of Budget Period 2	Successful completion of all work proposed in Budget Period 2.	
	Demonstrate greater than 50% enzyme activity retention after 200 days at target pH, temperature, and solvent concentration.	After 200 days of operation (achieved on September 7, 2012), enzyme activity remained at approximately 46%. Strong correlation between enzyme activity and film thickness suggests loss of activity primarily due to loss of film thickness.
	Demonstrate that the enzyme tolerates greater than 20 ppm SO_2 for at least 100 hours.	This milestone was met with lab-scale tests that concluded on May 24, 2012.
	Demonstrate a reboiler energy duty of 2.1 GJ/ t-metric (~900 Btu/lb) of CO_2 removed	Akermin demonstrated potential for 3.5 - 3.7 GJ/t CO_2 (1505 to 1591 Btu/lb) when using a simple solvent flow sheet with K_2CO_3. An alternate solvent and/or an advanced flow sheet is recommended to approach the original reboiler heat duty target.
	Submission of the final report, the final techno-economic analysis, and the final Aspen model of the Akermin technology in a 550 MW PC power plant.	Completed with this final report.

5.0 References

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Appendix A – PNNL Final Report

ADVANCED LOW ENERGY ENZYME CATALYZED SOLVENT FOR CO_2 CAPTURE

PNNL Final Report (9-30-13) – M. Bearden, G. Whyatt & C. Freeman

Revision C (12-17-13)

Task 6 –Aspen Plus Model Development (Lead Organization: PNNL and Battelle)

Subtask 6.4 – Revised Techno-Economic Analysis, Industrial Scale, Bench Unit Feedback (PNNL lead)

If an update is recommended by Battelle (Task 9.4), PNNL will update carbon capture modules in Aspen Plus based on feedback from the bench-scale tests. Update cost and performance estimates for alternative solvent systems based on updated models. Provide updated alkaline carbon capture (subsystem) module to Akermin.

Background:

Prior to the bench-scale testing phase of the project, PNNL worked with Akermin staff to provide Aspen modeling predictions for a full-scale power plant using K_2CO_3 solvent and Akermin's immobilized enzyme technology as part of the deliverable for Subtask 6.3 (Revised Techno-Economic Analysis, Industrial Scale, Wetted Wall Feedback). A key finding from the initial predictions was that elevating lean CO_2 loading levels and incorporating vacuum stripping in K_2CO_3 system could reduce the overall parasitic energy penalty (using equilibrium model) by approximately 30% relative to the MEA baseline. The modeling work also confirmed that K_2CO_3 solvents used without increased absorption kinetics (via enzymes or other means) required excessive tower height requirements, approaching 396 meters (1300 feet). An enzyme kinetic performance target equating to ~10 to 16 times enhancement in the overall CO_2 absorption flux in aqueous K_2CO_3 solutions relative to blank packing (no enzyme) was shown to proportionately reduce the absorber tower height to a level that was believed commercially feasible (i.e., approximately 25 to 40 meters). A 10-fold overall mass transfer enhancement would indicate a 10-fold reduction in absorber column height for equivalent area efficiency. This "10x" technical target (at temperature) was used by the project team in the subsequent design of the bench-scale system and used as technical target for this TEA analysis.

Guidance for Final Techno-Economic Analysis:

Upon successfully testing of the bench-scale system, Akermin was able to quantify the kinetic performance of the immobilized enzyme technology. Further, Akermin used the bench-scale performance data to determine a recommended process/operating configuration for the final techno-economic analysis. In addition to the current process/operating performance state, additional projections were made based on future kinetic performance targets proposed by Akermin.

The three main K_2CO_3/ Enzyme techno-economic modeling cases are detailed in Tables 1 through 3. Here Case 3A (6x1) represents the overall enzyme enhanced kinetic performance that is consistent with the bench-scale testing results. This performance equates to a 6-fold decrease in absorber column packed height due to enzyme enhanced kinetics, but no catalytic benefit is included in the stripper sizing (no enzyme in the stripper). Case 3A (10x1) represents an enzyme kinetic enhancement target in the absorber that equates to a 10-fold reduction in column height relative to no enzyme—the project technical target. Here still, there is no catalyst added to enhance kinetics in the stripper. Finally, Case 3A (10x5) represents conceptual performance with kinetic increases in both the absorber and the stripper. Here, a 5-fold reduction in stripper size with the same energy performance is assumed compared to the otherwise kinetically limited case. Conceptually, this last case helps quantify the cost savings with improved stripper kinetics. This stripper kinetic improvement would require exploring a catalyst coating on stripper packing, which would need to survive the elevated temperatures of that system.

Table 1. Operational Specifications and Model Inputs for Final TEA Cases (provided by Akermin)

Parameter	3A Cases
Net Power Production (MWe)	550
Flue Gas CO_2 concentration (dry basis)	15.9%
CO_2 Removal (%)	90%
K_2CO_3 Conc (wt% equiv as pure)	20%
Lean Loading (carbonate conversion)	0.35
Rich Loading (carbonate conversion)	0.70
Absorber: Bottom Pressure (bara)	1.07
Flue Gas Feed Temp (°C)	46
Lean Feed Temp: (°C)	40
Flood Fraction (per Aspen):	0.7
Packing Area Efficiency (%),	70%
Reboiler/Stripper: Stripper Top Pressure (bara):	0.55
Steam to Reboiler ΔT (°C)	10
Packing Area Efficiency (%), liquid load ($m^2/m^2/hr$)	70%, 55.7
Rich-Lean Cross Exchanger, Cold Side ΔT (°C):	5°
Trim Coolers Cooling Water Conditions per ISO: Water Inlet Temperature (15.5°C), Temperature rise, 11.1°C Minimum Approach ΔT (°C):	15.5°, 11.1°, 5°
Vacuum blower : (specified vacuum suction to discharge pressure of 1.6 bara) Isentropic Eff. (%)/ n-stages	83%, 2-stages
Suction/Discharge Pressure (bara/bara)	0.471/1.60
Compressor: (1.6 bara to 150 bara) Isentropic Eff (%)/ n-stages	86%, 6-stages*
Suction/Discharge Pressure (bara/bara)	1.6/150

*Matched number of stages to NETL Case-12 assumptions, which results in pressure ratio/stage of 2.1; however, according to WorleyParsons many CO_2 compressor manufacturers may specify PR/stage ~ 2.

For each of the cases modeled, the lean and rich loadings (variables X_{CL}, and X_{CR} respectively expressed as carbonate conversions to bicarbonate) were held at 0.35 and 0.70. All 3A cases were run with stripper top pressures of 0.55 bara. A single gas treatment train was assumed, with two (2) absorbers and one (1) stripper per train, having diameters of 16.7 m and 21 meters respectively. Note that the stripper diameter was chosen to roughly match the target liquid loadings; similarly, the absorber diameters were defined by the desired approach to flooding. The resulting liquid load (liquid flow per cross sectional area of packing) and approach to flooding for the full-scale design are consistent with the specified area efficiencies. (Tsai, 2010) The NETL Case 12 (30% MEA, 2010 updated reference case) was also reproduced with the assumption that one gas treatment train was deployed with two (2) absorbers and one (1) stripper per train.

Table 2. Absorber Sizing and Equilibrium Parameters for Aspen (provided by Akermin)

Parameter	Case 3A (6x1)	Case 3A (10x1)	Case 3A (10x5)
Number of Gas Treating Trains	1	1	1
Number of Absorbers per Train	2	2	2
Packing Type	M500X	M500X	M500X
Equivalent SPRX 23°C, lean loading ($X_{C,L}$) = 0.25 carbonate conversion to bicarbonate	~11.5	17	~17
Forward Pre-Exp Fact. [k_f] †	4.23E+13†	4.23E+13†	4.23E+13†
Forward Act. Energy [Ef] (cal/mol)	9120	8737	8737
Forward Temp. Exp. [n]	0.00	0.00	0.00
Reverse Pre-Exp Fact. [k_r]	2.1744E+9	2.1744E+9	2.1744E+9
Reverse Act. Energy [Er] (cal/mol)	25320	24937	24937
Reverse Temp. Exp. [n]	3.0638	3.0638	3.0638

† Catalyst performance is modeled in Aspen using an activation energy shift that is applied to both the forward and reverse reactions to preserve equilibrium. Kinetic parameters are specified for the CO_2 + $OH^- \rightarrow HCO_3^-$ reaction based on matching data for catalyst and blank (un-catalyzed) rate performance in laboratory and bench unit testing.

- Activation energy shift (6x1 case): 1755 cal/mol for the absorber, and 0 for the stripper.
- Activation energy shift (10x1 case): 2138 cal/mol for the absorber and 0 for the stripper.
- Activation energy shift (10x5 case): 2138 for both absorber and stripper modeling.

Supporting data is provided in Akermin's final report (Figure 20). Table 2 above also provides the "SPRX" reference multiplier, which is the overall mass transfer coefficient enhancement measured in the Akermin laboratory single pass reactor (SPR) under standard test conditions including lean loading of X_{CL} = 0.25 (carbonate conversion to bicarbonate) and room temperature.

Table 3. Stripper Sizing and Equilibrium Parameters for Aspen (provided by Akermin)

Parameter	Case 3A (6x1)	Case 3A (10x1)	Case 3A (10x5)
Stripper Columns per Train	1	1	1
Packing Type	M500X	M500X	M500X
SPRX 23°C, lean loading ($X_{C,L}$)= 0.25 carbonate conversion to bicarbonate	1	1	~17
Forward Pre-Exp Fact. [k_f]	4.23E+13	4.23E+13	4.23E+13
Forward Act. Energy [Ef] (cal/mol)	12975	12975	10837
Forward Temp. Exp. [n]	0.00	0.00	0.00
Reverse Pre-Exp Fact. [k_r]	3.31E+01	3.31E01	3.31E01
Reverse Act. Energy [Er] (cal/mol)	29000	29000	26862
Reverse Temp. Exp. [n]	6.1432	6.1432	6.1432
# Distribution Stages**	TBD	TBD	TBD

**Total height estimate (m) = pack height + 2 (n-1) + 5, where n = number of liquid distribution stages. SPRX is the mass transfer enhancement that would be measured under standard lab test conditions at 23°C.

Catalyst enhancement with temperature is predicted by Aspen based on the specified activation energy. The same catalyst is assumed for both the absorber and stripper in the 10x5 case, as previously noted. This is same catalyst that is assumed for the absorber in the 10x1 case. However, no catalyst is assumed in the stripper for the 10x1 and 6x1 cases.

Table 4 below summarizes packing costs based on budgetary quotes from Sulzer (5/24/2011 email to Akermin) for a large scale order >1 million square meters. Akermin estimated biocatalyst coating (immobilized enzyme) costs per unit area of packing ($/m2). The same unit cost is assumed for 6x and 10x catalysts, since the improved performance demonstrated in the laboratory was achieved through improvements in formulation and method and not by adding more material per square meter. Akermin estimated the cost of packing removal, recycling, and reinstall (RR&R) to be approximately 20% of the bare packing cost. For purposes of the current study Mellapak 500X (M500X) was specified in both the absorber and stripper packing since this is what was tested in the NETL-Akermin bench unit. The area efficiency of M500X is estimated to be 70% based on published correlation. (Tsai, 2010)

Table 4. Packing and Coating Cost Assumptions (from Akermin)

Description	Unit Cost ($/m^2 packing) – M500X	Unit Cost ($/m^2 packing) – M350Y	Comments
M500X Packing Cost (uncoated)	$ 4.32	$ 4.78	1st Install only. Sulzer quotes for > 1 MM m2 packing
Coating Cost	$ 5.56	$ 5.56	Per install. Includes chemicals, enzyme and Akermin mark-up
Packing RR&R (removal/recycle cost)	$ 0.86	$ 0.96	Packing handling and recycling for replacement. Includes removal, recycle and conditioning, and re-install handling

It was previously noted that if the catalyst coating can be improved through formulation development without increasing material costs, then the unit cost of catalyst per m^2 is the same for all cases. Since, improved catalysts will require less area for the given application, the installed cost is lower for more active catalysts. Also, future work should consider cost/benefit of using 350Y which may further reduce the cost of catalyst per install.

Akermin has set a commercial target of 2 to 3 year immobilized enzyme replacement cycle for this analysis. It is acknowledged that the enzyme performance at time of replacement will be lower than initial performance, but not accounted for in the performance modeling. Field testing thus far is too short (<2800 hrs) to project end of life performance at 15000 to 24000 hrs. Therefore, the 3-year projections are shown in this study to represent best case. No backup packing is to be assumed in the cost estimates, as packing core recycling is assumed and Akermin will hold the cost of holding backup/replacement stock packing as part of their business model.

Aspen Modeling Approach:

The reference cases for the current subtask: Case 11 and 12 from NETL report, "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity," Revision 2, DOE/NETL-2010/1397, November 2010. It is important to note that the Rev 2 baseline report utilizes a lower cross over steam temperature compared to Rev 1, which was used in the initial techno-economic analysis. The impacts of switching the two baselines on the analysis results are discussed below.

Cases 11 and 12 are based on a 550MW net output pulverized coal (PC) coal plant without and with 45% (approximately) MEA carbon dioxide capture technology and associated CO_2 compression,

transmission, and sequestration steps. For the present TEA, modeled unit operations were restricted to the cooling tower, steam cycle, absorber/stripper, and CO_2 compressor. Each of the study cases coal feed was adjusted to produce a 550 MWe net electric output. As such, scaling the power requirements of the upstream components of the plant (coal handling, boiler, fans etc. which are proportional to flue gas flow) was required.

Aspen Economic Analyzer was used to produce the capital equipment estimates for the carbon capture equipment only, through the vacuum blower system. Estimates were based on the Aspen Plus flow sheet input. No modifications to the library of Aspen equipment costs were made so as to assure a relative comparison to the MEA baseline (DOE/NETL, 2011 Rev 2). Note that the Aspen equipment costs were based on Q1 2012 values, compared to NETL reference values which were based on 2007. Note that the capital cost projections for non-capture components were scaled based on the same power law factors observed between the NETL baseline Case 12 relative to Case 11 (see Assumption 5 in Appendix A).

Table 5 shows the Aspen Plus energy predictions for the baseline cases and K_2CO_3 cases modeled. Table 6 gives additional data from the Aspen simulations with respect to absorber and stripper performance parameters (input variables identified). PNNL report appendix shows the other cost tables for the analysis (variable, fixed, and capital). The details associated with this modeling work (including assumptions) are also provided.

Table 5. Power and Fuel Estimates for Full-Scale Process/ Power Plant Simulations

(20% K_2CO_3 Cases with Akermin Technology and NETL Reference Case)

Fuel Costs	**Supercritical PC No Capture (NETL Case 11)**	**Supercritical PC MEA (NETL Case 12)**	**K2CO3 Capture (Akermin-3A) 6X1 CRF**	**K2CO3 Capture (Akermin-3A) 10X1 CRF**	**K2CO3 Capture (Akermin-3A) 10X5 CRF**	**Assumptions (see list in Appendix)**
GROSS TOTAL OUPUT POWER, kWe	580,400	662,800	675,475	675,475	675,475	1
AUXILIARY LOAD SUMMARY, kWe						
Coal Handling and Conveying	440	510	488	488	488	1
Pulverizers	2,780	3,850	3,685	3,685	3,685	1
Limestone Handling & Reagent Prep	890	1,250	1,197	1,197	1,197	1
Ash Handling	530	740	708	708	708	1
Primary Air Fans	1,300	1,800	1,723	1,723	1,723	1
Forced Draft Fans	1,660	2,300	2,202	2,202	2,202	1
Induced Draft Fan	7,050	11,120	10,644	10,644	10,644	1
SCR	50	70	67	67	67	1
Baghouse	70	100	96	96	96	1
Wet FGD	2,970	4,110	3,934	3,934	3,934	1
Capture Technology with Auxiliaries		20,600	21,052	21,052	21,052	1
CO2 Compression (total)		44,890	59,224	59,224	59,224	1
Miscellaneous Balance of Plant	2,000	2,000	1,914	1,914	1,914	1
Steam Turbine Auxiliaries	400	400	408	408	408	1
Condensate Pumps	800	560	846	846	846	1
Circulating Water Pumps	4,730	10,100	8,251	8,251	8,251	1
Ground Water Pumps	480	910	699	699	699	1
Cooling Tower Fans	2,440	5,230	6,264	6,264	6,264	1
Transformer Losses	1,820	2,290	2,334	2,334	2,334	1
TOTAL AUXILIARIES, kWe	30,410	112,830	125,735	125,735	125,735	2
NET POWER, kWe	549,990	549,970	549,740	549,740	549,740	2
Net Plant Efficiency (HHV)	39.3%	28.4%	29.7%	29.7%	29.7%	1
Net Plant Heat Rate (Btu/kWh)	8,687	12,002	11,493	11,493	11,493	2
Condenser Cooling Duty MkJ/hr		1,737	1,768	1,768	1,768	1
As-Received Coal Feed, kg/h	185,759	256,652	245,668	245,668	245,668	1
Percent CO2 Captured	0%	90%	90%	90%	90%	1
CO2 Released via Stack Gas, kg/hr	441,116	60,947	58,338	58,338	58,338	2,7
CO2 Captured, kg/hr	0	548,516	525,042	525,042	525,042	2
Limestone Sorbent, kg/hr	8,362.9	11,792	11,287	11,287	11,287	1
Thermal Input, kWt	1,400,162	1,934,519	1,851,727	1,851,727	1,851,727	7
Raw Water Withdrawal, m3/min	20	38.1	28.2	28.2	28.2	1
Raw Water Consumption, m3/min	16	29.3	21.4	21.4	21.4	1
Utilization Factor	85%	85%	85%	85%	85%	3
Annual Fuel Cost ($MM/year)	$58.2	$80.4	$77.0	$77.0	$77.0	4
COE - Fuel Cost (mills/kW-hr, 2007$)	14.2	19.6	18.8	18.8	18.8	2

An apparent discrepancy was noted between the cooling tower water circulation rate and cooling tower fan trends for NETL Case-12 and PNNL estimates of the same. Cooling tower flows were determined by the Aspen simulation, while cooling tower design conditions including wet bulb approach, cold water temperature, and temperature rise are the same as specified in the NETL

report. Where numbers weren't specified in the published report (for example, pump supply pressure and fan pressure drop) estimates were made based on input from local power producers and using best engineering judgment. Consistent trends are observed between the PNNL refit and PNNL predictions for Akermin Case 3A. While small differences are noted between the published NETL-12 and PNNL re-fit of Case-12, the overall economic impact was inconsequential.

