LOW-ENERGY SOLVENTS FOR CARBON DIOXIDE CAPTURE ENABLED BY A COMBINATION OF ENZYMES AND VACUUM REGENERATION

FINAL SCIENTIFIC/TECHNICAL REPORT

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ABSTRACT

An integrated bench-scale system combining the attributes of the bio-renewable enzyme carbonic anhydrase (CA) with low-enthalpy CO_2 absorption solvents and vacuum regeneration was designed, built and operated for 500 hours using simulated flue gas. The objective was to develop a CO_2 capture process with improved efficiency and sustainability when compared to NETL Case 10 monoethanolamine (MEA) scrubbing technology. The use of CA accelerates inter-conversion between dissolved CO_2 and bicarbonate ion to enhance CO_2 absorption, and the use of low enthalpy CO_2 absorption solvents makes it possible to regenerate the solvent at lower temperatures relative to the reference MEA-based solvent.

The vacuum regeneration-based integrated bench-scale system operated successfully for an accumulated 500 hours using aqueous 23.5 wt% K_2CO_3-based solvent containing 2.5 g/L enzyme to deliver an average 84% CO_2 capture when operated with a 20% enzyme replenishment rate per ~7 hour steady-state run period. The total inlet gas flow was 30 standard liters per minute with 15% CO_2 and 85% N_2. The absorber temperature was 40°C and the stripper operated under 35 kPa pressure with an approximate 77°C stripper bottom temperature. Tests with a 30°C absorber temperature delivered >90% capture. On- and off-line operational measurements provided a full process data set, with recirculating enzyme, that allowed for enzyme replenishment and absorption/desorption kinetic parameter calculations. Dissolved enzyme replenishment and conventional process controls were demonstrated as straightforward approaches to maintain system performance. Preliminary evaluation of a novel flow-through ultrasonically enhanced regeneration system was also conducted, yet resulted in CO_2 release within the range of temperature-dependent release, and further work would be needed to validate the benefits of ultrasonic enhanced stripping.

A full technology assessment was completed in which four techno-economic cases for enzyme-enhanced aqueous K_2CO_3 solvent with vacuum stripping were considered and a corresponding set of sensitivity studies were developed. The cases were evaluated using bench-scale and laboratory-based observations, AspenPlus® process simulation and modeling, AspenTech's CCE® Parametric Software, current vendor quotations, and project partners' know-how of unit operations. Overall, the DOE target of 90% CO_2 capture could be met using the benign enzyme-enhanced aqueous K_2CO_3-based alternative to NETL Case 10. The model-predicted plant COE performance, scaled to 550 MWe net output, was 9% higher than NETL Case 10 for an enzyme-activated case with minimized technical risk and highest confidence in physical system performance utilizing commercially available equipment. A COE improvement of 2.8% versus NETL Case 10 was predicted when favorable features of improved enzyme longevity and additional power output from a very low pressure (VLP) turbine were combined, wherein corresponding high capital and operational costs limited the level of COE benefit. The environmental, health and safety (EH&S) profile of the system was found to be favorable and was compliant with the Federal EH&S legislation reviewed. Further work on a larger scale test unit is recommended to reduce the level of uncertainty inherent in extrapolating findings from a bench-scale unit to a full scale PCC plant, and to further investigate several identified opportunities for improvement. Production feasibility and suitability of carbonic anhydrases for scale-up testing was confirmed both through the current project and through parallel efforts.

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ABBREVIATIONS AND NOMENCLATURE

~	Approximately
>	Greater than
<	Less than
%	Percent (per 100)
$	U.S. dollars
Ab.	Absorber
ACGIH®	American Conference of Governmental Industrial Hygienists®
a_i	Stoichiometric coefficient of component “i” in the reaction equation
aq.	Aqueous
atm	Standard atmospheric pressure
BP	Boiling point
Btu	British thermal units
Btu/kWh	British thermal units per kilowatt hour
°C	Degrees Celsius
CA	Carbonic anhydrase
C_i	Initial concentration
CAA	Clean Air Act
cal/mol	Calories per mole
CAPEX	Capital Expense
CCS	Carbon Capture and Storage (CCS)
CCE®	Capitol Cost Estimator® from AspenTech
CERCLA	Comprehensive Environmental Response and Liability Act of 1980
CF	Capacity factor
cm	centimeter
C/N	Carbon-to-nitrogen ratio
CO_2	Carbon dioxide
$CO_{2(aq)}$	Dissolved CO_2
$CO_{2(g)}$	Gaseous CO_2
CO_3^{2-}	Carbonate ion
COE	Cost Of Electricity
Conc.	Concentration
C_p	Heat capacity
cP	centipoise
CPVC	Chlorinated polyvinyl chloride
CTB	Carbonate To Bicarbonate
CWA	Clean Water Act
dB	Decibels
DCC	Direct Contact Cooler
DE-FOA	Department of Energy – Funding Opportunity Announcement
DI	Deionized
DOE	Department of Energy
DB, Doosan	Doosan Babcock Limited
DB1-5	Doosan Babcock Limited modelled Cases 1-5 for the TEA
Δ	Change between data points
ΔH_{rxn}	Enthalpy of reaction
DNA	Deoxyribonucleic acid

dyn/cm	Dyne per centimeter
e, exp	exponential
E	Activation energy
E.C.	Enzyme Commission (prefix for enzyme classification number)
EERC	Energy and Environmental Research Center
EH&S	Environmental, Health and Safety
EIA	Energy Information Administration
EOR	Enhanced Oil Recovery
°F	Degrees Fahrenheit
FGD	Flue Gas Desulfurization
Fl	Flowmeter
ft	Foot, feet
g	gram
g/g-[K_2CO_3-H_2O]	gram per gram aqueous potassium carbonate
g/mL	gram(s) per milliliter
g/L	gram(s) per Liter
gpm/MW_{net}	gallons per minute per Megawatt net
GJ/t	Gigajoules per tonne
h	hours
H^+	Hydrogen ion
HCO_3^-	Bicarbonate ion
H_2CO_3	Carbonic acid
Hg	Mercury (element)
HHV	Higher heating value
His	Histidine
H_2O	Water
H_3O^+	Hydronium ion
HP	High Pressure steam (2,415 psia)
HSS	Heat Stable Salts
Hz	Hertz
ID	Internal diameter
IN	Inlet
in, “	inches
IP	Intermediate pressure steam (565.5 psia)
J/g	Joules per gram
K	Kelvin
k	constant
k_2, k_{fwd}	Forward rate constant
k_3 k_{rev}	Reverse rate constant
K_2CO_3	Potassium carbonate
$KHCO_3$	Potassium bicarbonate
K_{eq}	Constant of equilibrium
kg	kilograms
kg/GJ	kilogram per Gigajoule
kg CO_2/kWh_e	kilograms CO_2 per kilowatt-hour electric
kg/MWh	kilograms per Megawatt hour
K_g, K_G	Overall mass transfer coefficient
kHz	Kilohertz
kJ	Kilojoules
kJ/kg-K	Kilojoules per kilogram per Kelvin

kJ/mol	Kilojoules per mole
kJe/kg	Kilojoules electric per kilogram
kJe/mol	Kilojoules electric per mole
KOH	Potassium hydroxide
kPa	Kilopascal(s)
kPa(a), kPaA	Kilopascal(s), absolute
kW	Kilowatt(s)
kW_e	Kilowatt(s) electric
kWh	Kilowatt hour
kWth	Kilowatt(s) thermal
L	Liter
lb	pound(s)
lb/10^6 Btu	pound(s) per million British thermal units (also lb/MMBtu)
lb/d	pound(s) per day
lb/hr, lb/h	pound(s) per hour
lb/MWh	pound(s) per Megawatt hour
lb CO_2/lb	pound(s) CO_2 per pound
lb/TBtu	pound(s) per trillion British thermal units
L/G	Liquid-to-Gas ratio
LCOE	Levilized Cost of Electrcity
ln	Natural logarithm
LP	Low pressure steam (73.5 psia, 570°F)
LPM, lpm	Liters per minute
LSFO	Limestone Forced Oxidation
m	meter
m^2	meter squared
mm	millimeter
MMBtu/hr	Million British thermal units per hour
MDEA	N-methyldiethanolamine
MEA	Monoethanolamine
MFC	Mass flow controller
MHz	Megahertz
µl	microliter(s)
µ Pa	micropascals
mills/kWh	Tenths of a cent per kilowatt hour
min	minute(s)
ml, mL	milliliter
ml/min, ml min^{-1}	milliliters per minute
mol	mole
mmol	millimoles
mmol/m^2/s/kPa	millimoles per meter squared per second per kilopascal
mmol/s	millimoles per second
mol/kg	mole(s) per kilogram
mol/L	mole(s) per liter
mol/min	mole(s) per minute
mol/s	mole(s) per second
MPa	Megapascal(s)
MSDS	Material Safety Data Sheet
MW	Megawatts
MWe	Megawatts electric