Table 5A: Cooling water pumps and fan duties compared in re-fit and Case-12

	NETL Case 12, R2	PNNL Case 12 (re-fit)	Akermin-3A
Circulating Water Pumps	10,100	9,786	8,251
Cooling Tower Fans	5,230	6,754	6,264
Raw Water Withdrawal (m^3/min)	38	31.9	28.2

Table 6 below specifies the column design inputs and the resulting height and diameter estimates based on detailed sizing analysis. The Akermin Case 3A-(6x1) was developed using an Aspen Plus simulation with absorber catalyst performance similar to what was demonstrated in the Akermin bench unit testing at the National Carbon Capture Center, and assuming no catalyst enhancement in the stripper. Stripper sizing includes bicarbonate dehydration reaction rate limitations consistent with data collected in the field testing. Case 3A-(10x1) case assumes that catalyst performance achieves a technical target of 10-fold column height reduction factor in the absorber, and scaled accordingly. Likewise, Case 3A-(10x5) case assumes catalyst performance achieves technical target of 10-fold column height reduction factor in the absorber and stripper size is reduced by factor of 5-fold relative to no catalyst.

Table 6. Absorber/ Stripper Projections

Case Description	K_2CO_3 Akermin Case 3A-(6X1)	K_2CO_3 Akermin Case 3A-(10X1)	K_2CO_3 Akermin Case 3A-(10X5)
Absorber			
Number of Columns per Train	2	2	2
Area Efficiency (input)	0.7	0.7	0.7
Flood Fraction (input)	0.7	0.7	0.7
Liquid Loading ($m^2/m^2/hr$)	46.4	46.4	46.4
Pump Discharge Pressure (bar)	8.7	8.7	8.7
Absorber Diameter (m)	16.7	16.7	16.7
Absorber Packing Height (m)	28.0	17.0	17.0
Stripper			
Number of Columns per Train	1	1	1
Area Efficiency (input)	0.7	0.7	0.7
Liquid Loading ($m^2/m^2/hr$, input)	58.9	58.9	58.9
Stripper Packing Height (m, input)	46	46	9.2
Stripper Diameter (m)	21	21	21
Flood Fraction	0.7	0.7	0.7
Pump Discharge Pressure (bar)	7.0	7.0	7.0
Stripper Reboiler Duty (MW_{th})	548.9	548.9	548.9
CO_2 release in stripper (t/hr)	525	525	525

Table 7 summarizes all of the individual costs into COE estimates for the baseline and catalyzed K_2CO_3 cases. The Cost of Electricity (COE) totals were then multiplied against a levelization factor (from the NETL reference report) to determine the Levelized Cost of Electricity (LCOE) for each case. Here, the total LCOE increase predictions for the catalyzed K_2CO_3 systems are 84%, 78% and 73%, compared to the no capture case. This is in comparison to an 81% increase for the NETL MEA baseline case.

Table 7. Summary of LCOE Estimates for Enzyme-Catalyzed K_2CO_3 and Reference Cases

(Based on results in Table 5 and other costing results presented in this appendix)

Fuel Cost	14.2	19.6	18.8	18.8	18.8	2
Capital Cost	31.7	59.6	61.6	59.0	55.2	2
Variable Cost	5.0	8.7	7.8	7.8	7.8	2
Enzyme Variable Cost	0.0	0.0	3.2	1.9	2.8	
Fixed Operating Cost	8.0	13.0	11.9	11.9	11.9	2
Transp, Sequesration & Monitoring (TSM)	--	5.6	5.4	5.4	5.4	14
Total COE	**58.9**	**106.5**	**108.7**	**104.8**	**101.9**	2
Levelization Factor	1.269	1.269	1.269	1.269	1.269	3
Total LCOE	**74.7**	**135.1**	**138.0**	**133.0**	**129.3**	2
Increase versus No Capture	***--***	***81%***	***85%***	***78%***	***73%***	2

Figure 1 presents the incremental contributions to levelized cost of electricity relative to no capture.

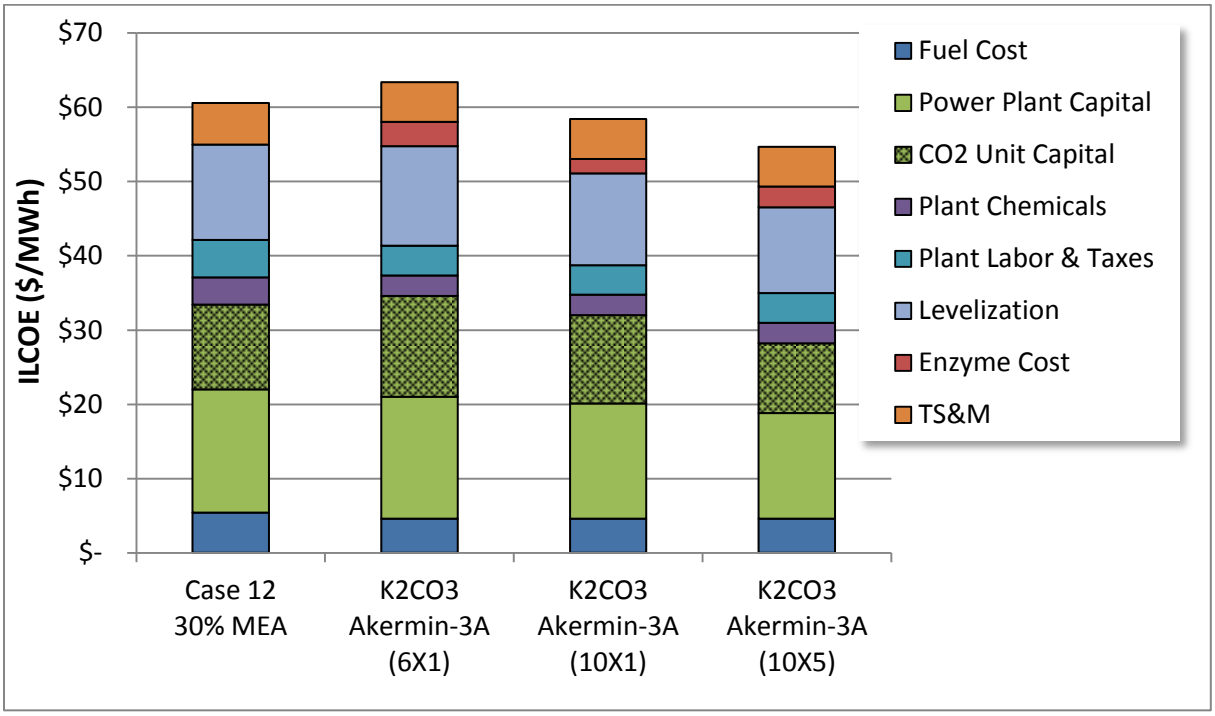

Figure 1. Comparison of Projected LCOE Increases over Case 11 baseline ($74.7/MWh net)

The preliminary techno-economic analysis performed as part of Subtask 6.3, prior to the bench-scale demonstration, projected an LCOE increase over Case 11 of approximately $41 per MWh. The primary reason for the higher LCOE values in the revised projections (Figure 1) is the increased capital cost estimates associated with the stripping system. In the preliminary techno-economic analysis equilibrium K_2CO_3 strippers were assumed (no reaction kinetic limitation) because adequate kinetic information was not available. The operation of the bench-scale test unit at the National Carbon Capture Center (NCCC) in Wilsonville provided the kinetic data necessary to validate rate-based simulations of both the absorbers and strippers for the uncatalyzed (blank) and enzyme-catalyzed K_2CO_3 systems. This data indicated that lower temperature stripping (under vacuum) required a much larger stripper, or required higher reboiler energy to produce the desired lean solvent. An additional concern, not addressed here, is the constructability of equipment of this size.

The second reason for the higher LCOE values (compared to the preliminary techno-economic analysis) is due to a change in the NETL MEA reference case used for benchmarking. The current analysis was developed from the NETL Case-12 Rev 2 instead of the Rev 1 version. The Rev 2 version drops the intermediate pressure turbine outlet pressure from approximately 135 psia to 75 psia, reducing the net equivalent work from 424 to 360 kWh/t CO_2. This provides additional power generation from the main steam cycle and reduces the crossover steam temperature to more closely match the MEA reboiler temperature in Case 12. However, despite even lower regeneration temperatures for enzyme-activated K_2CO_3, the lower crossover steam temperature results in a reduction in extracted power from the auxiliary let-down turbine at Rev 2 conditions. Nevertheless, even at Rev 2 conditions, the 60-80 MWe of additional power generated by the let-down turbine was still substantially greater than the power required for the vacuum stripping.

Note that the auxiliary let-down turbine assumption in the current techno-economic analysis may not be as economical as simply extracting low pressure steam from the main turbine equipment. During consultation with WorleyParsons it was suggested that a steam extraction system could be feasible, and may be afforded at a lower cost than adding a new let-down turbine as was done in this analysis. Nevertheless, the capital cost of the let-down turbine is retained in this study until a more detailed assessment of economics of the two options can be performed.

Case 3A (10x1) explores the economic potential of increased catalytic effect in the absorber. Indeed, advancements in catalyst performance can result in a LCOE decrease of nearly $4/MWh. Finally, Case 3A (10x5) is a hypothetical exploration of the potential economic benefit of catalytic enhancement in the stripping column, which would result in about $3.7/MWh. An important assumption here is that stripper performance could be obtained without unacceptable catalytic lifetime decay.

Conclusions:

The recent Akermin bench-scale results were used to update the initial techno-economic analysis. The cost projections for the enzyme-catalyzed system were higher than the initial techno-economic analysis. The primarily reason for this is due to the addition of rate-based kinetics in the stripper simulation in the present analysis, which is an outcome of the bench-scale testing feedback. This kinetic resolution helped project more accurate energy performance for the stripper reactor sizes, which are larger than in the initial analysis, impacting cost performance.

A due diligence assessment of the kinetic parameters fits/assumptions was also performed (see Appendix A). Although the due diligence identified the current kinetic fit used in this analysis as acceptable, some additional updates to those fits may determine better stripper performance than what is currently identified.

The other difference in the current study, compared to the preliminary TEA (PNNL, 2011) is that a smaller reduction in parasitic load was calculated. However, this difference is primarily due to the fact that the MEA reference case was updated from Rev 1 to Rev 2, where the intermediate steam pressures are correspondingly lower. NETL Case-12 Rev 2 is being used as the new baseline based on more recent NETL guidance toward that reference.

Works Cited

DOE/NETL. (2011 Rev 2). *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity.* DOE/NETL-2010/1397.

PNNL. (2011). *PNNL Progress Report (10-19-11).*

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PNNL Report Attachments:

Aspen Results and Assumptions for Full-Scale Process/ Power Plant Models

Modeling assumptions for Aspen cases that are referenced in Tables 5 and 7 of the main document and by the tables presented in this appendix is presented below:

Modeling Assumptions:

1. From simulation (Aspen Plus)
2. Calculated from above parameters
3. Same as Case 11/12
4. Calculated using NETL fuel cost
5. Capacity factored estimate used: $B/$A = (CapexB/CapexA)^n. Power law exponent *n*, determined from incremental cost increases between NETL Cases 11 and 12 for each piece of power boiler equipment. New capital estimates for this power boiler equipment was referenced to Case 11 costs. Likewise, for CO_2 compression (from 1.6 bar to 153 bar) a power law exponent of 0.61 was used.
6. From simulation (economic analyzer)
7. Interpolation with Case 11/12 coal flow
8. Use same fraction of total capture capital cost as Case 12
9. Assume 22.6% of TPC
10. Same as Case 12
11. Proportional to Case 12 water flow
12. Assume no refill required for K_2CO_3
13. 5-yr replacement assumed
14. Proportional to Case 12 coal flow
15. Assume not required for K_2CO_3
16. Assume equal to 80% of Case 12
17. Costs reported using 2007 US dollars.
18. Contingency costs are assumed equal to that specified in NETL Case-12, Revision 2. Since this is a solvent system, the construction of the basic CO_2 capture plant and power boiler systems have the same risk profile since its similar equipment.
19. All cases assume a 14 kPa (gauge) absorber bottom pressure, which is similar to Case 12. However, a lower pressure drop assumption (e.g., 7 kPa) could be explored in future work and this would be expected to decrease with column height improvement and elimination of overhead wash.
20. Two absorbers and one stripper column are assumed for all Akermin 3A cases.

Table A.1: Capital Cost Estimates (from Economic Analyzer) for K_2CO_3/ Enzyme Case 3A

Equipment ID	Equipment Description	Case 3A		
		(6x1) CRF	(10x1) CRF	(10x5) CRF
C-6620	Stripper vacuum blower	$19,735,626	$19,735,626	$19,735,626
D-6250	Flash tank	*$0*	$0	$0
D-6615-flash	1st stage vacuum blower water KO	$545,300	$545,300	$545,300
D-6635-flash	2nd stage vacuum blower water KO	$588,900	$588,900	$588,900
DCC.EC-6420	DCC cooler (P&F)	$903,618	$903,618	$903,618
DCC.P-6415	DCC circulating water pump	$4,555,300	$4,555,300	$4,555,300
DCC.T-6410	DCC vessel (absorber)	$14,976,100	$14,976,100	$14,976,100
EC-6220	Intercoolers	*$0*	$0	$0
EC-6550	Lean solvent trim cooler (plate & frame)	$802,137	$802,137	$802,137
EC-6610	Stripper Condenser	$10,018,500	$10,018,500	$10,018,500
EC-6625	Vacuum blower intercooler	$2,265,000	$2,265,000	$2,265,000
EC-6645	2nd stage vacuum blower after cooler	$2,042,500	$2,042,500	$2,042,500
EX-6530	Cross Exchanger (P&F)	$3,815,556	$3,815,556	$3,815,556
F-6500	FD fan to Absorber	$3,286,861	$3,286,861	$3,286,861
P-6515	Rich solvent pumps	$6,901,800	$6,901,800	$6,901,800
P-6545	Lean solvent pumps	$6,689,400	$6,689,400	$6,689,400
P-6560	Solvent water recycle	$110,100	$110,100	$110,100
P-6650	Solvent makeup water	$256,100	$256,100	$256,100
ST-7300	Let-down turbine	$7,329,957	$7,329,957	$7,329,957
T-6510	Absorber (with packing/ enzyme)	$90,279,000	$58,064,500	$58,064,500
T-6540	Stripper (with packing)	$102,920,000	$102,760,000	$27,476,900
T-6540-reb	Stripper reboilers	$16,154,300	$16,154,300	$16,154,300
VS-65XX	Lean Solvent Storage Tank	$1,302,400	$1,302,400	$1,302,400
ABS ENZYME	Cost for enzyme/ coating – Absorber	$34,171,828	$20,639,784	$20,639,784
STR ENZYME	Cost for enzyme/ coating – Stripper	$0	$0	$8,858,519
	Total Cost (with First Enzyme Install)	**$329,650,283**	**$283,743,739**	**$217,319,158**

Table A.2: LCOE Estimates from Capital Costs

Capital Costs (2007$/kWe)	Supercritical PC No Capture (NETL Case 11)	Supercritical PC MEA (NETL Case 12)	K2CO3 Capture (Akermin-3A) 6X1 CRF	K2CO3 Capture (Akermin-3A) 10X1 CRF	K2CO3 Capture (Akermin-3A) 10X5 CRF	Assumptions (see list)
Non-Carbon Capture Components:						
Coal & Sorbent Handling	$70	$85	$83	$83	$83	5
Coal & Sorbent Prep & Feed	$33	$41	$40	$40	$40	5
Feedwater & Misc. BoP Systems	$144	$186	$180	$180	$180	5
PC Boiler	$539	$671	$651	$651	$651	5
Flue Gas Cleanup	$234	$297	$288	$288	$288	5
Combustion Turbine/Accessories	$0	$0	$0	$0	$0	5
HRSG, Ducting & Stack	$68	$68	$68	$68	$68	5
Steam Turbine Generator	$211	$240	$236	$236	$236	5
Cooling Water System	$68	$111	$104	$104	$104	5
Ash/ Spent Sorbent Handling Sys	$23	$27	$26	$26	$26	5
Accessory Electric Plant	$93	$147	$138	$138	$138	5
Instrumentation & Control	$39	$47	$46	$46	$46	5
Improvements to Site	$26	$29	$29	$29	$29	5
Buildings & Structures	$101	$110	$109	$109	$109	5
Carbon Capture Components:						
CO2 Removal System (bare erected)	$0	$493	$600	$516	$395	6
CO2 Compression & Drying (bare erect	$0	$66	$64	$64	$64	5
Adders (H&O, fee & contingencies)	$0	$294	$349	$305	$242	8
Total Plant Cost (2007$/kWe)	$1,649	$2,911	$3,010	$2,882	$2,698	2
Owners Costs (2007$/kWe)	$377	$657	$680	$651	$610	9
Total Overnight Cost (2007$/kWe)	$2,026	$3,568	$3,690	$3,534	$3,308	2
Capital Charge Factor	0.116	0.124	0.124	0.124	0.124	10
COE - Capital Cost (mills/kW-hr, 2007$)	31.66	59.58	61.61	59.00	55.22	2

Table A.3: LCOE Estimates of Variable and Fixed Operating Costs

Variable Costs ($/yr)	Supercritical PC No Capture (NETL Case 11)	Supercritical PC MEA (NETL Case 12)	K2CO3 Capture (Akermin-3A) 6X1 CRF	K2CO3 Capture (Akermin-3A) 10X1 CRF	K2CO3 Capture (Akermin-3A) 10X5 CRF	Assump-tions (see list)
Non-Capture System:						
Maintenance Material Cost	$9,133,357	$15,721,656	$14,700,883	$14,700,883	$14,700,883	7
Water	$1,303,324	$2,457,806	$2,164,010.11	$2,164,010	$2,164,010	11
MU & WT Chem	$1,009,427	$1,903,577	$1,765,040	$1,765,040	$1,765,040	12
Limestone	$3,273,667	$4,610,586	$4,403,447	$4,403,447	$4,403,447	12
Ammonia (28% NH3)	$2,960,869	$4,090,854	$3,915,777	$3,915,777	$3,915,777	12
SCR Catalyst	$553,798	$765,005	$732,281	$732,281	$732,281	12
Flyash Disposal	$1,919,038	$2,651,418	$2,537,945	$2,537,945	$2,537,945	12
Bottom Ash Disposal	$479,759	$662,855	$634,487	$634,487	$634,487	12
Capture System:						
Solvent	$0	$1,017,164	$100,000	$100,000	$100,000	12
Enzyme/ coating (3-yr replacement)	$0	$0	$13,282,505	$7,944,089	$11,353,663	13
NaOH	$0	$976,789	$934,985	$934,985	$934,985	14
H2SO4	$0	$298,293	$0	$0	$0	15
Corrosion Inhibitor	$0	$6,769	$0	$0	$0	15
Activated Carbon	$0	$567,144	$0	$0	$0	15
Total (Non-Enzyme) ($/yr)	$20,633,239	$35,729,917	$31,888,856	$31,888,856	$31,888,856	2
Total (Enzyme) ($/yr)	$0	$0	$13,282,505	$7,944,089	$11,353,663	
COE - Variable Cost (mills/kW-hr, 2007$) =	5.03	8.72	7.79	7.79	7.79	2
COE - Enzyme Cost (mills/kW-hr, 2007$) =	0.00	0.00	3.24	1.94	2.77	
Fixed Costs ($/yr)						
Operating Labor	$5,524,319	$6,444,907	$6,444,907	$6,444,907	$6,444,907	10
Maintenance Labor	$6,088,905	$10,481,104	$8,384,883	$8,384,883	$8,384,883	16
Administrative & Support Labor	$2,903,306	$4,231,503	$4,231,503	$4,231,503	$4,231,503	10
Property Taxes and Insurance	$18,118,017	$32,040,467	$29,883,361	$29,883,361	$29,883,361	7
Total	$32,634,547	$53,197,981	$48,944,654	$48,944,654	$48,944,654	2
COE - Fixed Cost (mills/kW-hr, 2007$) =	7.96	12.98	11.95	11.95	11.95	2

Solvent reclaiming is not needed for K_2CO_3 system; therefore, sulfuric acid, corrosion inhibitors, and activated carbon are not expected to be required.

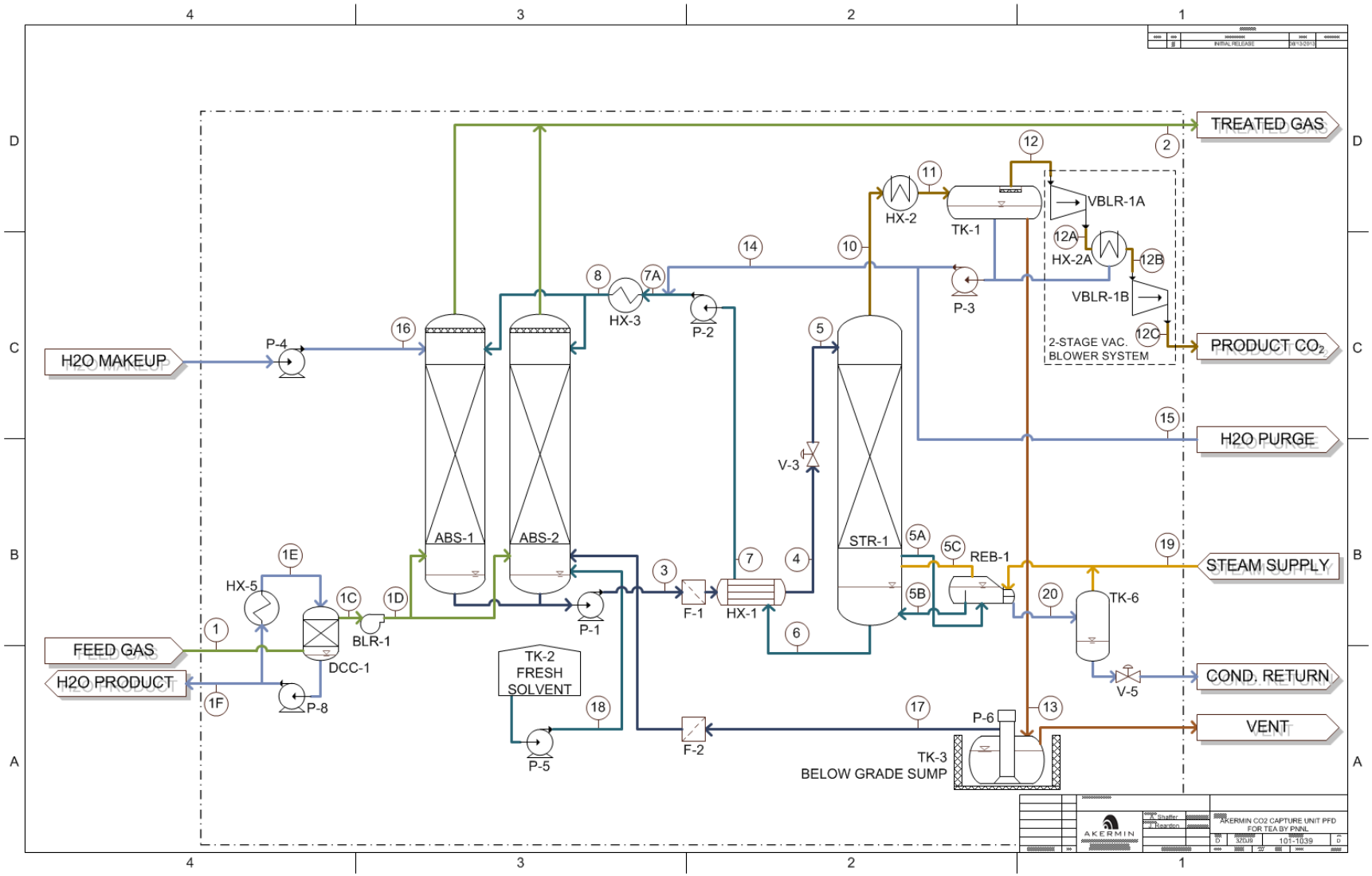


Figure A.1 Akermin Case 3A Process Flow Diagram

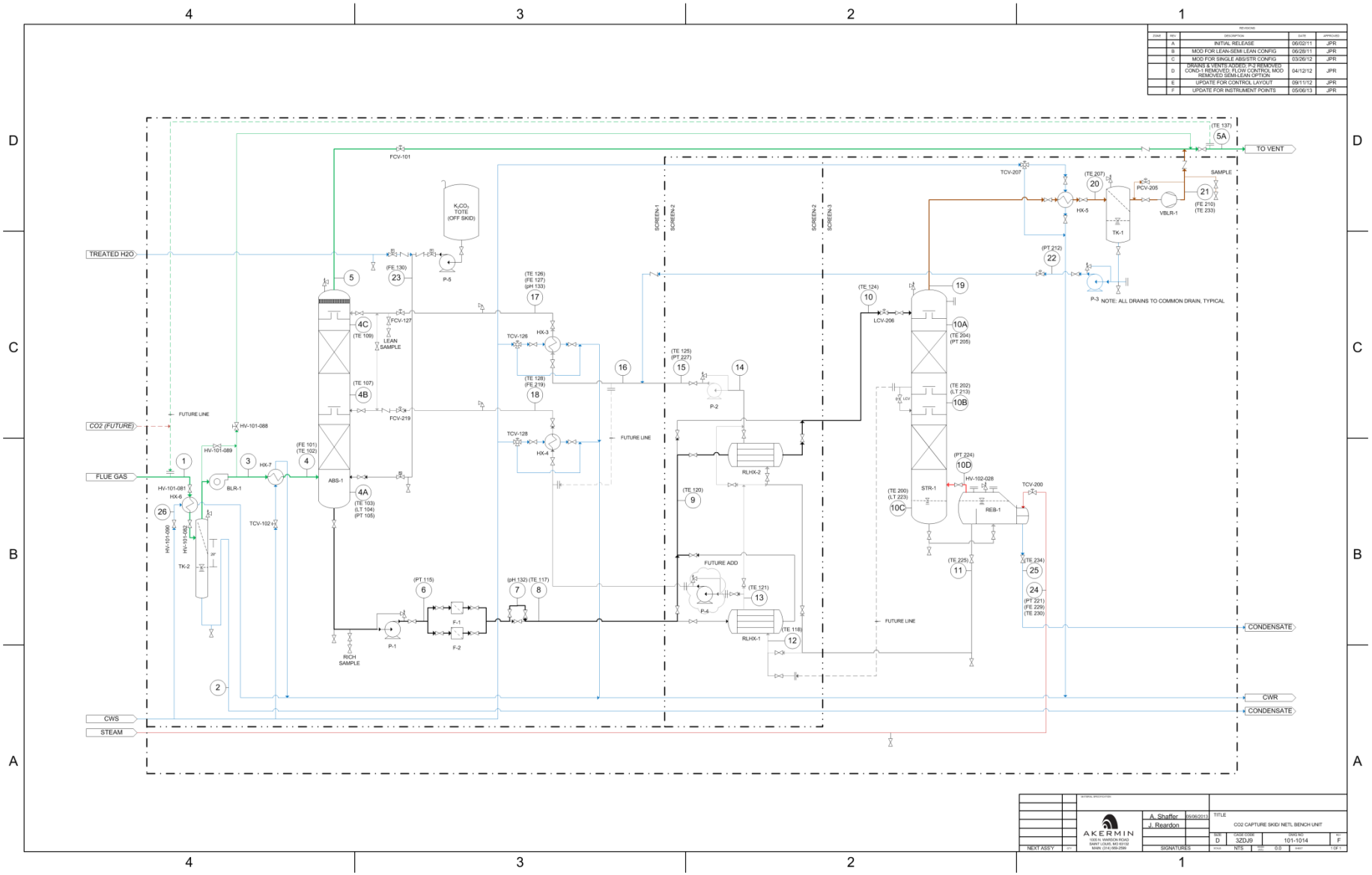
Table A.4 Stream Table for Akermin Process, Case 3A - Sheet 1

Stream Table - Page 1		1	1C	1D	1E	1F	2	3	4	5	5A	5B	5C	6	7	7A
Component Mole Flow																
N2	KMOL/HR	66997	66997	66997	0	0	66993	4	4	4	0	0	0	0	0	0
H2O	KMOL/HR	14679	6881	6881	299290	7798	5200	1022370	1022420	1022420	1053220	1008310	44910	1008310	1008330	1033680
CO2	KMOL/HR	13259	13259	13259	0	0	1326	27	77	77	14	0	14	0	4	4
HCO3-	KMOL/HR	0	0	0	0	0	0	47641	47546	47545	23839	23839	0	23839	23813	23826
CO3-2	KMOL/HR	0	0	0	0	0	0	10218	10264	10264	22108	22108	0	22108	22130	22124
K+	KMOL/HR	0	0	0	0	0	0	68078	68078	68078	68078	68078	0	68078	68078	68078
O2	KMOL/HR	2335	2335	2335	0	0	2335	0	0	0	0	0	0	0	0	0
AR	KMOL/HR	801	801	801	0	0	801	0	0	0	0	0	0	0	0	0
Component Mass Flow																
N2	KG/HR	1876820	1876810	1876810	0	2	1876700	120	120	120	0	0	0	0	0	0
H2O	KG/HR	264442	123955	123955	5391763	140486	93683	18418400	18419200	18419200	18974058	18165000	809058	18165000	18165400	18622000
CO2	KG/HR	583546	583524	583524	0	21	58352	1194	3375	3385	624	1	622	1	159	159
HCO3-	KG/HR	0	0	0	0	0	0	2906940	2901130	2901100	1454570	1454570	0	1454570	1453010	1453800
CO3-2	KG/HR	0	0	0	0	0	0	613195	615940	615954	1326730	1326730	0	1326730	1328050	1327660
K+	KG/HR	0	0	0	0	0	0	2661710	2661710	2661710	2661710	2661710	0	2661710	2661710	2661710
O2	KG/HR	74717	74717	74717	0	0	74708	9	9	9	0	0	0	0	0	0
AR	KG/HR	32012	32012	32012	0	0	32008	4	4	4	0	0	0	0	0	0
Total Mole Flow	KMOL/HR	98071	90273	90273	299290	7799	76655	1148340	1148390	1148390	1167284	1122360	44924	1122360	1122360	1147710
Total Mass Flow	KG/HR	2831530	2691020	2691020	5391763	140510	2135450	24601500	24601500	24601500	24418093	23608400	809693	23608400	23608400	24065400
Total Volume Flow	L/MIN	44196600	39975300	38211300	90269	2360	32842300	347328	354205	354312	353120	341411	40578386	341411	334351	341859
Temperature	C	56.85	40.00	47.28	30.00	40.00	40.36	46.09	81.50	81.59	87.00	87.00	87.00	87.00	51.09	50.60
Pressure	BAR	1.01	0.98	1.05	1.20	0.98	1.01	8.70	8.70	3.00	0.55	0.55	0.55	0.55	0.55	5.00
Liquid Fraction		0.000	0.000	0.000	1.000	1.000	0.000	1.000	1.000	1.000	1.000	1.000	0.000	1.000	1.000	1.000
Vapor Fraction		1.000	1.000	1.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.000	0.000
Solid Fraction		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mass Density	KG/CUM	1.07	1.12	1.17	995.50	992.11	1.08	1180.52	1157.59	1157.24	1152.49	1152.49	0.33	1152.49	1176.83	1173.26
Average Molecular Weight		28.87	29.81	29.81	18.02	18.02	27.86	21.42	21.42	21.42	20.92	21.03	18.02	21.03	21.03	20.97
Heat capacity - Mole Basis	J/KMOL-K	31156	30782	30843	75322	75172	29571	74224	75438	75468	--	76291	--	76291	74834	74814
Heat capacity - Mass Basis	KJ/KG-K	1.08	1.03	1.03	4.18	4.17	1.06	3.46	3.52	3.52	--	3.63	--	3.63	3.56	3.57
CO2 Loading	MOL/MOL	--	--	--	--	--	--	0.700	0.698	0.698	0.350	0.350	--	0.350	0.350	0.350