MWh_e	Megawatt-hour electric
MW_{th}	Megawatts thermal
N	Normal concentration
N_2	Nitrogen
N/A	Not Applicable
NCCC	National Carbon Capture Center
NETL	National Energy Technology Laboratory
NFPA	National Fire Protection Association
NH_3	Ammonia
NO_X	Nitrogen oxides
NR	Not reported
O&M	Operation and maintenance
OECD	Organization for Economic Cooperation and Development
OEM	Original equipment manufacturers
OH^-	Hydroxide ion
OPEX	Operational Expense
OSHA	Occupational Safety and Health Act
P	Pressure
PC	Pulverized Coal
PCC	Post Combustion Carbon Capture
P_{CO2}	Partial pressure of carbon dioxide
PFD	Process Flow Diagram
pH	negative logarithm (base 10) of the hydrogen ion activity in solution
P&ID	Process and Instrumentation Diagram
pKa	Acid dissociation constant
PM	Particulate Matter
PNNL	Pacific Northwest National Laboratory
ppm	parts per million
psia	Pounds per square inch, absolute
psig	Pounds per square inch, gauge
Q	Reboiler duty
QA	Quality Assurance
QC	Quality Control
r	rate
R	Universal gas constant, 8.314 Joules per Kelvin per mole
R^2	Correlation coefficient
REBIN	Reboiler inlet
REBOUT	Reboiler outlet
ρ	Density
Rxn	Aspen Plus® Kinetic Model reaction number
s	second(s)
S	Stripper
SARA	Superfund Amendments and Reauthorization Act
SCR	Selective catalytic reduction
SDS-PAGE	Sodium Dodecyl Sulfate – Polyacrylamide Gel Electrophoresis
SCR	Selective Catalytic Reduction
SLPM, slpm	Standard liters per minute
SO_2	Sulfur dioxide
SO_X	Sulfur oxides
Soln	Solution

STP	Standard Temperature and Pressure
TC	Thermocouple
TEA	Technical and Economic Analysis
T, Temp	Temperature
TLVs®	Threshold Limit Values®
Ton	Short ton (907 kg)
Tonne	Metric ton (1000 kg)
Tris	Tris(hydroxymethyl)aminomethane
TSCA	Toxic Substances Control Act
TSM, TS&M	Transportation, Sequestration & Monitoring
TWA	Time Weighted Average
UK-CAER	University of Kentucky's Center for Applied Energy Research
U.S.	United States of America
VLE	Vapor Liquid Equilibrium
VLP	Very Low Pressure steam (8 psia, 208°F)
vol%	volume of solute in 100 ml of total solution (solute + solvent)
W/cm^2	Watt per centimeter squared
WWC	Wetted Wall Column
wt%, kg/kg	weight of solute in 100 g of total solution (solute + solvent)
w/	with
w/w	weight per unit weight
x	When preceded by a numeral, x indicates fold change
y, yr	year
Zn, Zn^{2+}	Zinc (element)

EXECUTIVE SUMMARY

A project team, led by Novozymes North America, Inc. in collaboration with Pacific Northwest National Laboratory, University of Kentucky and Doosan Babcock Limited, was awarded DE-FE0007741 to complete a bench-scale study and a corresponding full technology and economic assessment of a solvent-based post-combustion carbon dioxide capture (PCC) system. The system integrates a low-enthalpy, aqueous potassium carbonate (K_2CO_3)-based solvent with a CO_2 absorption-enhancing carbonic anhydrase enzyme catalyst and low temperature solvent regeneration in a recirculating process configuration. The specific project objectives were to:

- Evaluate the effectiveness, physical characteristics and process robustness of the enzyme-solvent combination to capture CO_2 from simulated flue gas
- Determine the energy required to regenerate the solvent ultrasonically or using vacuum and very low pressure (VLP) steam approaches
- Successfully integrate all necessary process components to complete the 500 hour test
- Utilize test results in assessing the overall capital and operational cost of the integrated CO_2 capture system scaled for a 550 MWe net subcritical pulverized coal (PC) fired power plant
- Make a preliminary assessment of the environmental friendliness and safety of the materials and processes employed.

The rationale for using carbonic anhydrase is to promote inter-conversion between dissolved CO_2 and bicarbonate ion, which is the rate-limiting step for absorption and desorption in solutions that rely on ionic complexation of CO_2 for solvent loading. The rationale for using a CO_2 absorption solvent with a low enthalpy of reaction was to enable solvent regeneration at lower temperatures relative to existing CO_2 scrubber technologies. The study investigated both vacuum and novel flow-through ultrasonic technology options for providing the driving force needed for solvent regeneration at low temperature. Application of vacuum increases the driving force for solvent regeneration at moderate temperatures (50-80°C bulk liquid temperature) by decreasing the partial pressure of CO_2 in the gas phase, and it was projected that the ultrasonic phenomenon of rectified diffusion could substitute for the vacuum requirement at low stripping temperatures.

Work conducted during the first stages of this project determined that the magnitude of measured CO_2 release using flow-through ultrasonics regeneration was within the range of temperature-dependent release. This means, although application of ultrasonics resulted in significant visible bubble formation and was able to provide CO_2 release commensurate with thermal regeneration effects, further exploratory work would be required to determine whether rectified diffusion could deliver additional benefits. Therefore, to pursue the current project objectives, vacuum regeneration was selected as the focus for developing the integrated bench-scale system and was used for conducting the parametric and 500 hour testing.

The bench-scale study utilized a prototype microbial carbonic anhydrase enzyme catalyst to promote CO_2 absorption in 23.5 wt% K_2CO_3-based solvent and incorporated vacuum stripping to release CO_2 at a moderate temperature. The vacuum regeneration-based bench-scale system, sized for 15 L solvent inventory, demonstrated $\geq 90\%$ CO_2 capture during preliminary testing when the absorber temperature was 30°C, enzyme concentration was 3 g/L and reboiler heating fluid inlet temperature was 95°C. During the 500 hour test, an average of 84% CO_2 capture efficiency was maintained for a 450 hour period of routine enzyme replenishment. Stopping enzyme replenishment during the final test period resulted in decreased CO_2 capture efficiency, proving the importance of catalyst for CO_2 absorption in K_2CO_3-based solvents at ambient pressure. Overall, the system tolerated daily start-up/shut-down, foaming was controllable using antifoam, and the principle of using dissolved enzyme replenishment to achieve stable operation was demonstrated. The system tolerated turbidity during operation. Solvent could be clarified using proper filtration. Although performance instability occurred – attributed to (protein) solids accumulation on reboiler surfaces – this was corrected by rinsing the system. At a practical level, stabilizing the vacuum condition in the bench-scale unit required continuous control due to the high chance of foaming in the presence of prototype enzyme. The bench-scale regeneration energy requirement with K_2CO_3 (no-enzyme) was 1600 kJ/mol giving 19% CO_2 capture and was 313 kJ/mol for K_2CO_3 with enzyme giving 84% capture; compared to a full scale simulation of 147 kJ/mol for the DB1 main case and 156 kJ/mol for 30 wt% MEA (NETL Case 10).

A technical and economic feasibility assessment was carried out to evaluate five cases consisting of a subcritical PC fired power plant with different PCC plant configurations. The power plant design was based on a PC steam generator firing Illinois No. 6 coal and a steam turbine. The entire coal-fired power plant, including the integrated PCC plant, was modelled and optimized for 550 MWe net output to allow for a meaningful comparison among the five cases and the baseline cases of NETL Case 9 (subcritical PC boiler without CO_2 capture) and NETL Case 10 (subcritical PC boiler with amine based CO_2 capture). Four cases utilizing the enzyme-activated solvent and one case with solvent containing no enzyme, all using vacuum regeneration at different pressures with different sources of steam, were evaluated. For the case without enzyme, the model predicted a maximum of 18% CO_2 capture with aqueous K_2CO_3 alone, clearly illustrating why non-activated K_2CO_3 solvent has not been considered viable for ambient pressure flue gas scrubbing applications. The best enzyme-activated case in terms of minimized technical risk with highest confidence in physical system performance utilizing commercially available equipment and related process technologies had a model predicted plant COE performance 9% higher than NETL Case 10. However, the likelihood of a lower environmental impact and potential for further process improvements, particularly with regards to enzyme development, could result in a model predicted reduction of 1% in COE for this case compared to NETL Case 10. A COE improvement of 2.8% versus NETL Case 10 was predicted when favorable features of improved enzyme longevity and additional power output generated from a very low pressure (VLP) turbine were combined, however the capital and operational costs required for vacuum creation and subsequent CO_2 compression and for installation of the VLP turbine diminished the magnitude of the benefits, highlighting the importance of capital cost considerations. The preliminary environmental, health and safety (EH&S) risk assessment found that potential emissions pose no significant concerns and were compliant with the Federal EH&S legislation reviewed. The commercial scale feasibility of systems incorporating the beneficial features identified would need to be further assessed and validated through scale-up. Beyond the specific cases evaluated, a number of recommendations have been made that could result in further system improvements, such as improved solvent cyclic capacity, improved enzyme longevity, alternative stripper configurations and potentially taking advantage of low temperature exhaust steam sources.