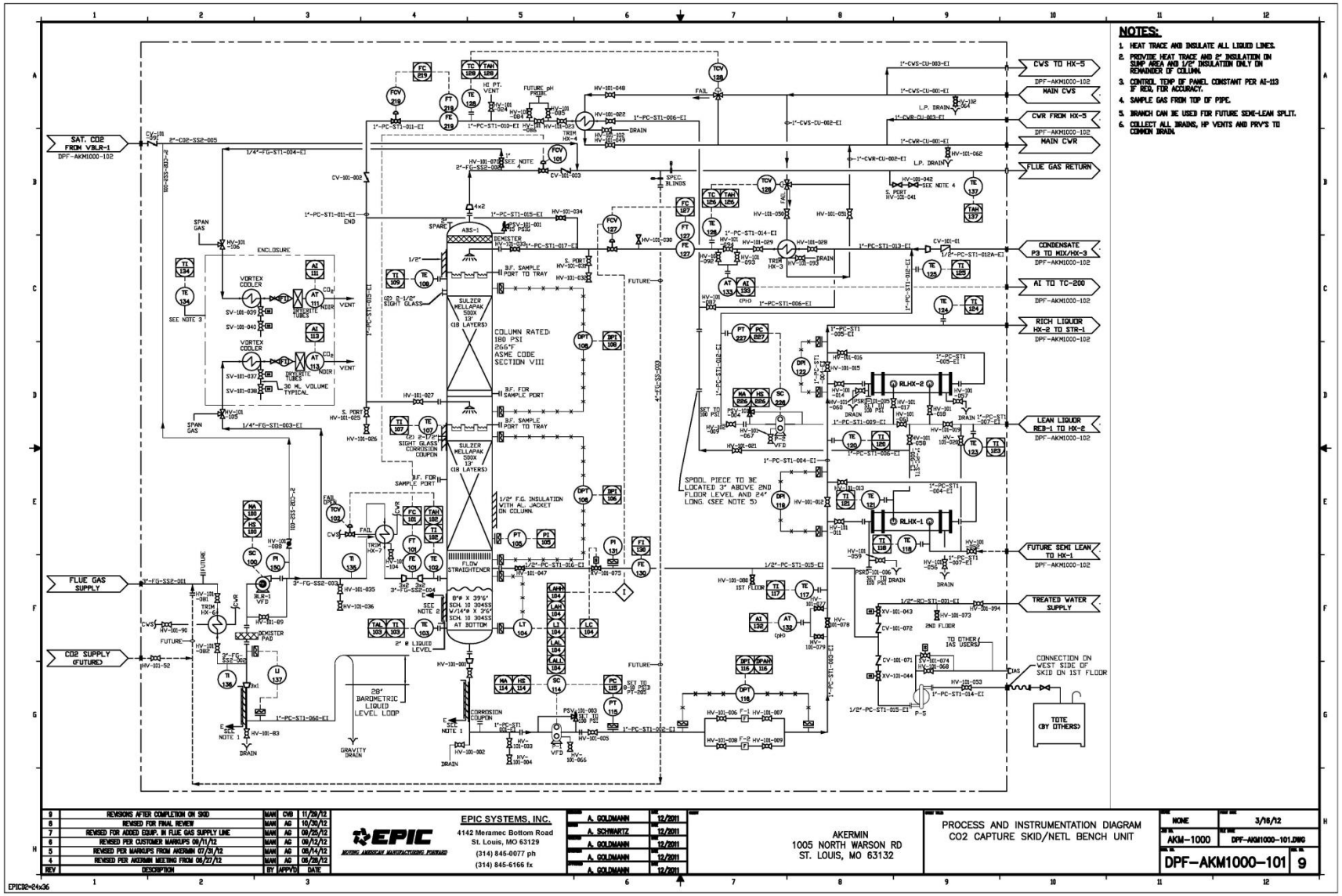
Table A.5 Stream Table for Akermin Process, Case 3A - Sheet 2

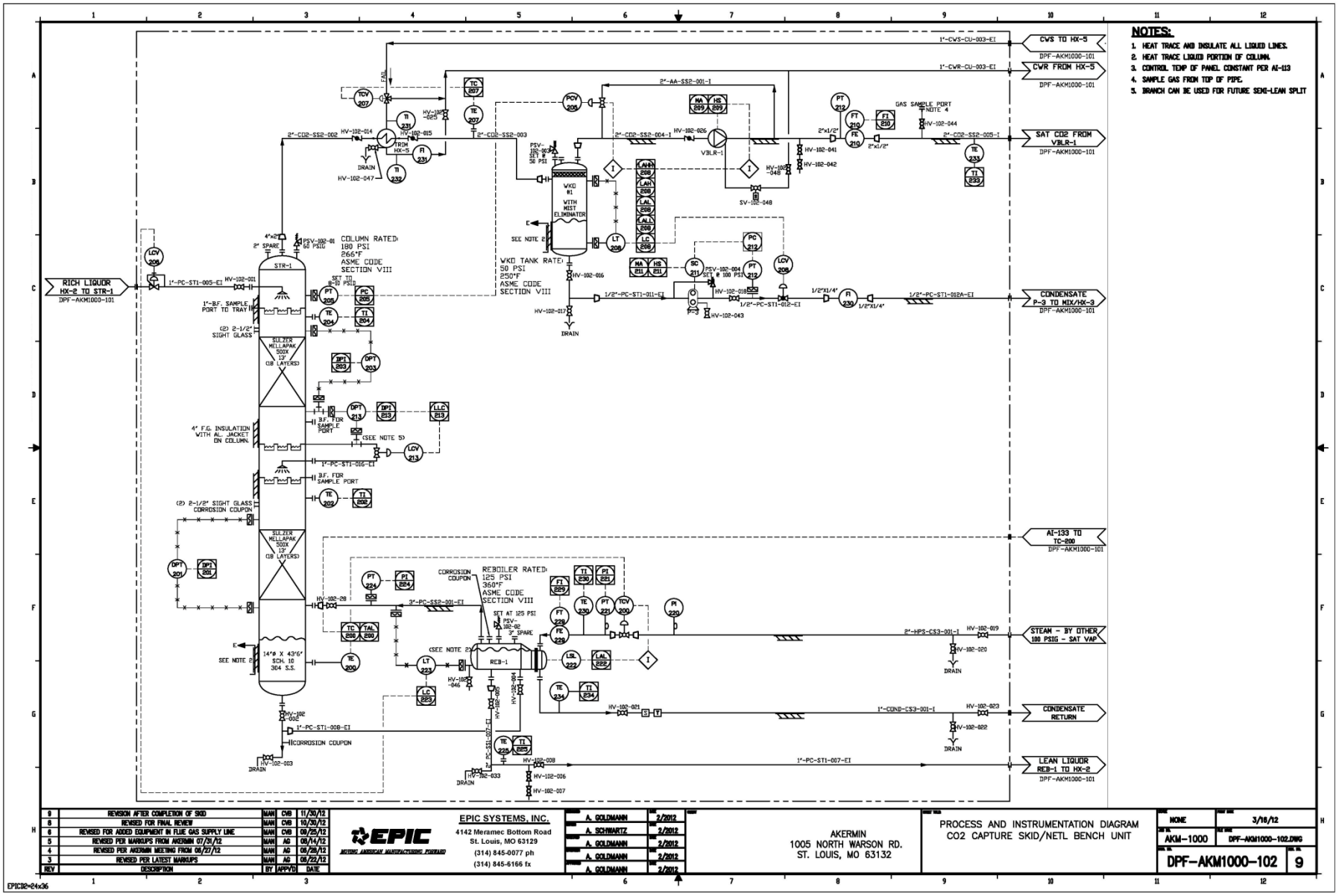
Stream Table - Page 2		8	10	11	12	12A	12B	12C	14	15	16	17	18	19	20
Component Mole Flow		0	0	0	0	0	0	0	0	0	0	0	0	0	0
N2	KMOL/HR	0	4	4	4	4	4	4	0	0	0	0	0	0	0
H2O	KMOL/HR	1033680	25953	25952	1106	1106	603	603	25349	1077	0	0	0	46704	46704
CO2	KMOL/HR	3	11939	11939	11933	11933	11933	11933	6	0	0	0	0	0	0
HCO3-	KMOL/HR	23826	0	0	0	0	0	0	0	0	0	0	0	0	0
CO3-2	KMOL/HR	22125	0	0	0	0	0	0	0	0	0	0	0	0	0
K+	KMOL/HR	68078	0	0	0	0	0	0	0	0	0	0	0	0	0
O2	KMOL/HR	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AR	KMOL/HR	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Component Mass Flow		0	0	0	0	0	0	0	0	0	0	0	0	0	0
N2	KG/HR	0	120	120	120	120	120	120	0	0	0	0	0	0	0
H2O	KG/HR	18622000	467542	467540	19926	19926	10867	10867	456673	19404	0	0	0	841386	841386
CO2	KG/HR	113	525446	525444	525172	525172	525162	525162	283	0	0	0	0	0	0
HCO3-	KG/HR	1453820	0	2	0	0	0	0	2	0	0	0	0	0	0
CO3-2	KG/HR	1327710	0	0	0	0	0	0	0	0	0	0	0	0	0
K+	KG/HR	2661710	0	0	0	0	0	0	0	0	0	0	0	0	0
O2	KG/HR	0	9	9	9	9	9	9	0	0	0	0	0	0	0
AR	KG/HR	0	4	4	4	4	4	4	0	0	0	0	0	0	0
Total Mole Flow	KMOL/HR	1147710	37896	37896	13044	13044	12541	12541	25356	1077	0	0	0	46704	46704
Total Mass Flow	KG/HR	24065400	993120	993120	545231	545231	536161	536161	456959	19404	0	0	0	841386	841386
Total Volume Flow	L/MIN	340312	34547600	10719400	10925200	7094470	5860870	3802530	7649	325	0	0	0	87077000	14302
Temperature	C	40.00	76.38	30.00	29.81	79.15	30.00	79.16	29.86	29.86	0.00	--	--	65.00	65.00
Pressure	BAR	4.80	0.53	0.51	0.50	0.89	0.89	1.60	5.00	0.51	0.00	--	--	0.25	0.25
Liquid Fraction		1.000	0.000	0.656	0.000	0.000	0.000	0.000	1.000	1.000	0.000	--	--	0.000	1.000
Vapor Fraction		0.000	1.000	0.344	1.000	1.000	1.000	1.000	0.000	0.000	0.000	--	--	1.000	0.000
Solid Fraction		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	--	--	0.000	0.000
Mass Density	KG/CUM	1178.59	0.48	1.54	0.83	1.28	1.52	2.35	995.63	995.63	0.00	--	--	0.16	980.48
Average Molecular Weight		20.97	26.21	26.21	41.80	41.80	42.75	42.75	18.02	18.02	0.00	--	--	18.02	18.02
Heat capacity - Mole Basis	J/KMOL-K	74502	35812	62147	37256	39412	37481	39719	75166	75166	0	--	--	33863	75324
Heat capacity - Mass Basis	KJ/KG-K	3.55	1.37	2.37	0.89	0.94	0.88	0.93	4.17	4.17	0.00	--	--	1.88	4.18
CO2 Loading	MOL/MOL	0.350	--	--	--	--	--	--	--	--	--	--	--	--	--

Appendix B – Final Bench Unit Process Flow Diagram (PFD)



Appendix C – Bench Unit Piping & Instrumentation Diagram (P&ID)




NOTES:
1. HEAT TRACE AND INSULATE ALL LIQUID LINES.
2. HEAT TRACE LIQUID PORTION OF COLUMN.
3. CONTROL TEMP OF PANEL CONSTANT PER AI-113
4. SAMPLE GAS FROM TOP OF PIPE.
5. BRANCH CAN BE USED FOR FUTURE SEMI-LEAN SPLIT
RICH LIQUOR HX-2 TO STR-1
DPF-AKM1000-101
CWS TO HX-5
CWR FROM HX-5
SAT CO2 FROM V3LR-1
CONDENSATE P-3 TO MIX/HX-3
AI-133 TO TC-200
STEAM - BY OTHER 100 PSIG - SAT VAP
CONDENSATE RETURN
LEAN LIQUOR REB-1 TO HX-2
COLUMN RATED: 180 PSI 266°F ASME CODE SECTION VIII
WKD TANK RATED: 50 PSI 250°F ASME CODE SECTION VIII
REBOILER RATED: 125 PSI 350°F ASME CODE SECTION VIII
EPIC SYSTEMS, INC.
4142 Meramec Bottom Road
St. Louis, MO 63129
(314) 845-0077 ph
(314) 845-6166 fx
AKERMIN
1005 NORTH WARSON RD.
ST. LOUIS, MO 63132
PROCESS AND INSTRUMENTATION DIAGRAM
CO2 CAPTURE SKID/NETL BENCH UNIT
DPF-AKM1000-102
9

Appendix D – General Arrangement (Isometric)

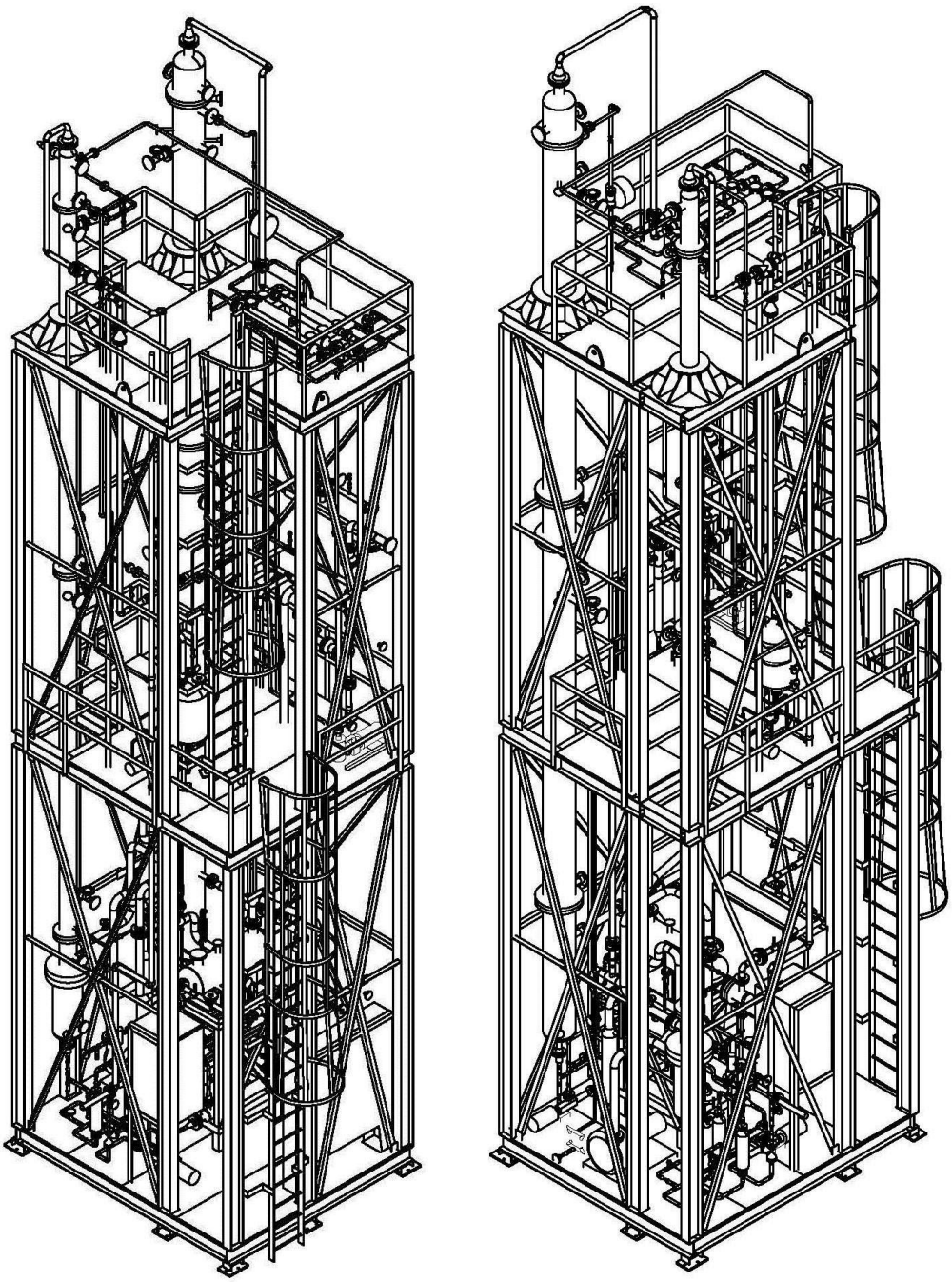


Figure 50: Isometric Views of the Akermin-NETL "Bench Unit" Skid by EPIC Systems Inc.