1 INTRODUCTION

According to the U.S. Department of Energy (DOE) Energy Information Administration's (EIA) International Energy Outlook 2013 [1] Reference Case (which does not include prospective greenhouse gas reduction policies), coal remains the second largest energy source worldwide, contributing more than one-fourth of the world's total primary energy supply, and one-third of the fuel used for electricity generation. World energy consumption will grow by 56 percent between 2010 and 2040, and worldwide energy-related carbon dioxide emissions will increase by 46 percent, from about 31 billion metric tons in 2010 to 45 billion metric tons in 2040. Within this period, coal consumption is predicted to increase by 50 percent, from 147 quadrillion Btu in 2010 to 220 quadrillion Btu in 2040. In the EIA Outlook, total coal consumption for Organization for Economic Cooperation and Development (OECD) countries remains near 2010 levels while coal consumption in non-OECD countries increases at a pace of 1.8 percent per year, led by China. Coal consumption in India is projected surpass the United States by 2030. As a result, increased use of coal in non-OECD countries accounts for nearly all the growth in world coal consumption over the period. Coal's share of global fuel consumption for electricity generation is projected to decline from 43 percent in 2010 to 37 percent in 2040 [1]. In the United States, coal consumption declined from 20.8 quadrillion Btu in 2010 to 17.8 quadrillion Btu in 2012 as a result of lower demand for power and displacement of coal-fired generation in response to lower natural gas prices and rising delivered prices for coal. Although coal's share of total U.S. electricity generation (Figure 1) is projected to decline from 45 percent in 2010 to 35 percent in 2040 as consumption of alternative fuels such as natural gas and renewables increase to meet growing energy demands [1], coal power generation remains a very significant share of the global energy mix and, for the foreseeable future, coal will continue to play a critical role in powering the world's electricity generation, especially for base-load power plants.

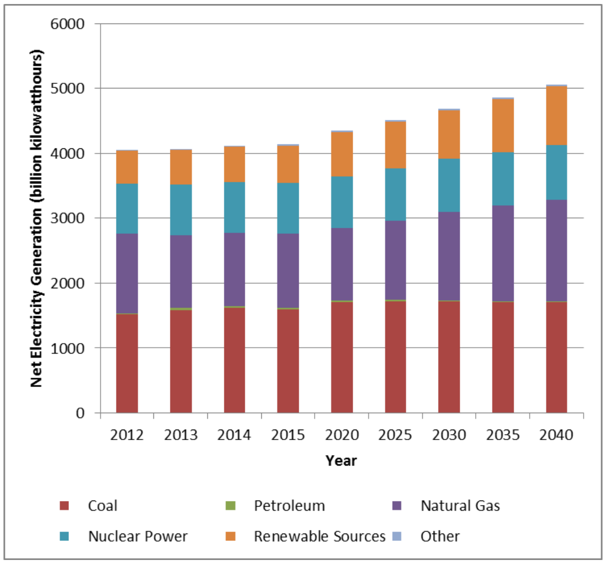


Figure 1. U.S. Electricity generation by fuel type.

Emissions of greenhouse gases, such as CO_2, have increased over the past century and have been linked to increasing climate disruption [2]. Coal, the most carbon-intensive fossil fuel, will continue to be the leading source of energy-related carbon dioxide emissions through 2040, accounting for 45 percent of energy-related emissions globally. The amount of CO_2 produced from the combustion of fossil fuels in the United States reached 5.6 billion metric tons in 2010 and is expected to remain around this level, reaching 5.7 billion metric tons in 2040 according to the EIA, with about 30% coming from the coal-fired electric power sector [1]. During the past decades, since the passage of the Clean Air Act [3], coal-fired power plants have made significant progress in reducing emissions of damaging flue gas components such as sulfur dioxide (SO_2), nitrogen oxides (NOx), particulate matter (PM), and mercury (Hg). For example, U.S. electric power sector emissions of 3 and 1.5 million metric tons for sulphur dioxide and nitrogen oxide, respectively, and 24 metric tons for mercury in 2014 are expected to decrease even further to 1.3 and 1.4 million metric tons for SO_2 and NO_2, respectively, and to 6 metric tons for mercury by 2020 [4], illustrating the beneficial impact of these regulations. Currently there are no national limits on CO_2 emissions, however, steps towards reductions are being taken through the proposed Clean Power Plan, issued by the Environmental Protection Agency in June 2014, with the goal of reducing carbon pollution from the power sector by 30 percent compared to 2005 levels [5]. This sets a carbon dioxide equivalents emissions target of 1.7 billion metric tons. For reference, total greenhouse gas emissions from U.S. electricity generation in 2013 were 2 billion metric tons of carbon dioxide equivalents [6]. Implementation of CO_2 capture technologies at large stationary CO_2-emitting sources is one of the key strategies to help meet the Clean Power Plan CO_2 emissions control goals while continuing to benefit from coal's competitive stature as a base-load fuel and the security of its domestic supply.

The U.S. DOE National Energy Technology Laboratory (NETL) issued Funding Opportunity Announcement DE-FOA-000403 "Bench-Scale and Slipstream Development and Testing of Post Combustion Carbon Dioxide Capture and Separation Technology for Application to Existing Coal-Fired Power Plants," specifically focused on developing advanced technologies for CO_2 capture and purification that can be retrofitted to existing pulverized-coal (PC) power plants [7]. Sixteen projects were awarded in August 2011 totalling \$41 million. The DOE program objective for projects in the solvent-based, post-combustion category was to develop technologies that can achieve 90% CO_2 removal from PC power plants, and demonstrate progress toward the DOE target of < 35% increase in levelized cost of electricity (LCOE). A project team, led by Novozymes North America, Inc. in collaboration with Pacific Northwest National Laboratory, University of Kentucky and Doosan Babcock Limited, was awarded DE-FE0007741 to conduct bench-scale tests and techno-economic assessment of a novel potassium carbonate-based post-combustion carbon dioxide capture (PCC) process with potential to improve CO_2 capture process efficiency.

The PCC process evaluated under DE-FE0007741 included application of a carbonic anhydrase enzyme catalyst to promote CO_2 absorption in a low enthalpy potassium carbonate-based solvent and the incorporation of a vacuum or ultrasonic stripping process to release CO_2 at a moderate temperature. Low temperature regeneration processes were predicted to offer energy benefits, therefore, the goal was to demonstrate performance at bench-scale as well as evaluate overall system cost scaled for a 550 MWe net output PC plant, including considerations of enzyme longevity. Evaluating ultrasonically-enhanced regeneration was of interest because of the potential for a phenomenon known as rectified diffusion to force dissolved CO_2 into gas bubbles at ambient pressure, thereby eliminating the need for additional compression, which is required if vacuum regeneration is used to supply driving force.

1.1 Background

Fossil fuels will play a dominant role in base-load power generation for the foreseeable future, incurring high levels of CO_2 emissions. Therefore, carbon capture and storage (CCS) is considered to be a critical component in the portfolio of low-carbon energy technologies needed to mitigate climate change and limit long-term global average temperature increase to 2 °C [8]. Depending on the combustion technology employed, three routes for CO_2 capture from coal-derived power generation are possible – post-combustion capture, pre-combustion capture, and oxy-combustion – each with advantages and disadvantages [9]. Chief advantages for post-combustion CO_2 capture approaches are the applicability of the technology to the majority of existing coal-fired power plants and the potential to retrofit these plants with post-combustion CO_2 controls. In the post-combustion option, conventional combustion using air produces a flue gas mixture containing dilute CO_2 and a large amount of nitrogen with other minor gas components at ambient pressure. As a result, a large amount of flue gas needs to be processed in order to remove the CO_2 fraction, requiring large capacity equipment, and the CO_2 produced is at low pressure compared to sequestration requirements. Therefore, technology developments are needed to overcome the techno-economic obstacles presented by these challenges.