Appendix E (Battelle Report)

Report on Review of Final Bench Unit Mass and Energy Balance and Column Sizing

Prepared by:
M.A. Brundage, R. Peterson, M.I. Zilka, G.B. Chadwell

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December 15, 2011

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1.0 Introduction

Akermin is developing a proprietary enzyme catalyzed carbonate-based solvent technology to remove carbon dioxide from industrial gas streams including ambient pressure post combustion flue gas, high pressure syngas, and upstream natural gas applications. Having demonstrated catalyst performance in laboratory reactors, the company is ready to build a *"bench-scale"* modular pilot plant to demonstrate 90% CO_2 removal from 500 SLPM of post combustion flue gas, conceptually equivalent to 5 kWe of a coal fired electric power plant.

This report is submitted in fulfillment of Milestone B2 of Akermin's Advanced Low Energy Enzyme Catalyzed Solvent for CO_2 Capture project (DOE Award Number DE-FE0004228). It details Battelle's review of final bench-unit mass and energy balance and column sizing for Akermin's enzyme-enhanced CO_2 capture process.

2.0 Background

Appendix A contains the proposed process flow diagram (Drawing 101-1014, Rev C). The proposed system incorporates two absorption towers, operating in series, and two regeneration towers also operating in series. The regeneration towers have the provision to operate the lower stage at a pressure regulated above the upper stage through a pressure control valve.

At the end of September, Pacific Northwest National Laboratory in Richland (PNNL), Washington, delivered Excel worksheets with mass and energy balance data for numerous bench unit operating conditions (500 SLPM flue gas, 200 to 400 kg/hr circulation rate, and heat duties from 2.8 kW to 11 kW). These worksheets were forwarded to Battelle after Akermin completed its internal review in mid-October. As directed by Akermin, Battelle focused its review on only two cases: case B3-K1X, which is the blank case without enzyme enhanced kinetics, and case B3_v2 that has the enzyme enhanced 10x's kinetics as compared to the blank case, and meets the 90% CO_2 capture requirement. Akermin and PNNL have been working on demonstration of the enhanced enzyme kinetics performance of the capture system ("10x" performance over the non-enzymatic case).

Appendix B contains the Aspen flow sheet and Excel mass and energy balances for case B3-K1X. Appendix C contains the Aspen flow sheet and Excel mass and energy balances for case B3_v2.

3.0 Column Design and Packing

The current column design is a 6" (15.3 cm) diameter tower that is 15.3 m in height filled with Sulzer Mellapak M350Y. The absorber is designed to operate at 20 to 60°C and the stripper is designed to operate at 65 to 140°C.

Information on the Sulzer Mellapak M350Y was obtained from the Sulzer web site: http://www.sulzerchemtech.com/portaldata/11/Resources//brochures/mtt/Structured_Packings_April_2010.pdf. Pages 8-10 in the *.pdf file contain information on M350Y. The special features of the Mellapak are:

- 0.3-1.0 mbar pressure drop per theoretical stage
- 2 mbar/m pressure drop at 70-80% flooding
- Minimum liquid load: 0.2 $m^3/m^2/hr$ (approx)
- Maximum liquid load: up to more than 200 $m^3/m^2/hr$

3.1 Aspen Mass and Energy Balance Review

Heat and mass balances and calculations were reviewed for the system without the enzyme (B3-K1X) in Appendix B and with enzyme-enhanced absorption (B3_V2) in Appendix C. The overall mass balance and overall CO_2 balance in both cases closed to within 99.9%. All temperature changes across unit operations were linked with an associated heat source or sink. The liquid-liquid heat exchanger, RLHX-1, had a pinch point approach temperature that was at least 5°C in both cases. The heat exchanger efficiencies for the enzyme-enhanced absorption and blank cases were 87.3% and 88.1%, respectively, calculated as the heat transferred over the heat transferred in an exchanger of infinite area. It was confirmed for the blank case that the vapor stream from the first flash, FLASH-1, is very small, explaining the constant temperature across the flash. Stream pressures in all instances justified the stream flow directions. Elemental balances on hydrogen, carbon, and oxygen around the absorbers and strippers closed to within 99.9% in both cases.

Calculations for the potassium carbonate conversion, potassium balance, ion balance, potassium carbonate concentration, CO_2 capture per absorber and CO_2 removal in the strippers were reviewed and validated. The steam calculation for the second stripper, STR-2, reboiler was reviewed, and the vapor pressure equation was compared to the IAPWS 1997 steam tables. Equation-generated values matched the steam table values to within 99.9% over a range ± 20 K from the 362.7 K reboiler temperature. All molecular weights and unit conversion factors were confirmed for both cases.

Absent from the Aspen model flow sheets is any provision for heat loss in the operation. Heat loss from the operation could change the operating temperature of the column and its performance to capture CO_2. Typical heat loss from chemical plants is usually modeled at 10% and should be included in future models.

It is concluded that the simulation converged correctly and the calculations are sound in both cases. However, heat loss was not included in the Aspen model and should be included before the final design.

3.2 Column Review

To evaluate the performance of the absorption column design, the wetting characteristics were checked. For structured metal packings, such as Mellapak 350Y, satisfactory performance has

been reported down to 0.1 gpm/ft^2 and down to 0.05 gpm/ft^2 for structured wire mesh packings (ref: Kister, Henry A, Distillation Design, McGraw-Hill (1992) p 515).

Taking the liquid flow rate into the column, Stream #9 from the Aspen models in Appendix B (B3-K1X) and Appendix C (B3_V2 and), both liquid flow rates are ~ 5.6 l/min. For the 6" (~15.3 cm) column design, the column ID is 6.065" (sch 40 pipe), the internal area is 28.9 in^2. Thus the liquid load is 7.44 gpm/ft^2, which is well above the minimum liquid load of 0.1 gpm/ft^2.

Figure 1 shows the effect of pipe diameter on the liquid load from the Aspen model (solid blue line) (dotted green line is discussed below). The lowest liquid load shown on the y-axis is at 0.1 (gpm/ft^2), the lowest reported satisfactory performance for corrugated structured packings. As Figure 1 shows, the design point (shown as a red circle) the absorption column liquid load is almost 2 orders of magnitude above the minimum liquid load. A pipe diameter of around 17", will still result in the liquid load being an order of magnitude higher than the minimum liquid load.

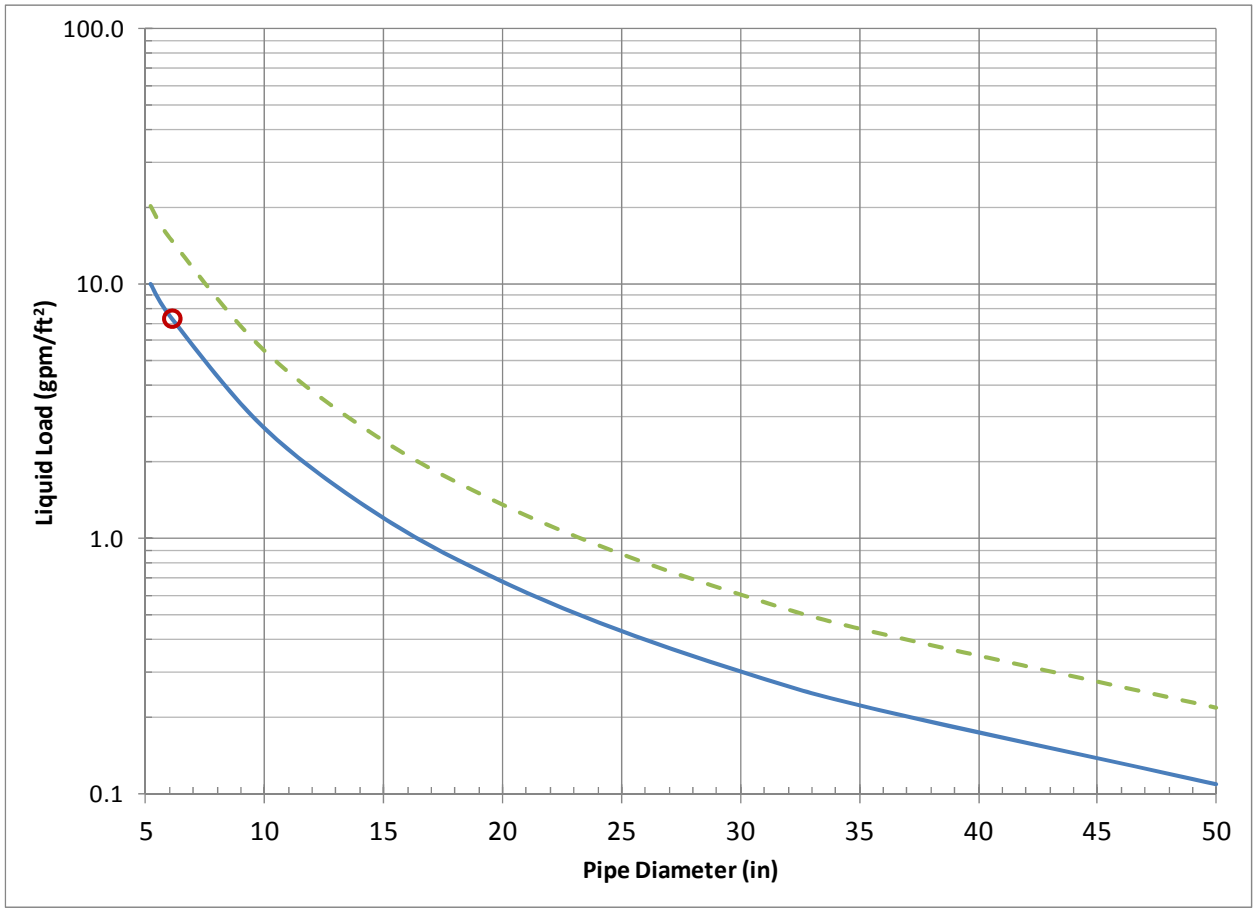


Figure 1. Effect of Diameter on Liquid Load

Given the successful demonstration of the "10x" kinetic enhancement demonstrated by Akermin and PNNL, it is concluded that the absorption column is properly sized for the designed liquid load.

3.3 Pressure Drop

To determine the pressure drop in the Mellapak packing, Sulzer uses an F factor, which is the superficial gas velocity times the square root of the gas density. Taking the gas flow rate into the column, Stream #1 from the Aspen models in Appendix B (B3-K1X) and Appendix C (B3_V2 and), both gas flow rates are ~ 567 l/min. For the 6" column, the gas flow rate of 567 l/min corresponds to a superficial gas velocity of 0.51 m/s. The gas density from Stream#1 is ~ 1.2 g/l, thus the F factor is ~0.55 $Pa^{½}$. Figure 2 shows the effect of diameter on the F factor from the Aspen models (solid blue line). Figure 2 also shows that increasing the pipe diameter decreases the F Factor.

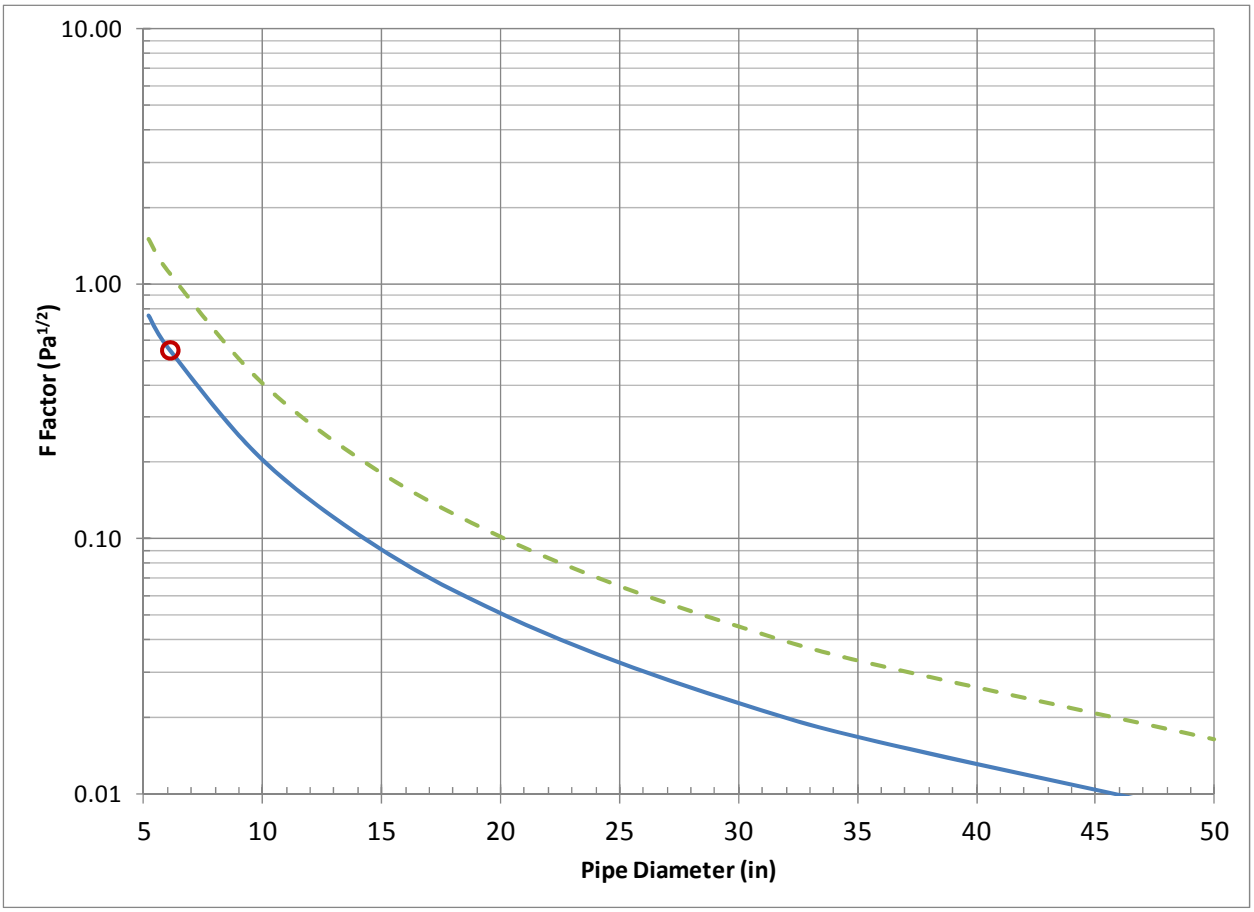


Figure 2. Effect of Pipe Diameter on F Factor

Figures 3 and 4 show the separation efficiency and pressure drop respectively from Sulzer literature. Included in the plots are various head pressures from 50 to 960 mbar. As shown in Figures 3 and 4, for an F factor of less than 1.5 $Pa^{½}$, the head pressure does not affect the separation efficiency or pressure drop.

Figure 3 shows that at an F factor of ~0.55 $Pa^{½}$ (shown as the open circle) corresponds to a HETP of ~0.25/m column for the separation efficiency. Figure 4 shows that at an F factor of ~0.55 (shown as the open circle) correlates to a pressure drop of ~0.2 mbar/m. Taking these

values, the minimum pressure drop is ~12 mbar per absorption column, for a total of 24 mbar. If the F factor is doubled to 1, the minimum pressure drop becomes 48 mbar.