CO_2 capture technologies are already used commercially for natural gas upgrading, biogas upgrading, production of liquefied natural gas, hydrogen production, fertilizer production, production of merchant gas for applications such as beverage carbonation and dry ice production, removal of CO_2 from enclosed environments such as submarines and spacecraft, and separation of CO_2 in various industrial processes [10]. Projects [11] at Sleipner (0.9 Mt CO_2/yr), Weyburn (1 Mt CO_2/yr), In Salah (1.2 Mt CO_2/yr), and Snøhvit (0.7 Mt CO_2/yr) are examples of end-to-end CCS operations that have successfully captured, compressed, transported and injected CO_2 into deep geologic storage formations, yet it would require the combined scale of these projects to capture and store the CO_2 from one 500 MW coal fired power plant (3 Mt CO_2/yr) [12]. Also, in commercial processes, the CO_2 can optionally be recovered and used or can be vented to the atmosphere, by-passing the sequestration compression requirement. With the growing concerns of climate change, technologies to efficiently separate and prevent CO_2 emissions from accumulating in the atmosphere are needed, yet the scale of operations required to have meaningful impact on current emissions is far larger than the techno-economic capability of current commercial processes. Therefore, the U.S. Department of Energy established targets to reduce the cost of CO_2 capture to < \$40 per metric ton by 2025 [13] and has provided significant financial incentives to encourage rapid development and deployment of new efficient CO_2 scrubbing technologies. Through these efforts, an increasing number of demonstration projects are being carried out in the U.S. and globally [14], recently including the world's first operational full-scale post combustion carbon capture system for base-load power generation at Boundary Dam which utilizes the captured CO_2 for enhanced oil recovery (EOR) [15]. In the long term, geologic storage is seen as the only option for sequestering CO_2 at billion-ton scale. The path towards storage is being established by demonstration projects where emissions sources are in close proximity to well-suited geologic formations ([16], [17]), as well as commercially-oriented projects, such as the one at Boundary Dam [18], utilizing compressed CO_2 for EOR, where it is estimated that one metric ton of CO_2 can be geologically sequestered for every 2.5

barrels of oil produced over the life of the project [19], and recent surveys indicate CO_2-EOR projects now produce about 350,000 barrels of oil per day [20].

1.2 Overall Process Concept for Post-Combustion CO_2 Capture

In the power generation sector, burning fuels (e.g. coal, methane, oil, biomass) by combustion with air in a boiler is used to heat water and produce steam at high pressure. This high pressure steam is delivered to a series of turbines in the power block, where thermal energy is converted to electrical energy. The by-product of fuel combustion is a flue gas containing a mixture of gaseous (primarily N_2 and CO_2) and particulate components, as well as water vapor. In order to meet regulatory limits on the composition of flue gas emitted to the atmosphere, the flue gas is passed through pollution control systems to remove nitrogen oxides (NOx), particulate matter (PM) and sulfur dioxide (SO_2). Removal of CO_2 from the flue gas is envisioned to occur as a next step after the standard pollution controls, resulting in a gas stream emitted to the atmosphere that is primarily composed of N_2 and water vapor. Condensers are used to recover water vapor from the CO_2 removed during the CO_2 capture process before being compressed to high pressure for efficient transportation to an end use, such as EOR, or to geologic storage. A simplified block diagram illustrating a power plant with post-combustion CO_2 capture process is shown in Figure 2. The separation of CO_2 from flue gas in the CO_2 capture process is challenging because a high volume of gas (≈2 million cubic feet per minute for a 550-MWe plant) must be treated, the CO_2 is dilute (typically below 15 percent volume CO_2, wet basis), the flue gas is at atmospheric pressure, trace impurities (PM, SO_2, NOx, etc.) can degrade capture media, and compressing captured CO_2 from near-atmospheric pressure to pipeline pressure (about 2,200 pounds per square inch absolute [psia]) requires a large auxiliary power load [13]. Chemical solvent-based technologies currently used in industrial CO_2 capture applications are being evaluated for installation at power plants, however, solvent-based processes require relatively large volumes of low-pressure steam from the power block to release CO_2 from the solvent. This use of steam for solvent regeneration is a key factor causing reduced electrical generation output of the plant, and creates an economic obstacle to deploying CO_2 capture technologies.

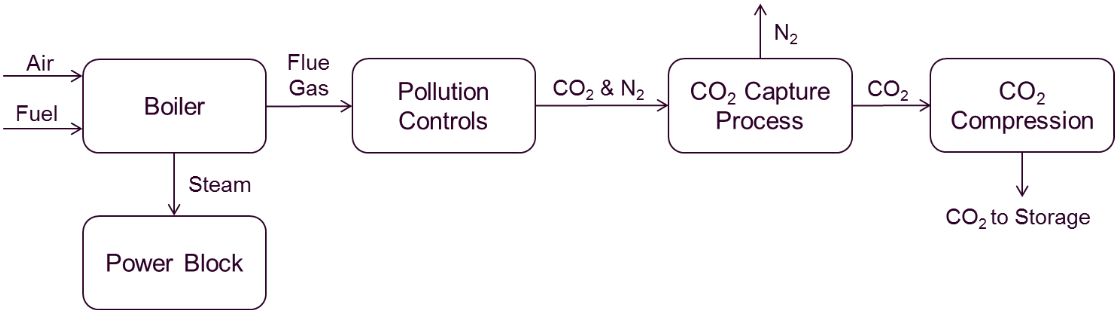


Figure 2. Block diagram of power plant with Post-Combustion CO_2 Capture.

Solvent-based post-combustion CO_2 capture systems are typically benchmarked against the performance of aqueous monoethanolamine (MEA), which, combined with a proprietary corrosion inhibitor system, was introduced in the 1980s to separate CO_2 for food and chemical process industries and enhanced oil recovery (EOR) applications [21]. A main attribute of MEA is the ability to form MEA-carbamate, resulting in rapid reaction kinetics at relatively low temperature and CO_2 partial pressure. However, the relatively high heat of absorption requires a high desorption temperature and energy to overcome the strong chemical bond formed between CO_2 and the sorbent. An NETL study based on costs compared in 2007$ estimated the cost of electricity increase of adding MEA-based post combustion CO_2 removal and compression ("NETL Case 10") to subcritical coal-fired power plants without capture ("NETL Case 9") at more than 80% (Exhibit ES-2 of [22]), therefore alternatives are urgently needed and are under investigation in the U.S. ([9], [23], [24]) and globally [25]. An increasing number of studies have given evidence that CO_2 capture processes utilizing the CO_2 absorption enhancing biocatalyst carbonic anhydrase could contribute to developing these necessary alternatives.

1.3 Enzymes as Catalysts for Industrial Processes

Enzymes are protein-based biological catalysts that selectively enable essential biochemical reactions to occur at useful rates by virtue of an 'active site' located within the complex three dimensional protein structure. Enzymes are produced by all living organisms according to a genetic blueprint, are vital to life, but are not themselves alive. The chemical functionality and spatial orientation of amino acid side-groups in the active site enables chemical recognition and binding of the reactant compound, called the 'substrate,' in a way that lowers the activation energy for the specific chemical reaction to occur [26]. Both the overall protein structure and chemical composition of functional groups in and around the active site contribute to the selectivity, efficiency and robustness of enzymes.

Enzymes are established, beneficial, and cost-effective catalysts in many industrial processes. Around 150 different industrial processes based on enzymes are estimated to be in use, spanning industries including household care, food, feed, textiles, biofuels, industrial cleaning, and paper production, where the action of enzymes reduces chemical, water and energy consumption [27]. Enzymes can be obtained directly from their natural source, such as by extraction from plant, animal or microbial cells, or can be produced in non-native host microorganisms using recombinant DNA and bio-manufacturing techniques. For commercial bio-manufacturing (Figure 3), a common approach is to insert donor DNA for the enzyme of interest into the gene sequence of a microbial host capable of secreting the enzyme from the cell into the surrounding fermentation broth during production. The soluble secreted enzymes are separated from the host cell by a series of filtration, purification and recovery processes that enable the scalable and economical production of enzymes in large industrial quantities [28].