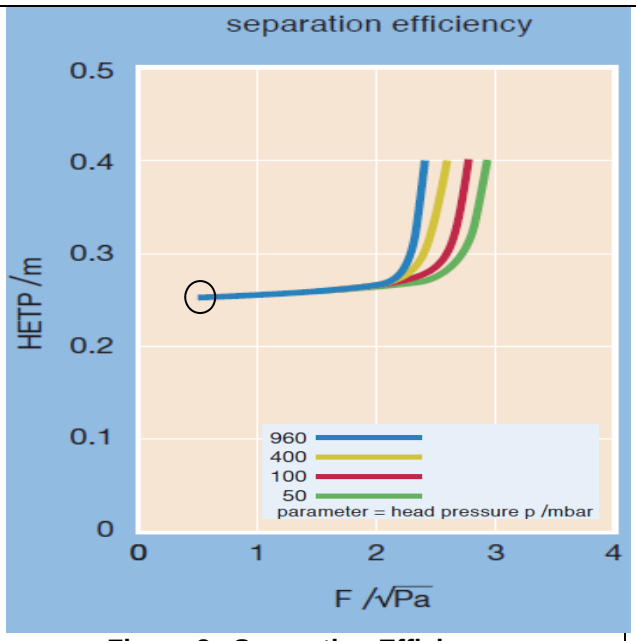


Figure 3. Separation Efficiency

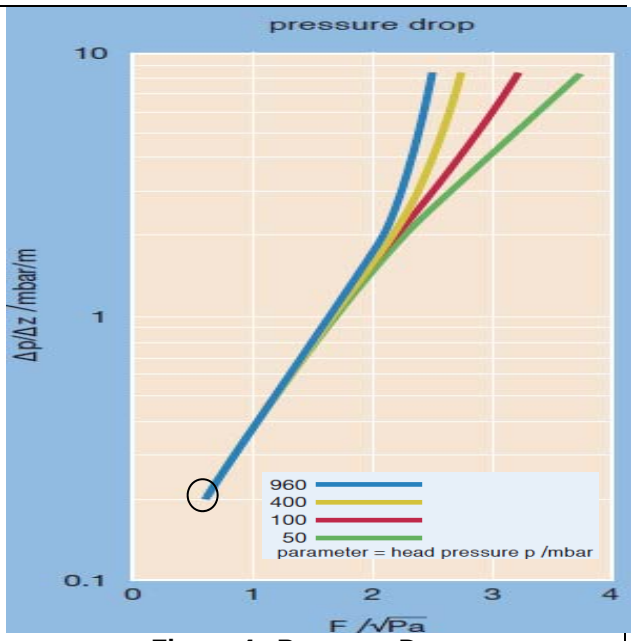


Figure 4. Pressure Drop

The F factor of ~0.55 is at the lower limit of Figures 3 and 4. Running at the lower limits of the vendor data is concerning, and may not allow for turning down the operation of the column. Increasing the gas flow rate would increase the F factor, but will also increase the pressure drop. The dashed lines in Figures 1 and 2 show the effect of doubling the liquid flow and gas flow, respectively. The dashed lines show that the column seems to have capacity for twice the flow, though it should be verified with Sulzer that flooding would not occur at that flow rate.

In addition, there also does not seem to be an allowance for an additional pressure drop through the flow distributors. There may be a need to have periodic flow distribution in a packed column with 15 meters of packing. Also, in the second column, there may be additional pressure drop from the mist eliminator (unless Sulzer does not think one is required).

The fan in the Aspen Model is set at 40 mbar, but should be set higher to allow for potential flow distributers, mist eliminators, and higher pressure drop than anticipated through the absorption column.

It is concluded that the absorption column design is at the low end of Sulzer's data. This may limit the turn down ability of the absorption column. Increasing flow rate or decreasing column diameter would move the absorption column operating point away from the low end from Sulzer's data.

Additionally, the pressure drop in the Aspen model is low. It should be verified that the vendor has included additional pressure drop for the other column internals (flow distributer and mist eliminator) in its submittal and include this pressure drop in the fan specifications.

4.0 Conclusions and Recommendations

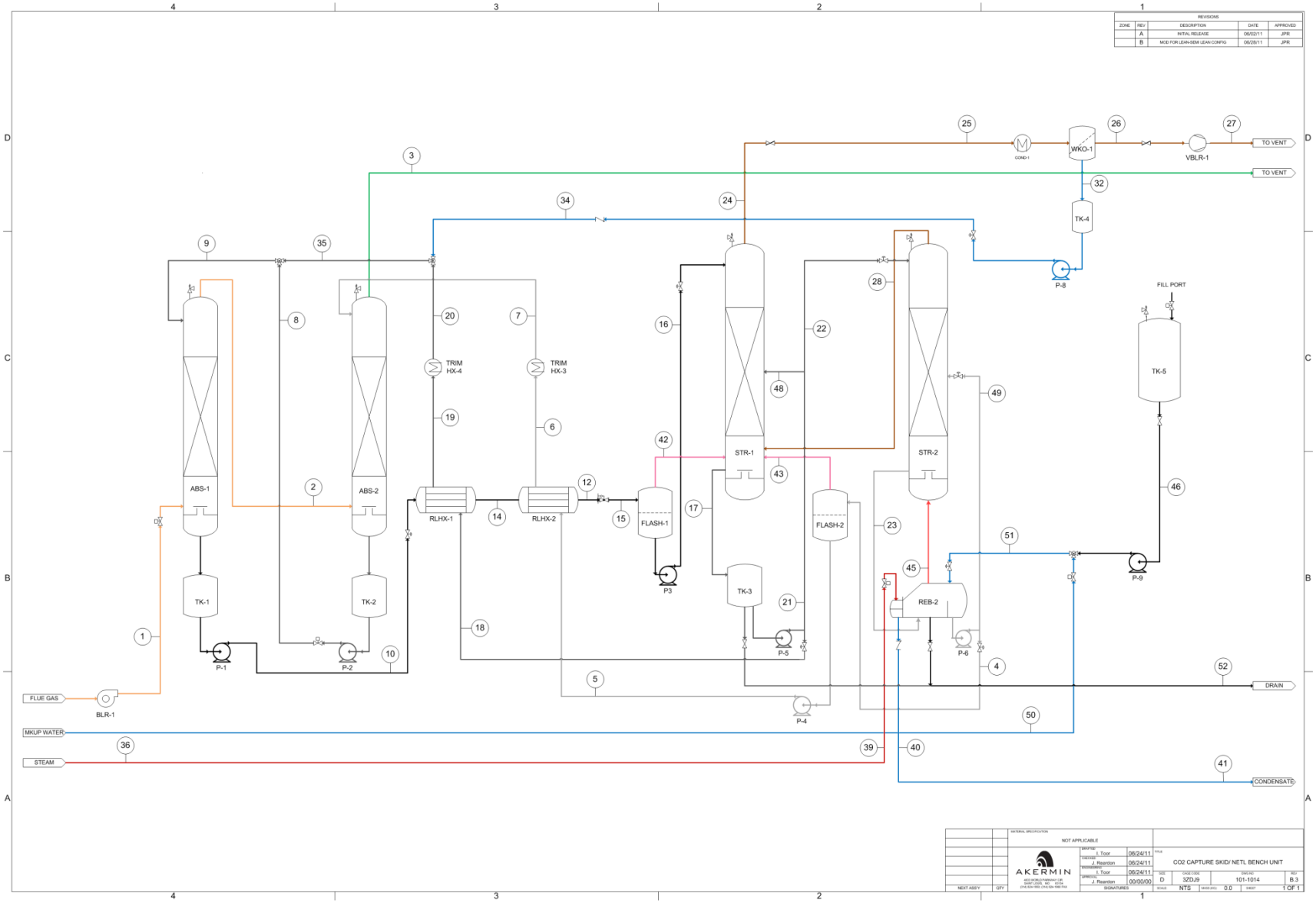
The material and energy balances from the Aspen simulations converged correctly and the calculations are sound in both models. However, heat loss was not included in the Aspen simulation. It is recommended that a 10% heat loss be included in the Aspen model before the final design is finalized.

The column design appears sound as the liquid load of the column is sufficient. However, the operating point of the column is at the low end of the F factor vendor data, which may limit the turndown ability of the column. It appears the 6” diameter was selected as a reasonable trade-off between performance and physical practicality (length to diameter ratio). Akermin may consider further investigation of additional column diameters. A smaller diameter will increase the F factor and pressure drop, but will increase the ability to turn down the absorption column. A larger diameter will decrease an already small F factor and pressure drop, and will decrease the ability to turn down the column. If different diameters are considered, the column liquid load and flooding should be verified with Sulzer to make sure they are good.

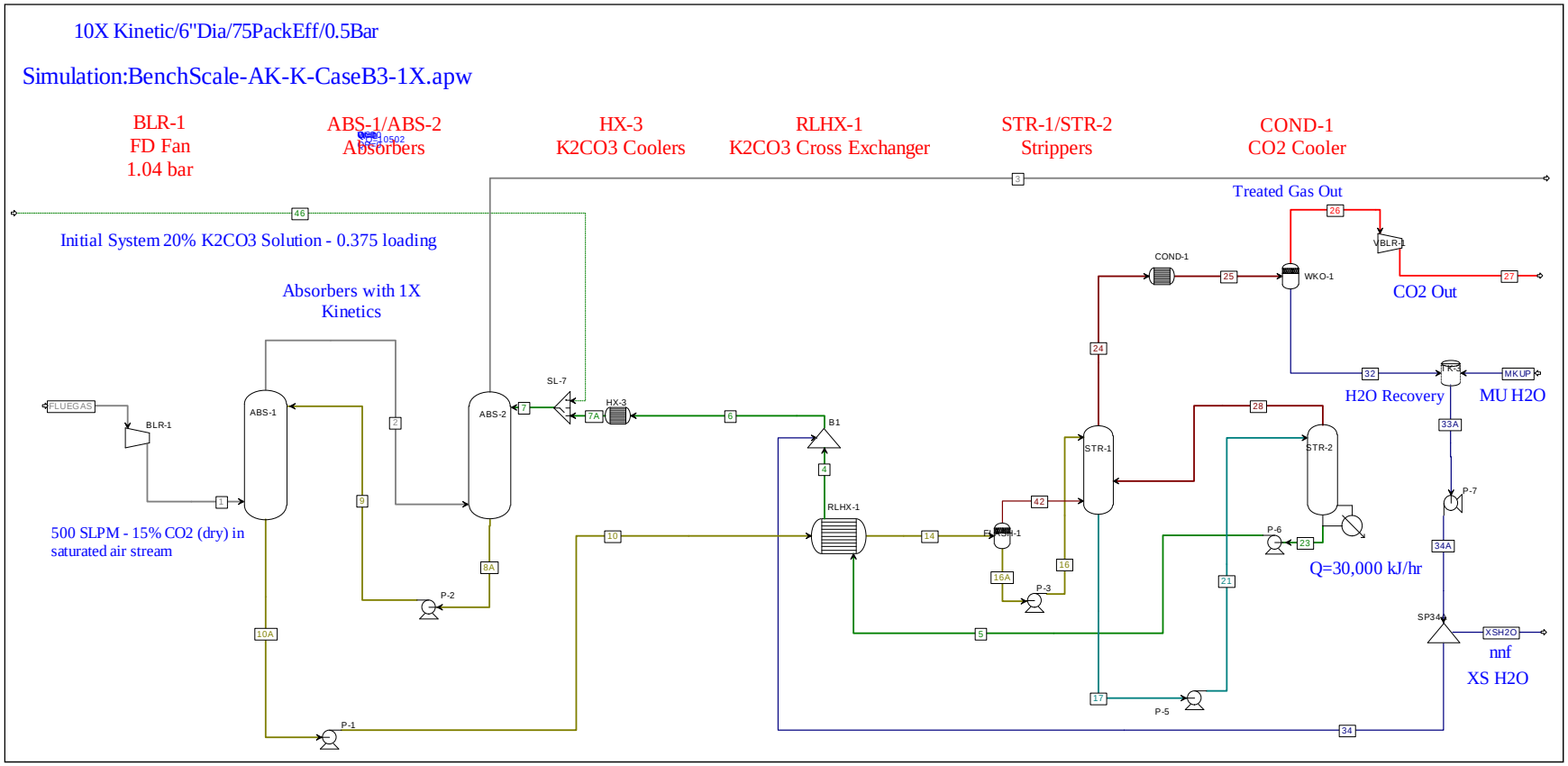
The pressure drop in the Aspen model may be low. There may be additional pressure drop due to flow distributers and mist eliminators. It is recommended that Akermin consider verifying with Sulzer what equipment is needed for the two absorption columns and what pressure drop is expected in the design then to add that pressure drop to the Aspen model. The fan then can be designed from that data.

Equipment sizing and selection should include some safety factor (5 to 10%) to allow for operational adjustments and inefficiencies.

Appendix A Akermin Process Flow Diagram, Rev C.



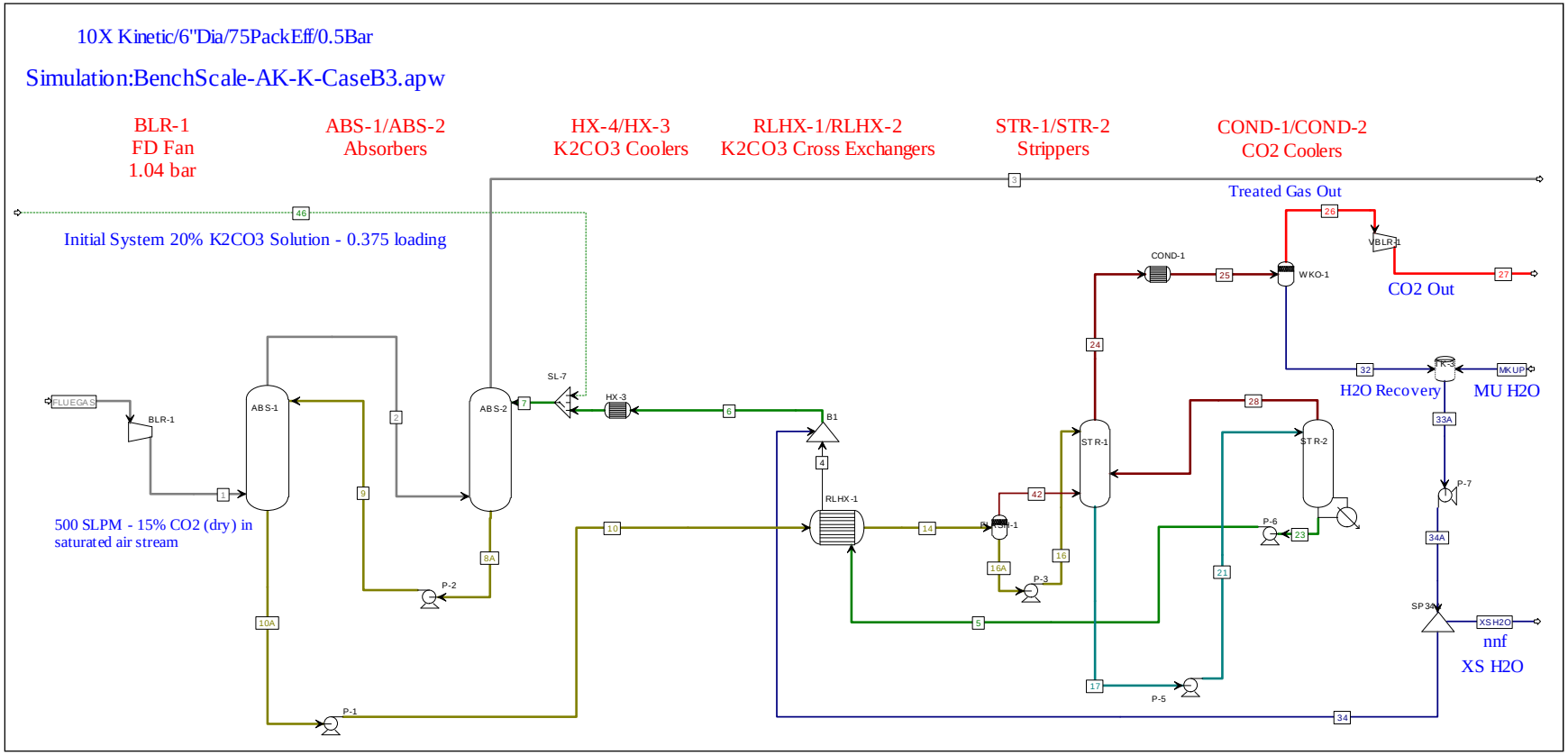
Appendix B PNNL ASPEN Model without enzyme