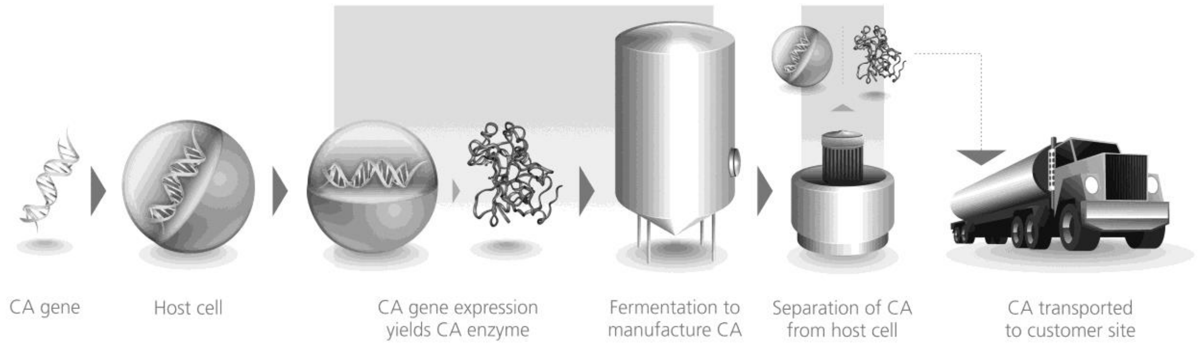


Figure 3. Simplified schematic of enzyme production. *Reprinted from Novel Materials for Carbon Dioxide Mitigation Technology, Salmon and House, Chapter 2, Enzyme-catalyzed solvents for CO_2 separation, Figure 1, Page 26, Copyright 2015* [28], *with permission from Elsevier.*

1.4 Enzyme Enhanced CO_2 Capture Processes

The enzyme carbonic anhydrase (CA) has broad potential for use together with CO_2 separation processes that utilize the chemical conversion between CO_2 and bicarbonate as part of the separation process [28]. The enzyme has been investigated and described by an increasing number of researchers as a catalyst for aqueous solvent-based CO_2 separation processes. The general features of several selected studies are presented in Table 1. Topics on enzyme-based carbon dioxide capture have been reviewed by Russo et al. [29], Pierre [30], González and Fisher [31], Dilmore [32], Lacroix [33], Savile and Lalonde [34], and Yong et al. [35]. The common goal in applying enzymes for CO_2 capture is to help overcome challenges long associated with industrial gas processing ([36], [37], [38]), especially aimed at improving energy efficiency and reducing environmental impact. Process intensification and hybrid reactor approaches developed in general for solvent-based separation processes, such as use of advanced contactors to enhance gas-liquid contact for improved absorption and desorption efficiency, including membrane reactors ([39], [40], [41], [42]), rotating packed beds [43], horizontal spray reactors [44], jet bubble reactors ([45], [46]), acoustic and cavitation ([47], [48], [49]) reactors, and use of techniques for providing desorption driving force, such as direct steam injection [50] and single or multi-stage/multi-pressure sweep gas approaches ([41], [51], [52], [53]) that could, for example, use inlet air to the combustor as “air stripper” gas in membrane or direct contact configurations [54], are equally relevant for solvents catalyzed by CA. Processes in which flue gas desulfurization (FGD) and CO_2 absorption are combined have also been envisioned ([50], [55], [56]) where the action of CA could promote CO_2 absorption into the alkaline aqueous mixtures used for FGD ([57], [46]). Such combinations could, for example, result in a single stage absorption where SO_2 reacts with the aqueous alkaline liquid to produce calcium sulfate precipitates and CO_2, catalyzed by CA, reacts with the liquid to produce bicarbonate. After solid-liquid sulfate reclamation, the process liquid containing bicarbonate could be sent to desorption for CO_2 release and recycling, with chemical adjustment to account for consumed reagents. Indications are that CA tolerates exposure to oxygen, and could be improved for even greater tolerance in combination with limestone forced oxidation (LSFO) which is the preferred FGD control technology [58]. In such cases, CA catalyzed systems could offer benefits compared to conventional CO_2 absorption chemicals that suffer from oxidation instability. CA could be used in various forms, such as dissolved, immobilized on fixed surfaces, or immobilized in or on materials, such as nano- or microparticles, to position the biocatalyst optimally near the gas-liquid interface. Using the biocatalyst in different forms can also enable different types of reactor configurations where, for example, the biocatalyst is either held in a particular reaction zone or is carried along with the process liquid. CA has been repeatedly shown to enhance CO_2 absorption rates in a wide variety of aqueous CO_2 absorption solvents and solvent mixtures, where important features in common among these solvents are the ability to absorb CO_2 through a bicarbonate-based chemical absorption mechanism and the ability to become “loaded” with CO_2 in the form of bicarbonate by virtue of solvent alkalinity and pH buffer capacity. Different enzyme forms, solvent options, and reactor configurations can lead to optimal gas mass transfer performance and solvent loading for both absorption and desorption while also extending enzyme longevity for robust performance at industrial scale.

The work initiated in the current project was distinguished from these important adjacent efforts by specific focus on the CO_2 capture energy reductions to be gained through modifications to the regeneration process in order to take full advantage of catalyzed low enthalpy conditions. Both vacuum regeneration and ultrasonically-enhanced atmospheric pressure regeneration were evaluated. Furthermore, the current project involved demonstration of bench-scale system operating with carbonic anhydrase catalyst dissolved in and recirculating along with the potassium carbonate-based solvent to minimize kinetic limitations throughout the process, and provide a straightforward liquid replenishment approach to maintaining system performance over time. At the time this project was initiated, availability of sufficiently robust carbonic anhydrase in the amounts needed to carry out the 500 hour testing had not been shown previously. Availability and suitability of carbonic anhydrases for scale-up testing has now been confirmed both through the current project and through parallel efforts.

Table 1. Selected Investigations of Carbonic Anhydrase for CO_2 Capture

Investigator/ Award	General Features of the Study	Observations
Burk, 1961 [59]	Presented manometric testing techniques and CO_2 scrubbing systems for submarines and industrial applications that could benefit from CA enhanced absorption.	Proposed CA enhancement of conventional amine-based CO_2 scrubber liquids or replacement with more benign liquids, e.g. potassium carbonate catalyzed by CA.
Graf, 1966 [52]/ USAF Contract No. 33(615)-2553	Parametric evaluation of CA in a lab-scale disc column reactor as a model system for CO_2 capture using a packed reactor for CO_2 removal from closed space capsule atmospheres.	Maintained greater than 60% CO_2 removal for several hours using CA in aqueous Tris solutions, demonstrated cycling of absorption (10°C) and air-sweep desorption (40°C), and conducted simulations to show the feasibility for man-sized systems.
Alper and Deckwer, 1983 [60]	Discussion of the theory and mechanisms by which small catalyst particles suspended in gas absorption liquids can provide gas absorption enhancement.	Demonstrated significant CO_2 gas absorption enhancement for CA immobilized as microparticles having dimensions less than the thickness of the liquid film.
Trachtenberg, et al, 1999 [39]	CA immobilized on membranes improved CO_2 selectivity for CO_2 absorption from a mixed gas stream.	Demonstrated significant improvement in CO_2 selectivity and CO_2 capture rate using CA-based membranes.
Bond et al, 2001 [61]/ EPRI Contract No. WO9000-26	Biomimetic CO_2 capture and sequestration in seawater or brines through inorganic carbonate formation accelerated by CA and estimations of solids produced.	CA accelerates hydration and precipitation of calcium carbonate and retains activity in seawater-type solutions. Solids production estimated as 5-times the coal consumption.
Bhattacharya et al., 2004 [62]	Evaluation of CA immobilized in a porous matrix inside packed reactor configurations to minimize pressure drop of the gas flow while using water spray for CO_2 absorption.	CO_2 absorption increased as CA load in the immobilization matrix increased.
Carbozyme, 2009 [63]/ DE-FC26-07NT43084	Evaluated several high surface area membrane-based gas permeator reactors as well as a novel electrodialytic CO_2 absorber/ stripper that used resin wafer technology and *in situ* pH swing to promote capture and of release of CO_2, catalyzed by CA.	Demonstrated effective permeator performance in lab-scale with both dissolved and immobilized enzyme for periods up to 10 days with high CO_2/N_2 selectivity, and demonstrated CA enhancement of electrodialytic CO_2 separation in lab scale.
Illinois State Geological Survey, 2012 [50], [64]/ DE-FC26-08NT0005498	Integrated Vacuum Carbonate Process (IVCAP) utilizing CA catalyzed potassium carbonate/ bicarbonate solvent using direct injection of (low temperature) exhaust steam for stripping. Evaluated enzyme immobilization, temperature stability, kinetics, and other process aspects.	Showed dissolved enzyme tolerance to simulated flue gas contaminants (e.g. SOx, NOx). Provided fundamental VLE data for K_2CO_3-based solvents in ambient/moderate temp/pressure regimes. Predicted lower LCOE versus MEA process.
Codexis, Inc., 2012 [65]/ DE-AR0000071	Directed evolution used to develop protein engineered CAs from *Desulfovibrio vulgaris* with improved stability in MDEA. Conducted pilot test in packed column-flash tank stripper system with ~150 lb CO_2/d CO_2 capture rate.	Demonstrated CA longevity in non-natural environments (high pH/ temperature) and 60-70% CO_2 capture efficiency of over 60 hours using 25 wt% MDEA. LCOE estimated at 97 mills/kWh versus 121.9 mills/kWh for DOE/NETL Case 12.
Akermin, Inc., 2013 [66]/ DE-FE0004228	Developed an immobilization system for integration of CA in CO_2 separation processes, leading to commercially-relevant performance longevity, including tolerance of actual post-FGD flue gas conditions.	Demonstrated stable CO_2 capture performance for 5 months at the NCCC under real post-FGD flue gas conditions using absorber packing coated with immobilized CA biocatalyst and aqueous potassium carbonate and another non-volatile solvent.
LLNS, 2013 [67] / DE-AR0000099	Developed and evaluated polymer-encapsulated carbonate solvents incorporating a synthetic chemical analog of the CA active site to enhance reaction rates.	Zinc-cyclen and zinc-acyclic proline CA active site mimic compounds accelerate CO_2 hydration and are stable at ≥75°C, and can be inhibited by bicarbonate.
CO2 Solutions, Inc., 2015 [68]	Evaluated a proprietary CA in EERC pilot test facility for CO_2 capture from natural gas and coal flue gases in a packed column absorber and stripper, using hot water from domestic water heaters as heat source and operating stripper under partial vacuum.	Based on techno-economic comparison versus DOE Cases 11 and 12, and use of all stripping heat from outside the steam cycle, an effective parasitic load of 0.2 GJ/t for CO_2 capture was claimed.