Appendix B PNNL ASPEN Model without enzyme

	1	2	3	4	5	6	7	7A	8A	9	10	10A	14	16	16A	17	21	23	24	25	26	27	28	32	33A	34	34A	42	46	FLUEGAS	MKUP	XSH2O
Temperature C	45	41.6	40.1	47.7	84.7	47.4	40	40	41.2	41.4	42.7	42.6	79	79.1	79	82	82.2	84.5	80.6	40	40	133.4	82.3	40	39.9	40	40	79	40	40	26.9	
Pressure bar	1.04	1.02	1.02	2.66	3	2.66	2.31	2.31	1.02	3	3	1.02	2.66	3	0.52	0.5	3.5	0.5	0.5	0.43	0.43	1.04	0.5	0.43	0.43	3	3	0.52	1.5	1	3	
Vapor Frac	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0.169	1	1	1	0	0	0	0	1	0	1	0	
Mole Flow kmol/hr	1.339	1.295	1.25	18.499	18.499	18.967	18.967	18.967	18.976	18.976	18.979	18.979	18.979	18.978	18.978	19.101	19.101	18.499	0.557	0.557	0.094	0.094	0.654	0.463	0.468	0.468	0.468	0.001	19.044	1.339	0.004	0
Mass Flow kg/hr	40.557	38.678	36.926	386.242	386.242	394.673	394.673	394.673	396.425	396.425	398.303	398.303	398.303	398.29	398.29	399.383	399.383	386.242	12.061	12.061	3.711	3.711	13.141	8.35	8.431	8.431	8.431	0.013	400	40.557	0.081	0
Volume Flow l/min	567.102	550.391	531.433	5.462	5.577	5.602	5.585	5.585	5.61	5.61	5.635	5.635	5.745	5.745	5.745	5.781	5.781	5.577	544.426	94.484	94.344	50.756	641.637	0.14	0.142	0.142	0.142	0.545	5.655	582.228	0.001	0
Enthalpy MMBtu/hr	-0.091	-0.075	-0.059	-5.213	-5.164	-5.34	-5.35	-5.35	-5.365	-5.365	-5.381	-5.381	-5.332	-5.331	-5.331	-5.35	-5.349	-5.165	-0.138	-0.158	-0.033	-0.032	-0.156	-0.125	-0.126	-0.126	-0.126	0	-5.407	-0.091	-0.001	
Mass Flow kg/hr																																
N2	23.141	23.141	23.14	0	0	0	0	0	0.002	0.002	0.002	0.002	0.002	0	0	0	0	0	0.002	0.002	0.002	0.002	0	0	0	0	0	0.001	0	23.141	0	0
O2	7.093	7.093	7.092	0	0	0	0	0	0.001	0.001	0.001	0.001	0.001	0	0	0	0	0	0.001	0.001	0.001	0.001	0	0	0	0	0	0.001	0	7.093	0	0
AR	0.396	0.396	0.396	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.396	0	0
CO2	8.216	6.383	4.799	0.001	0.002	0.001	0.001	0.001	0.005	0.001	0.002	0.007	0.006	0.006	0.006	0.008	0.005	0	3.42	3.42	3.417	3.417	2.306	0.003	0.003	0.003	0.003	0.002	0.002	8.216	0	0
H2O	1.711	1.665	1.5	300.504	300.495	308.931	308.932	308.932	308.45	308.449	307.745	307.747	307.742	307.735	307.735	310.394	310.393	300.494	8.639	8.639	0.292	0.292	10.835	8.347	8.428	8.428	8.428	0.008	308.717	1.711	0.081	0
KHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3O+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K+	0	0	0	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	0	0	0	0	0	0	0	0	0	0	44.207	0	0	0
HCO3-	0	0	0	14.957	14.986	14.966	14.964	14.964	19.345	19.354	24.433	24.419	24.435	24.429	24.429	21.346	21.355	14.993	0	0	0	0	0	0	0	0	0	0	25.868	0	0	0
OH-	0	0	0	0.002	0.011	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.005	0.005	0.005	0.007	0.007	0.011	0	0	0	0	0	0	0	0	0	0	0.001	0	0	0
CO3--	0	0	0	26.57	26.54	26.565	26.567	26.567	24.414	24.409	21.912	21.919	21.904	21.907	21.907	23.42	23.416	26.536	0	0	0	0	0	0	0	0	0	0	21.205	0	0	0
K2CO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
KHCO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mass Frac																																
N2	0.571	0.598	0.627	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.118	0	0.571	0	
O2	0.175	0.183	0.192	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.065	0	0.175	0	
AR	0.01	0.01	0.011	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.004	0	0.01	0	
CO2	0.203	0.165	0.13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.284	0.284	0.921	0.921	0.175	0	0	0	0	0.174	0	0.203	0	
H2O	0.042	0.043	0.041	0.778	0.778	0.783	0.783	0.783	0.778	0.778	0.773	0.773	0.773	0.773	0.773	0.777	0.777	0.778	0.716	0.716	0.079	0.079	0.825	1	1	1	1	0.64	0.772	0.042	1	
KHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
K2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
H3O+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
K+	0	0	0	0.114	0.114	0.112	0.112	0.112	0.112	0.112	0.111	0.111	0.111	0.111	0.111	0.111	0.111	0.114	0	0	0	0	0	0	0	0	0	0	0.111	0	0	
HCO3-	0	0	0	0.039	0.039	0.038	0.038	0.038	0.049	0.049	0.061	0.061	0.061	0.061	0.061	0.053	0.053	0.039	0	0	0	0	0	0	0	0	0	0	0.065	0	0	
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
CO3--	0	0	0	0.069	0.069	0.067	0.067	0.067	0.062	0.062	0.055	0.055	0.055	0.055	0.055	0.059	0.059	0.069	0	0	0	0	0	0	0	0	0	0	0.053	0	0	
K2CO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
KHCO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Mole Flow kmol/hr																																
N2	0.826	0.826	0.826	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.826	0	0
O2	0.222	0.222	0.222	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.222	0	0
AR	0.01	0.01	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0	0
CO2	0.187	0.145	0.109	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.078	0.078	0.078	0.078	0.052	0	0	0	0	0	0	0.187	0	0
H2O	0.095	0.092	0.083	16.681	16.68	17.148	17.148	17.148	17.122	17.122	17.082	17.083	17.082	17.082	17.082	17.23	17.229	16.68	0.48	0.48	0.016	0.016	0.601	0.463	0.468	0.468	0.468	0	17.136	0.095	0.004	0
KHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3O+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K+	0	0	0	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	0	0	0	0	0	0	0	0	0	0	1.131	0	0	0
HCO3-	0	0	0	0.245	0.246	0.245	0.245	0.245	0.317	0.317	0.4	0.4	0.4	0.4	0.4	0.35	0.35	0.246	0	0	0	0	0	0	0	0	0	0	0.424	0	0	0
OH-	0	0	0	0	0.001	0	0	0	0	0	0	0	0	0	0	0	0	0.001	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO3--	0	0	0	0.443	0.442	0.443	0.443	0.443	0.407	0.407	0.365	0.365	0.365	0.365	0.365	0.39	0.39	0.442	0	0	0	0	0	0	0	0	0	0	0.353	0	0	0
K2CO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
KHCO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mole Frac																																
N2	0.617	0.638	0.661	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.001	0.001	0	0	0	0	0	0.092	0	0.617	0	0
O2	0.166	0.171	0.177	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.044	0	0.166	0	0
AR	0.007	0.008	0.008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.002	0	0.007	0	0
CO2	0.139	0.112	0.087	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.139	0.139	0.827	0.827	0.08	0	0	0	0	0.086	0	0.139	0	0
H2O	0.071	0.071	0.067	0.902	0.902	0.904	0.904	0.904	0.902	0.902	0.9	0.9	0.9	0.9	0.9	0.902	0.902	0.902	0.86	0.86	0.173	0.173	0.92	1	1	1	1	0.776	0.9	0.071	1	0
KHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3O+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K+	0	0	0	0.061	0.061	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.059	0.059	0.061	0	0	0	0	0	0	0	0	0	0	0.059	0	0	0
HCO3-	0	0	0	0.013	0.013	0.013	0.013	0.013	0.017	0.017	0.021	0.021	0.021	0.021	0.021	0.018	0.018	0.013	0	0	0	0	0	0	0	0	0	0	0.022	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO3--	0	0	0	0.024	0.024	0.023	0.023	0.023	0.021	0.021	0.019	0.019	0.019	0.019	0.019	0.02	0.02	0.024	0	0	0	0	0	0	0	0	0	0	0.019	0	0	0
K2CO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
KHCO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SOLINDEX																																
KHCO3(S)				0.073	0.029	0.069	0.064	0.064	0.079	0.079	0.093	0.093	0.05	0.05	0.05	0.039	0.039	0.029											0.092			
PH				9.888	9.874	9.883	9.906	9.906	9.748	9.747	9.588	9.589	9.557	9.557	9.557	9.649	9.648	9.841		4.186				4.186	4.188	4.188	4.188		9.555		6.969	

Appendix C PNNL ASPEN Model with enzyme



Appendix C PNNL ASPEN Model with enzyme

CaseB3-F4Q3V2	1	2	3	4	5	6	7	7A	8A	9	10	10A	14	16	16A	17	21	23	24	25	26	27	28	32	33A	34	34A	42	46	FLUEGAS	MKUP	XSH2O
Temperature C	45	42.1	40.1	50.3	84.7	49.9	40	40	41.6	41.7	45.3	45.1	79.2	77.1	76.9	78.2	78.4	84.5	75.6	40	40	133.4	79.4	40	39.4	39.6	39.6	76.9	40	40	26.9	
Pressure bar	1.04	1.02	1.02	2.66	3	2.66	2.31	2.31	1.02	3	3	1.02	2.66	3	0.52	0.5	3.5	0.5	0.5	0.43	0.43	1.04	0.5	0.43	0.43	3	3	0.52	1.5	1	3	
Vapor Frac	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0.358	1	1	1	0	0	0	0	1	0	1	0	
Mole Flow kmol/hr	1.339	1.209	1.15	18.603	18.603	18.989	18.989	18.989	19.002	19.002	19.008	19.008	19.009	18.949	18.949	19.034	19.034	18.603	0.576	0.576	0.206	0.206	0.525	0.37	0.387	0.387	0.387	0.083	19.044	1.339	0.017	0
Mass Flow kg/hr	40.557	34.994	32.72	390.109	390.109	397.077	397.077	397.077	399.351	399.351	404.913	404.913	404.913	402.791	402.791	402.031	402.031	390.109	14.804	14.804	8.144	8.144	11.922	6.661	6.968	6.968	6.968	2.123	400	40.557	0.307	0
Volume Flow l/min	567.102	515.025	489.126	5.524	5.634	5.639	5.616	5.616	5.647	5.647	5.72	5.72	5.826	5.788	5.788	5.792	5.792	5.633	554.684	207.09	206.98	111.352	511.433	0.112	0.117	0.117	0.117	77.49	5.655	582.228	0.005	0
Enthalpy MMBtu/hr	-0.091	-0.043	-0.023	-5.256	-5.21	-5.361	-5.374	-5.374	-5.394	-5.394	-5.441	-5.441	-5.395	-5.373	-5.373	-5.373	-5.372	-5.211	-0.155	-0.171	-0.072	-0.071	-0.133	-0.1	-0.104	-0.104	-0.104	-0.022	-5.407	-0.091	-0.005	
Mass Flow kg/hr																																
N2	23.141	23.141	23.14	0	0	0	0	0	0.002	0.002	0.002	0.002	0.002	0	0	0	0	0	0.002	0.002	0.002	0.002	0	0	0	0	0	0.002	0	23.141	0	0
O2	7.093	7.093	7.092	0	0	0	0	0	0.001	0.001	0.001	0.001	0.001	0	0	0	0	0	0.001	0.001	0.001	0.001	0	0	0	0	0	0.001	0	7.093	0	0
AR	0.396	0.396	0.396	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.396	0	0
CO2	8.216	2.761	0.716	0.002	0.005	0.002	0.001	0.001	0.002	0.002	0.011	0.009	0.029	0.021	0.021	0.021	0.013	0	7.503	7.503	7.501	7.501	4.162	0.002	0.002	0.002	0.002	1.05	0.002	8.216	0	0
H2O	1.711	1.603	1.377	301.552	301.547	308.516	308.517	308.517	307.907	307.907	305.785	305.784	305.791	305.147	305.147	307.615	307.611	301.545	7.299	7.299	0.64	0.64	7.76	6.658	6.965	6.965	6.965	1.07	308.717	1.711	0.307	0
KHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3O+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K+	0	0	0	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	44.207	0	0	0	0	0	0	0	0	0	0	44.207	0	0	0
HCO3-	0	0	0	20.509	20.521	20.516	20.515	20.515	26.182	26.181	41.285	41.291	41.239	38.349	38.349	32.001	32.023	20.535	0	0	0	0	0	0	0	0	0	0	25.868	0	0	0
OH-	0	0	0	0.002	0.007	0.002	0.001	0.001	0.001	0.001	0	0	0.002	0.002	0.002	0.003	0.003	0.007	0	0	0	0	0	0	0	0	0	0	0.001	0	0	0
CO3--	0	0	0	23.838	23.821	23.834	23.836	23.836	21.049	21.05	13.623	13.62	13.643	15.064	15.064	18.184	18.173	23.814	0	0	0	0	0	0	0	0	0	0	21.205	0	0	0
K2CO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
KHCO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mass Frac																																
N2	0.571	0.661	0.707	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.001	0	0.571	0	
O2	0.175	0.203	0.217	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.175	0	
AR	0.01	0.011	0.012	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0	
CO2	0.203	0.079	0.022	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.507	0.507	0.921	0.921	0.349	0	0	0	0	0.495	0	0.203	0	
H2O	0.042	0.046	0.042	0.773	0.773	0.777	0.777	0.777	0.771	0.771	0.755	0.755	0.755	0.758	0.758	0.765	0.765	0.773	0.493	0.493	0.079	0.079	0.651	1	1	1	1	0.504	0.772	0.042	1	
KHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
K2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
H3O+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
K+	0	0	0	0.113	0.113	0.111	0.111	0.111	0.111	0.111	0.109	0.109	0.109	0.11	0.11	0.11	0.11	0.113	0	0	0	0	0	0	0	0	0	0	0.111	0	0	
HCO3-	0	0	0	0.053	0.053	0.052	0.052	0.052	0.066	0.066	0.102	0.102	0.102	0.095	0.095	0.08	0.08	0.053	0	0	0	0	0	0	0	0	0	0	0.065	0	0	
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
CO3--	0	0	0	0.061	0.061	0.06	0.06	0.06	0.053	0.053	0.034	0.034	0.034	0.037	0.037	0.045	0.045	0.061	0	0	0	0	0	0	0	0	0	0	0.053	0	0	
K2CO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
KHCO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Mole Flow kmol/hr																																
N2	0.826	0.826	0.826	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.826	0	0
O2	0.222	0.222	0.222	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.222	0	0
AR	0.01	0.01	0.01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.01	0	0
CO2	0.187	0.063	0.016	0	0	0	0	0	0	0	0	0	0.001	0	0	0	0	0	0.17	0.17	0.17	0.17	0.095	0	0	0	0	0.024	0	0.187	0	0
H2O	0.095	0.089	0.076	16.739	16.738	17.125	17.125	17.125	17.091	17.091	16.974	16.974	16.974	16.938	16.938	17.075	17.075	16.738	0.405	0.405	0.036	0.036	0.431	0.37	0.387	0.387	0.387	0.059	17.136	0.095	0.017	0
KHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3O+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K+	0	0	0	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	1.131	0	0	0	0	0	0	0	0	0	0	1.131	0	0	0
HCO3-	0	0	0	0.336	0.336	0.336	0.336	0.336	0.429	0.429	0.677	0.677	0.676	0.628	0.628	0.524	0.525	0.337	0	0	0	0	0	0	0	0	0	0	0.424	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO3--	0	0	0	0.397	0.397	0.397	0.397	0.397	0.351	0.351	0.227	0.227	0.227	0.251	0.251	0.303	0.303	0.397	0	0	0	0	0	0	0	0	0	0	0.353	0	0	0
K2CO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
KHCO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mole Frac																																
N2	0.617	0.683	0.718	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.001	0	0.617	0	0
O2	0.166	0.183	0.193	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.166	0	0
AR	0.007	0.008	0.009	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.007	0	0
CO2	0.139	0.052	0.014	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.296	0.296	0.827	0.827	0.18	0	0	0	0	0.286	0	0.139	0	0
H2O	0.071	0.074	0.066	0.9	0.9	0.902	0.902	0.902	0.899	0.899	0.893	0.893	0.893	0.894	0.894	0.897	0.897	0.9	0.704	0.704	0.173	0.173	0.82	1	1	1	1	0.713	0.9	0.071	1	0
KHCO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K2CO3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H3O+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
K+	0	0	0	0.061	0.061	0.06	0.06	0.06	0.06	0.06	0.059	0.059	0.059	0.06	0.06	0.059	0.059	0.061	0	0	0	0	0	0	0	0	0	0	0.059	0	0	0
HCO3-	0	0	0	0.018	0.018	0.018	0.018	0.018	0.023	0.023	0.036	0.036	0.036	0.033	0.033	0.028	0.028	0.018	0	0	0	0	0	0	0	0	0	0	0.022	0	0	0
OH-	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO3--	0	0	0	0.021	0.021	0.021	0.021	0.021	0.018	0.018	0.012	0.012	0.012	0.013	0.013	0.016	0.016	0.021	0	0	0	0	0	0	0	0	0	0	0.019	0	0	0
K2CO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
KHCO3(S)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SOLINDEX																																
KHCO3(S)				0.091	0.036	0.086	0.08	0.08	0.096	0.096	0.124	0.124	0.067	0.071	0.071	0.061	0.06	0.036											0.092			
PH				9.69	9.685	9.686	9.714	9.714	9.542	9.541	9.126	9.127	9.113	9.188	9.187	9.353	9.352	9.652		4.186				4.186	4.196	4.196	4.196		9.555		6.969	

Appendix F (WorleyParsons Report)

WP Summary Analysis of the PNNL TEA Report

Prepared for:

AKERMIN, Inc.

Prepared by:

WorleyParsons

Disclaimer

This report has been prepared on behalf of and for the use of Akermin, Inc.; WorleyParsons accepts no liability or responsibility whatsoever for it in respect of any use of or reliance upon this report by any third party.