1.5 Technical Challenges

Although solvent-based systems, typically employing amine-based chemical solvents, are in commercial use for separating CO_2 from industrial flue and process gases, these systems are only beginning to be applied for removing the large volumes of CO_2 encountered in flue gas from a commercial-scale coal-fired utility boiler, due to a number of key remaining technical challenges. These challenges, as outlined in the Funding Opportunity Announcement DE-FOA-0000403 [7], are shown in Table 2 along with a description of how the present project sought to overcome those challenges. The key challenge for solvent-based post-combustion CO_2 capture technologies is the high energy requirement for solvent regeneration. Additional challenges specific to the unique technical aspects of the project are shown in Table 3.

Table 2. General Technical Challenges for Solvent-based CO_2 Absorption Systems

General Challenges	Project Approach
High energy penalty associated with solvent regeneration	Utilize aqueous potassium carbonate solvent which has a low enthalpy of reaction for regeneration compared to MEA
Low (atmospheric) CO_2 desorption pressures	Evaluate the potential for ultrasonics to promote CO_2 desorption at low temperature without requiring vacuum conditions
Mismatch between regeneration temperature and steam quality available in an existing PC plant	TEA Case Study
Solvent degradation due to flue gas contaminants and other solvent losses	Utilize aqueous potassium carbonate solvent which has no vapor pressure and is less-reactive towards flue gas contaminants compared to MEA
Solvent recovery and reclaiming	Evaluate cook-and-filter process for separating spent enzyme from the solvent to enable straightforward solvent recovery
Water usage and quality management	Utilize biodegradable enzyme catalyst and biocompatible solvent components to simplify process water disposal
Handling of two-phase solvents (e.g. salt-based solvents and solvents with phase change)	Potassium carbonate concentration was maintained below the solubility limit of bicarbonate (rich loaded solvent) at 30°C, which was considered to be the critical temperature for maintaining solubility at a power plant site.
Process equipment footprint and cost	Utilize carbonic anhydrase enzyme to accelerate the rate of CO_2 absorption in potassium carbonate solvent, resulting in reduced absorption tower height.

Table 3. Project-Specific Technical Challenges

Specific Challenges	Project Approach
Sufficiently fast absorption rate to minimize tower size	Evaluate chemical auxiliaries as rate enhancement boosters. Increase enzyme dose to maximal levels.
Ability of ultrasonics to deliver required lean loading	Evaluate different ultrasonic/liquid flow orientations, and adaptations, such as cyclone for improved bubble release. Considered but not explored: • Alternative ultrasonic frequencies • Alternative geometries for delivering acoustic energy • Inclusion of microparticles to enhance mixing.
Ability of vacuum stripping to deliver required lean loading (at 30 SLPM scale)	Equipment adjustment to ensure proper performance. Evaluate potential for enzyme to improve stripper kinetics. Considered but not explored: • Evaluate alternative stripper geometry or packing arrangement.
Enzyme compatibility with absorber conditions (e.g. adsorption on surfaces, foaming, solids)	Implement antifoam, filters, and system cleaning protocol as needed.
Enzyme compatibility with stripper conditions (e.g. temperature, foaming, solids)	Determine the upper allowable limit for reboiler skin surface temperature. Monitor potential enzyme losses over the range of stripper temperatures, and implement corresponding enzyme replenishment program. Use increased or repeated enzyme dosing to overcome enzyme inactivation. Implement antifoam addition to control foaming. Implement filtration to control solids accumulation in the liquid. Considered but not explored: • alternative CA enzyme with higher thermal stability • constrain CA enzyme to the absorber only • chemically modify or immobilize CA to improve the thermal stability
Dissolved enzyme concentration requirement	Optimize concentration during parametric testing. Considered but not explored: • Evaluate alternative/advanced contactors
Dissolved enzyme longevity	Replenishment program to maintain system performance with “cook and filter” approach to induce spent enzyme aggregation, insolubility, and removal via filtration.

2 PROJECT OBJECTIVES

The overall project objective was to make significant progress towards meeting the DOE's target of no more than a 35% increase in the levelized cost of electricity (LCOE), while capturing at least 90% of the carbon dioxide (CO_2) released from coal-fired power plants, by conducting integrated bench-scale testing and a techno-economic feasibility study of a novel process that combined attributes of the thermo-stable carbonic anhydrase (CA) enzyme catalyst, a low-enthalpy potassium carbonate (K_2CO_3) solvent, and vacuum regeneration utilizing very low pressure (VLP) steam or a novel ultrasonically-enhanced regeneration process. Based on initial simulations, these integrated technologies had the potential for achieving up to a 50% reduction in energy demand versus the benchmark monoethanolamine (MEA) solvent. Therefore, specific project objectives were to develop key information on the effectiveness and robustness of the enzyme-solvent combination to capture CO_2 from flue gases, evaluate physical characteristics and process robustness, determine the energy required to regenerate the solvent ultrasonically or using the vacuum and VLP steam approach, successfully integrate all necessary process components to complete the 500 hour test, utilize test results in assessing the overall capital and operational cost of the integrated CO_2 capture and compression system scaled for a 550 MWe pulverized coal power plant, and make a preliminary assessment of the environmental friendliness and safety of the materials and processes employed.

2.1 Scope of Work

Novozymes North America, Inc. (Novozymes), partnered with the University of Kentucky's Center for Applied Energy Research (UK-CAER), Doosan Babcock Ltd. (Doosan), and Pacific Northwest National Laboratory (PNNL), designed and conducted integrated bench-scale testing of a novel post-combustion CO_2 capture process that combined the attributes of the bio-renewable CA enzyme catalyst, a low-enthalpy K_2CO_3 solvent, and an ultrasonically-enhanced or vacuum regeneration process utilizing VLP steam. During Budget Period 1, the individual unit operations and the solvent/enzyme formulation were optimized, a detailed design of the bench-scale system was completed for operation at 30 SLPM inlet gas flow, and the initial technical and economic feasibility study was conducted. During Budget Period 2, all major components of the bench-scale system were procured and pre-tested in unit-based shakedown testing, resulting in selection of the vacuum regeneration approach for assembly into the final integrated bench-scale system on an instrumented host rig located at UK-CAER. During Budget Period 3, parametric and long-term testing of the integrated bench-scale system with synthetic gas that approximates flue gas (~15% CO_2) was conducted for 500 hours.

2.2 Tasks Performed

Project objectives were addressed through the collaborative completion of seven tasks during a 45 month period by the project team. Novozymes led the overall Project Management and Planning (Task 1). Process Optimization (Task 2) was divided into subtasks (led as indicated) for Ultrasonic Unit Optimization (PNNL), Solvent and Enzyme-Solvent Compatibility Optimization (Novozymes), Solvent Physical Properties and Kinetic Measurements (UK-CAER), and Design of the Integrated Bench-Scale System (Novozymes). Bench Unit Procurement and Fabrication (Task 4) was divided into subtasks for Absorber Procurement and Fabrication (UK-CAER), Ultrasonic Regenerator Procurement and Fabrication (PNNL), Bench-Scale Host Rig Procurement and Fabrication with Vacuum Regeneration Capability (UK-CAER), and Enzyme Supply for Bench-Scale Testing (Novozymes).

Within the Unit Operations and Shakedown Testing and Integration (Task 5), UK-CAER led Absorber and Vacuum Regenerator Testing, PNNL led Kinetic-Based Stripping Simulation and Supporting Experimentation, and Novozymes led Long-Term Enzyme Stability and Reclamation evaluations. UK-CAER led Bench-Scale Testing (Task 6), including Parametric Testing and Long-Term Operation comprising 500 hours of total run time at steady-state conditions. The Initial (Task 3) and Final (Task 7) Technical and Economic Feasibility Studies were led by Doosan, including an Environmental, Health and Safety (EH&S) Risk Assessment. In addition to routine progress reports and status presentations, three Topical Reports were prepared and submitted, including the Preliminary Technical and Economic Feasibility Study [69], Preliminary EH&S Assessment [70], and Final Technical and Economic Feasibility Study [71].

Further tasks performed in support of the project outside of the project budget were: production of prototype carbonic anhydrase enzyme by Novozymes in sufficient amounts to supply the project for completion of the tasks; loan of bench-scale ultrasonic equipment to conduct unit operation pre-testing by PNNL as a procurement risk mitigation within Task 4; and, operation of the bench-scale unit by UK-CAER using 30% MEA solvent to provide supplementary system performance benchmarking results beyond those identified in the statement of work.

The bench-scale system was initially designed as essentially three stand-alone components with two regeneration options: an absorber column “host” rig equipped with vacuum regeneration and sized to accommodate the ultrasonic regenerator, an ultrasonic regenerator, and a potassium carbonate-based solvent recipe containing enzyme catalyst. This allowed preliminary testing of each component in parallel by the respective project partner experts prior to final assembly. A simplified schematic of the bench-scale system planned for incorporating ultrasonic regeneration is shown in Figure 4. A simplified schematic of the bench-scale system planned for incorporating vacuum regeneration is shown in Figure 5.

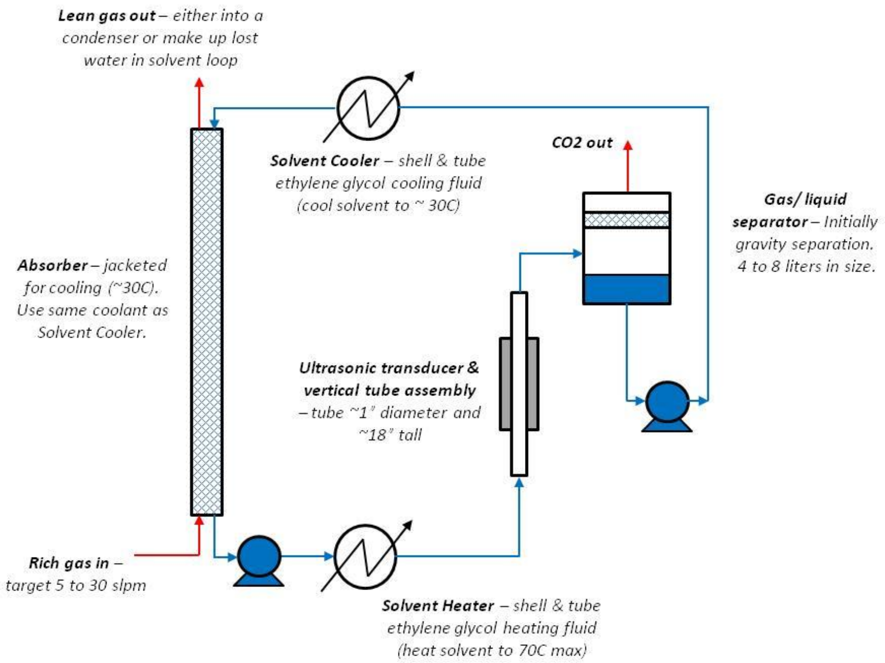


Figure 4. Schematic bench-scale CO_2 capture system with ultrasonic regeneration.

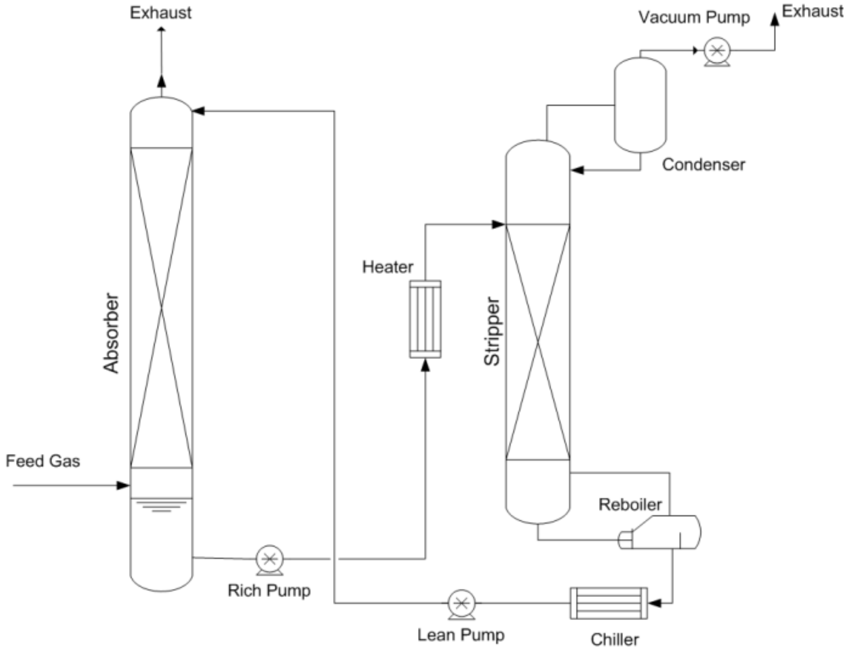


Figure 5. Schematic bench-scale CO_2 capture system with vacuum regeneration. *Reprinted from Novel Materials for Carbon Dioxide Mitigation Technology, Salmon and House, Chapter 2, Enzyme-catalyzed solvents for CO_2 separation, Figure 4, Page 44, Copyright 2015* [28], *with permission from Elsevier*.

2.3 Summary of Project Success Criteria and Milestone Accomplishments

Successful completion of project tasks required meeting targeted milestones, with the collaborative accumulation of knowledge required to respond to outlined project success criteria. While Project Management, Planning and Reporting requirements were considered among the project success criteria and milestones, this report is focused on summarizing technical goals and achievements, as outlined in Table 4.

Table 4. Summary of Technical Project Success Criteria and Milestones

Project Success Criteria or Milestone	**Accomplishment**
Enzyme and Solvent tasks part 1 – before construction of the bench-unit	
Down-select to the optimal enzyme-solvent formulation for integrated bench-scale testing	Initial laboratory scale tests using a wetted wall column identified 20 wt% K_2CO_3 with 3 g/L active enzyme as an initial baseline solvent. Further work in the bench-unit found that greater solvent loading, while still balancing bicarbonate solubility, was achieved with 23.5 wt% K_2CO_3, and that an enzyme dose of 2.5 g/L was sufficient to ensure the absorber was not kinetically limited. Laboratory scale (bubble tank) tests were also conducted with various stable salts, including phosphate, sulfate, borate, and borax, and the substituted amino acid bicine. Of these, borax (sodium tetraborate decahydrate) gave the best performance, but was unable to surpass 23.5 wt% K_2CO_3 in terms of solvent loading. A mixture of borax with carbonate was tested in the bench-unit, and gave similar results to carbonate alone. Thus, the optimal enzyme-solvent formulation selected for the project comprised 23.5 wt% K_2CO_3 with 2.5 g/L active enzyme.
Demonstrate CO_2 absorption kinetics with the optimal enzyme-solvent formulation that are at least 50% as fast as the benchmark 30 wt% MEA solvent, under identical process conditions, and measured using a wetted wall column.	An overall mass transfer rate (K_g) of 0.55 mmol m^{-2} s^{-1} kPa^{-1} for the baseline solvent (20 wt% K_2CO_3, 3 g/L active enzyme) at 30°C was measured, and achieved the target of ≥ 50% of the rate of benchmark 30% MEA measured under identical process conditions. Tests with the down-selected optimal select were not conducted as the target was achieved with the baseline solvent.
Enzyme and Solvent tasks part 2 – during operation of the bench-unit	
Soluble enzyme demonstrates sufficient physical and longevity compatibility with bench-scale operation at targeted conditions to proceed with parametric testing. Sufficient physical compatibility is evidenced by unobstructed recirculation of the enzyme-containing absorption liquid (no uncontrolled accumulation of solids or foaming) for ≥ 20 hours cumulative at steady-state operating conditions. Sufficient enzyme longevity compatibility during unit shakedown and operational extremes testing is evidenced by cumulative steady-state operation of ≥ 20 hours at between 70 to 80°C bulk reboiler temperature with no negative alteration of lean/rich CTB conversion compared to the initial 4 hour steady-state period. And, for parametric and long-term tests, an active enzyme replenishment dosing program will be established at <10% of the initial charge used per 100 hours of steady-state operation.	Sufficient enzyme physical compatibility achieved by implementing daily filter cleaning/replacement to mitigate solids accumulation, and by application of antifoam to control foaming. Enzyme longevity during shakedown and operational extremes testing was determined according to two approaches: one based on measurement of percent enzyme activity remaining in offline samples taken from the bench unit, and another based on changes in online CO_2 capture performance over time measured on the unit. Offline % enzyme activity remaining indicated approximately 20-fold higher enzyme activity loss (~20% per run day) relative to what would be expected from online CO_2 capture performance loss (~ 1% per run day). Thus, offline metrics were taken as a "worst case" scenario (to ensure adequate enzyme supply for a dosing routine during parametric and long-term tests, even in a "worst case" scenario); and that based on online % CO_2 capture, was taken to represent a probable active enzyme replenishment rate. The stark deviation between measured enzyme activity loss and online CO_2 performance loss continued into parametric and long-term testing, such that in order to avoid a 1% loss in CO_2 capture performance per run day, an ~ 20% active enzyme replenishment was required, which was significantly higher than the target of the dosing program. The long residence time and maximum temperature conditions (i.e. reboiler skin temperature) in the 500 hour test were more detrimental to enzyme longevity than anticipated. Improvements in enzyme longevity or process conditions may reduce the required replenishment dose.