PROJECT 108101-06452

REV	DESCRIPTION	ORIG	REVIEW	WORLEY-PARSONS APPROVAL	DATE	CLIENT APPROVAL	DATE
A	Issue for Comments	V.Vaysman	J. Simpson	S. Jain	11 Nov 2013	J. Reardon	14 Nov 2013
B	Final	V.Vaysman	J.Simpson	S. Jain	14 Nov 2013		
C	Add'l cmnts	.V.Vaysman	J. Simpson	S. Jain	19 Dec 2013	J. Reardon	23 Dec 2013

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Background

As part of the existing project funded by a grant from the US DOE NETL, Akermin and its project partner, the Pacific Northwest National Laboratory (PNNL), developed a techno-economic assessment (TEA) of Akermin's Biocatalyst Delivery System for application to coal-fired power plants. Akermin has provided PNNL with inputs that include: assumptions, flow sheets, mass and energy balances based upon simulation models, test data, and other information. PNNL utilized Akermin inputs to assess the cost and performance of Akermin's technology applied to capture 90% CO_2 from a coal-fired boiler designed to produce a net output of 550 MWe for a direct comparison with NETL's Case No. 12 (Reference DOE NETL Report No. DOE/NETL-2007/1281, 2010, Rev. 2).

Scope of Work:

Akermin retained Worley-Parsons (W-P) services [1] to conduct a summary analysis of the PNNL report and provide a report that comments on the following:

1. A brief summary of the work that W-P has performed leading to the resulting comments, calculations, and conclusions.
2. Where feasible, W-P to provide a general review and assessment of Cases 3A and 3C1 from the PNNL, summary tables and prepare a report that addresses:
    - **a.** The 'reasonableness' of key assumptions
    - **b.** Conversely, comment on any key assumptions that do not appear 'reasonable'
    - **c.** Spot check key calculations to comment on their accuracy
3. W-P to take the PNNL output from the report and validate PNNL calculations of the following, using the DOE NETL Carbon Capture Cost Model:
    - **a.** Cost of Electricity (COE) for the Akermin cases
    - **b.** Avoided Cost of CO_2 Capture for the Akermin cases

Summary of the Work Performed by WorleyParsons

The review of the PNNL report and the cost worksheet was conducted in two stages. During the first stage, WorleyParsons reviewed, commented and discussed with PNNL and Akermin the preliminary report [2] and the work sheet [3]. Subsequently, PNNL and Akermin provided an updated report [4] and worksheet [5], incorporating WorleyParsons preliminary comments.

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1 Services Contract between Akermin and WorleyParsons Group Inc. dated September 18, 2013

2 Advanced Low Energy Enzyme Catalyzed Solvent For Co_2 Capture, *PNNL Final Report (9-30-13) – M. Bearden, G. Whyatt & C. Freeman,* PNNL TEA Report for Akermin 20130930_v5.doc

3 LCOE Estimates vs NETL Baselines 6 – Akermin's projections.xls

4 Advanced Low Energy Enzyme Catalyzed Solvent For CO2 Capture, PNNL Final Report (9-30-13) – M. Bearden, G. Whyatt & C. Freeman, PNNL TEA Report for Akermin – Updated 10-30-13.doc

5 PNNL's LCOE Estimates vs NETL Baselines – Updated 10-30-13 (Rev 2).xls

General Overview of the PNNL Report

The PNNL report is described as an update of an earlier conducted techno-economic analysis that preceded the bench testing of the Akermin system. As such, the report appears to rely on the earlier prepared report for the description of the Akermin process, including process description, and process flow diagrams (PFD). The heat and material balances (HMB) for the update are also not included with the report, which makes it difficult to follow the discussion in the report. The process information contained in the PNNL report is limited to the performance summary of a power plant equipped with the Akermin CO_2 separation system and model input information for the Akermin system. Hence, this WorleyParsons review is based on the information deduced from the summary tables.

It is recommended to amend the PNNL report with the process related information (PFD, or block diagrams, HMB, etc.), especially if the PNNL report is intended as a standalone product.

> **PNNL report was updated on 12/3/13 to include a Process Flow Diagram (PFD) of the CO_2 Capture Unit and Heat and Mass Balance Data Table for the Akermin 3A Case, 550 MWe.**

In general the PNNL report meets the specified objectives, provided that the WorleyParsons comments are resolved to the Akermin satisfaction. The independent calculation of the Cost of Electricity performed by WorleyParsons validated the PNNL results. It should be noted that the WorleyParsons calculation was based the capital and operating costs estimated by PNNL.

Key Assumptions

The following major assumptions provide background for the design cases developed for this techno-economic analysis:

- The kinetics of the absorption process of the K_2CO_3 based solvent can be enhanced by a factor of 10 by utilization of the enzyme impregnated packing in the absorber column, and
- The kinetics of the desorption process of the K_2CO_3 based solvent can be enhanced by a factor of 5 by utilization of the enzyme impregnated packing in the stripper column.

The 10x improvement in the solvent reaction rate performance (as compared to the un-promoted K_2CO_3 based solvent) was targeted for the bench scale tests. However, the achieved performance enhancement during the bench-scale testing was observed and reported as equivalent to a 6x reaction rate improvement. The report does not identify the reasons/rationale for missing the design target of 10x. Nor does the report discuss if enhancements (changes in the catalyst) are required for the bench scale design to improve the reaction rate from 6x to 10x.

> **Supporting data is provided the Akermin's final report to which this report is an appendix. The coating process scale-up for the Bench Unit demonstration is also discussed. Akermin reports that quality assurance samples of the scaled-up coating production showed similar performance to what was reported in bench unit testing. Therefore, laboratory testing is a valid indication of enhancement at the next scale. Akermin provides data (Figure 20) from**

most recent coating development formulation which achieved ~10-fold enhancement at 45°C (and 17x at 25°C).

The utilization of the enzymes to improve the stripper kinetics is contingent upon an assumption that the enzymes could survive, and their performance does not degrade at the elevated temperature conditions in the stripper column. The report was not fully clear on the basis for the assumption of the 5x improvement in the desorption rate at the stripper temperatures.

The same catalyst is assumed for both the absorber and stripper and this is modeled with an activation energy shift. The activation energy shift specified in the Aspen model results in a 10-fold reduction in absorber height at 40 to 45°C and a 5-fold reduction in stripper column height at 80 to 85°C. According to the principle of micro-reversibility the same catalyst enhances the forward (CO_2 hydration) and reverse ($KHCO_3$ dehydration) reactions to the same extent because equilibrium must be preserved. The activation energy shift input to the Aspen model is applied to both the forward and reverse reactions to maintain accurate equilibrium prediction. Aspen's prediction of column height reduction is temperature dependent because the enzyme catalyzed reaction and the blank (un-catalyzed) reaction have different overall activation energies.

We think that the report would greatly benefit from inclusion of the following topics:

- The rationale for the expected absorber reaction rate improvement from 6X to 10X, and a description of the design features (improvements to the pilot design) that could enable such improvement
  - **See Figure 20 of the Akermin final report to which this document is attached.**
- The rationale for the enzyme performance under the elevated temperature conditions in the stripper column
  - **See Figure 20 of the final report to which this document is attached. See also the discussion above where it is noted that Aspen's prediction of column height reduction is temperature dependent because the enzyme catalyzed reaction and the blank (un-catalyzed) reaction have different overall activation energies.**

Spot Check of Key Calculations

Since the HMB is not included with the report, only the trend of some of the PNNL scaled auxiliary loads and costs were reviewed for reasonableness. The following findings have been noted:

1. The auxiliary load for the circulating water (CW) pumps is higher for the NETL Case 12 as compared to the Akermin design cases. However, the cooling tower (CT) fans auxiliary load for the Akermin cases is higher as compared to the NETL Case 12. Typically, both CT fan and CW pump auxiliary loads are proportional to the total cooling load.
   a. **PNNL has addressed this question in its updated report.**

2. There was an inconsistency in description of the Akermin system configuration, which was described as 2 x 16.7 m absorber column on page 3, but a single 23.6 m DIA absorber column (Table 6). What configuration was used as a basis for estimating FD fan auxiliary load, and the absorber capital and operating costs?
    a. **The basis for estimation was 2 x 16.7 m absorber columns, as shown in the PFD, and report was updated for clarity. One FD fan is assumed.**

3. The enzyme /coating replacement costs are estimated to be higher for the 6x case than the 10x and the 10X5 cases. The enzyme costs are expected to be higher for the 10X and 10X5 cases.
    a. **The enzyme cost per m^2 is the same since the same amount of immobilization material is coated per m^2; however, the performance is improved due to improved formulation. A more active formulation requires less total surface area for the same CO_2 capture.**

Cost of Electricity, Cost of Capture, and Avoided Costs of CO_2 Captured

The cost of electricity (COE) present in the PNNL report was independently validated and the avoided costs of CO_2 capture were calculated by W-P using the date presented in the PNNL report.

The COE ($/MWh) is calculated using the following equation from the DOE/NETL Cost and Performance Baseline for Fossil Energy Plants Volume 1 Report[6].

$$COE = \frac{\begin{matrix}\text{first year}\\ \text{capital charge}\end{matrix} + \begin{matrix}\text{first year}\\ \text{fixed operating}\\ \text{costs}\end{matrix} + \begin{matrix}\text{first year}\\ \text{variable operating}\\ \text{costs}\end{matrix}}{\begin{matrix}\text{annual net megawatt hours}\\ \text{of power generated}\end{matrix}}$$

$$COE = \frac{(CCF)(TOC) + OC_{FIX} + (CF)(OC_{VAR})}{(CF)(MWH)}$$

Where:

6 United States Department of Energy (DOE), National Energy Technology Laboratory (NETL). (2010). Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity Rev. 2. (DOE/NETL-2010/1397).Pittsburgh, Pennsylvania: U.S. DOE.

COE = cost of electricity, revenue received by the generator ($/MWh) during the power plant's first year of operation (expressed in base-year dollars) assuming that the COE escalates thereafter at a nominal annual rate equal to the general inflation rate

CCF = capital charge factor based on financial structure and determined using the NETL PSFM. This factor takes into account the financial structure and construction period to distribute the costs of the plant operational life (unitless)

TOC = total overnight capital costs, expressed in base-year dollars ($)

OC_{FIX} = the sum of all fixed annual operating costs, expressed in base-year dollars ($)

OC_{VAR} = the sum of all variable operating costs (fuel and variable O&M costs), expressed in base-year dollars ($/MWh)

CF = Capacity factor (unit-less)

MWH = Total generation from facility operating for 1 year, 8760 hours (MWh).

The cost of CO_2 captured is calculated using the following equation:

$$CO_2\ Capture\ Cost = \frac{COE_{Capture} - COE_{NoCapture}}{CO_2\ Feed_{Capture} - CO_2\ Emissions_{Capture}}$$

Where:

$COE_{Capture}$ = COE of generation facility with CO_2 capture ($/MWh)

$COE_{No\ Capture}$ = COE of generation facility without CO_2 capture ($/MWh)

CO_2 $Feed_{Capture}$ = CO_2 feed from generation facility with CO_2 capture (tonne CO_2/MWh) to the CO_2 capture unit

CO_2 $Emissions_{Capture}$ = CO_2 emissions from generation facility after CO_2 capture (tonne CO_2/MWh).

The cost of CO_2 avoided is calculated using the following equation:

$$CO_2\ Avoided\ Cost = \frac{COE_{Capture} - COE_{NoCapture}}{CO_2\ Emissions_{NoCapture} - CO_2\ Emissions_{Capture}}$$

Where:

$COE_{Capture}$ = COE of generation facility with CO_2 capture ($/MWh)

$COE_{No\ Capture}$ = COE of generation facility without CO_2 capture ($/MWh)

CO_2 $Emissions_{Capture}$ = CO_2 emissions from generation facility after CO_2 capture (tonne CO_2/MWh)

CO_2 $Emissions_{No\ Capture}$ = CO_2 emissions from generation facility without CO_2 capture (tonne CO_2/MWh).

The economic analysis assumptions were taken from the original DOE/NETL report. [6] The global assumptions are summarized in Exhibit 1. The financial structure for low risk (no-capture) and high risk (capture) projects and the resulting factors are summarized in Exhibit 2. Additionally, consistency in coal price between these calculations and the DOE/NETL Baseline report was maintained at $38.15/ton.[6]

Exhibit 1 Global Economic Assumptions

Parameter	Value
TAXES	
Income Tax Rate	38% (Effective: 34% Federal, 6% State)
Capital Depreciation	20 years, 150% declining balance
Investment Tax Credit	0%
Tax Holiday	0 years
CONTRACTING AND FINANCING TERMS	
Contracting Strategy	Engineering Procurement Construction Management (owner assumes project risks for performance, schedule and cost)
Type of Debt Financing	Non-Recourse (collateral that secures debt is limited to the real assets of the project)
Repayment Term of Debt	15 years
Grace Period on Debt Repayment	0 years
Debt Reserve Fund	None
ANALYSIS TIME PERIODS	
Capital Expenditure Period	5 years
Operational Period	30 years
Economic Analysis Period (used for IRROE)	35 years (capital expenditure period plus operation period)
Treatment of Capital Costs	
Capital Cost Escalation During Capital Expenditure Period (nominal annual rate)	3.6%[1]
Distribution of Total Overnight Capital over the Capital Expenditure Period (before escalation)	10%, 30%, 25%, 20%, 15%
Working Capital	Zero for all parameters
% of Total Overnight Capital that is Depreciated	100% (this assumption introduces a very small error even in a substantial amount of TOC is actually non-depreciable
ESCALATION OD OPERATING REVENUES AND COSTS	
Escalation of COE (Revenue), O&M Costs, and Fuel Costs (nominal annual rate)	3%[2]

Notes:

1. The nominal average rate of 3.6 percent is assumed for escalation of capital costs during construction. This rate is equivalent to the nominal average annual escalation rate for process plant construction costs between 1947 and 2008 according to the *Chemical Engineering* Plant Cost Index.
2. An average annual inflation of 3.0% is assumed. This rate is equivalent to the average annual escalation rated between 1947 and 2008 for the US Department of Labor's Producer Price Index for Finished Goods, the so-called "headline" index of the various Producer Price Indices.

Exhibit 2 Financial Structure for Investor Owned Utility

Finance Structure	High Risk CO_2 Capture Cases		Low Risk Non – CO_2 Capture Cases	
	Debt	Equity	Debt	Equity
Percent of Total	45%	50%	50%	50%
Current (Nominal) Dollar Cost	5.50%	12.00%	4.50%	12.00%
Weighted Current (Nominal) Cost	2.48%	6.60%	2.25%	6.00%
Weighted Current (Nominal) Cost Combined	9.08%		8.25%	
After Tax Weighted Cost of Capital	8.13%		7.39%	
Capital Charge Factor	0.124		0.116	
Levelization Factor	1.268		1.268	

Results of Economic Analysis

A comparison of the Akermin and WP COE's are provided in the following table. The W-P calculations validate the COE values from the PNNL report. The differences in the last significant figure are assumed to be related to the rounding of the numbers.

The following table presents results from WorleyParsons' calculation of cost of CO_2 capture and the cost of avoided CO_2.

Table 1: Summary of COE calculations and cost of avoided CO_2 determination

	Akermin-3A 6x1		Akermin-3A 10x1		Akermin-3A 10x5	
Total Plant Costs ($/kW)	2,997		2,869		2,685	
Total Overnight Cost (2007$/kw)	3,690		3,534		3,308	
Total Overnight Cost (2007$x1,000)	2,028,542		1,942,782		1,818,541	
Total As Spent Capital (2007$)	4207		4029		3771	
Annual Fixed Operating Costs ($/yr)	48,944,654		48,944,654		48,944,654	
Variable Operating Costs ($/MWh)	11.01		9.70		10.53	
COE($/MWh, 2007$)	Akermin	W-P	Akermin	W-P	Akermin	W-P
CO2 TS&M Costs	5.4	5.4	5.4	5.4	5.4	5.4
Fuel Costs	18.8	18.8	18.8	18.8	18.8	18.8
Variable Costs	11.0	11.0	9.7	9.7	10.6	10.5
Fixed Costs	11.9	12.0	11.9	12.0	11.9	12.0
Capital Costs	61.6	61.6	59.0	59.0	55.2	55.2
COE($/MWh, 2007$)	**108.7**	**108.7**	**104.8**	**104.8**	**101.9**	**101.9**
Cost of CO_2 Avoided ($/tonne)	71.64		66.03		61.80	
Cost of CO_2 Captured ($/tonne)	52.25		48.16		45.08	

The cost of CO_2 captured and the cost of avoided CO_2 can be compared the DOE/NETL Baseline report, revision 2 results: $47.84/tonne CO_2 captured and $68.95/tonne CO_2 avoided.