Rate enhancement provided by enzyme on the bench-scale unit is quantified for absorption and regeneration processes, which is expected to result in ≥ 5x CO_2 absorption rate enhancement versus K_2CO_3 baseline solvent alone based on indications from completed WWC tests.	CO_2 capture efficiency of the bench-scale unit increased 5-fold upon enzyme addition (Parametric Test #1) to K_2CO_3 baseline solvent (Parametric Test #10).
Enzyme-enhanced solvent working capacity achieves 0.3 mol CO_2/mol K_2CO_3 equivalent (0.019 kg CO_2/kg solvent).	Enzyme-enhanced solvent working capacity achieved for the long term testing conditions (Parametric Test #1) was 0.2 mol CO_2/mol K_2CO_3 equivalent (0.013 kg CO_2/kg solvent), an ~ 7-fold improvement over the no enzyme case, yet lower than the target. Balancing loading capacity with bicarbonate solubility proved to be a challenge in using a K_2CO_3 solvent alone, and future work should consider alternative solvents, or process configurations capable of handling insoluble bicarbonate.
Ultrasonics tasks	
Determine the optimal batch-mode ultrasonic regenerator operating conditions, such that at 70°C, lab ultrasonics demonstrates a lean loading (with 1 atmosphere of water-saturated CO_2 in the headspace) equivalent to lean loading achieved with vacuum stripping at 70°C. Graduate to testing with a flow-through prototype ultrasonics regenerator unit and make go/no-go decision on purchase of ultrasonic equipment for solvent regeneration in the bench-unit.	Batch-mode ultrasonics was less effective relative to vacuum stripping, and achieved 30% of the CO_2 desorption working range target set by Aspen Plus® -simulation. CO_2 re-dissolution into the large volume of solvent used in batch tests was suspected to be a main contributor to the low performance. A flow-through prototype ultrasonic configuration was also tested, which could provide more efficient energy transfer and bubble release versus batch-mode tests; however, the magnitude of measured CO_2 release was within the range of temperature-dependent release, therefore, the separate benefit of ultrasonics could not be verified. Vacuum regeneration was the reference case for ultrasonics, although data on low temperature vacuum regeneration was lacking. Thus, vacuum regeneration, which was the reference case for ultrasonics, but lacked data was selected for the bench-unit testing.
Integrated Bench-unit construction and operation tasks	
Complete fabrication and construction of an integrated bench-scale unit capable of treating a maximum gas flow of 30 SLPM and fitted with conventional and vacuum regeneration. Use kinetic simulations of the stripper to predict bench-scale stripper performance between 70-100°C at variable stripper pressures to contribute to test matrix design, and to help inform stripper height required to achieve targeted CO_2 removal.	Integrated bench-scale unit constructed with a vacuum system, and also a hot oil system to provide the necessary heat for solvent regeneration. Absorber column was constructed of transparent chlorinated polyvinyl chloride and the stripper was stainless steel. Both columns had 7.6 cm ID and 2 m packed height, with 6x6 mm Raschig rings as the packing. System was capable of treating 30 SLPM of simulated flue gas containing ~15% CO_2 balanced with N_2, and CO_2 removal performance was close to target conditions.
Integrated bench-scale equipment fitness for parametric testing demonstrated by: CO_2 stripping performance between 70 and 90°C achieves lean solvent loading of ≤ 40% carbonate-to-bicarbonate (CTB) conversion; and absorber performance achieves rich solvent loading of ≥ 50% (absent enzyme) and ≥ 60% (with ≤ 3 g/L enzyme) CTB conversion at a nominal solvent	Shakedown target CTB conversions were achieved with a reboiler heat source temperature of 90°C, and with vacuum applied such that reboiler bulk liquid temperature was ≤ 80°C. The addition of 0.3 g/L enzyme was sufficient to meet the shakedown target 20% CTB conversion (0.2 mol CO_2/mol K_2CO_3 cyclic capacity). Without enzyme, the CTB conversion was 3% (0.03 mol CO_2/mol K_2CO_3).

concentration of 20 wt% K_2CO_3, absorber temperature of 40°C and L/G of 10 (w/w).	
Stable, reproducible operability of the integrated bench-scale system is confirmed across the range of conditions required for parametric testing.	Bench-unit operation was stable and reproducible across three test days at the operational extremes expected for parametric testing, including maximum liquid flow rate (700 ml min^{-1}), minimum stripper pressure (0.3 atm) and minimum absorber temperature (30°C), with minimum – maximum enzyme dose range of 0.3 – 3 g/L.
Identify the optimal operating conditions, including temperature and pressure of the absorber and regenerator units for the long-term integrated bench-scale test.	Long-term operating conditions selected, including 40°C absorber, 95°C reboiler heating source temperature, and 0.35 atm stripper top pressure.
Complete at least 500 hours of integrated bench-scale testing.	Long term (500 hour) bench unit operation completed. Average 84% CO_2 capture efficiency was maintained when replenishing 10-20% of the active enzyme per an average 7 hour steady state run day.
Modeling tasks	
Complete kinetics-based vacuum stripping simulation in Aspen Plus® including bench-scale and 550MW scale components, and validate against data collected from the bench-scale system.	Kinetic-based absorber simulations of the bench-scale system were completed, and parameters applied in Aspen Plus® (Section 7) for use in full scale predictions .
Prediction for CO_2 regeneration energy is made based on preliminary bench-scale shakedown measurements including reboiler and vacuum pump energy. Measurements continue into long-term testing, are corrected as appropriate for heat and power losses due to equipment size, and provided to the final techno-economic assessment to help validate the CO_2 regeneration energy predicted for Vacuum Stripping Case 2 of the Preliminary TEA (9.566 kg CO_2/kWh_e).	Un-optimized shakedown tests achieved >90% CO_2 capture, corresponding to >75% CO_2 capture improvement and 36% energy demand reduction, enabled by enzyme addition. Initial Aspen Plus® prediction (based on the bench-scale system configuration) indicated potential for lower regeneration energy than was actually measured during bench-scale tests. Later refinements to the model used to translate bench-scale measurements into full-scale performance estimates also indicated potential for lower regeneration energy than measured on the unit. Potential reasons for the difference are discussed in the project full Technical and Economic Assessment (Appendix I, [71]) and in Section 7.3. For Case DB1 in the full TEA, the calculated CO_2 regeneration energy was 4.71 kg CO_2/kWh_e. Regeneration energy was calculated using the model predicted CO_2 captured divided by the sum of the vacuum pump power requirement and reboiler steam equivalent electric power penalty.
Final assessment tasks	
Complete Preliminary EH&S Assessment	Assessment completed [70]. Potential emissions pose no significant environmental, health or safety concerns and were compliant with the Federal EH&S legislation reviewed. Further work during scale-up studies would be required to confirm these findings.
Complete Final Technical and Economic Feasibility Study	Study completed [71]. Various aspects of the process were considered for technical and economic feasibility, including low pressure and very low pressure steam for reboiler heating supply, and different vacuum pressures for low-temperature stripping. Best cases showed this benign solvent achieved similar LCOE to NETL baseline Case 10 [72]. Further work during scale-up studies would reduce uncertainties present when modeling a 550 MW_e net power plant from bench-unit data for the feasibility study.

3 BASIS FOR SELECTION OF SOLVENT AND ENZYME CATALYST

Potassium carbonate (K_2CO_3), ammonia and MDEA are examples of materials that bond less strongly to CO_2 and require less energy for desorption, but they have slow absorption kinetics due to the rate limiting step of converting dissolved CO_2 to bicarbonate ion [36]. In spite of their slow kinetics, potassium carbonate based aqueous solvents have been used for CO_2 separation in natural gas processing for many years (i.e. the “Benfield” or “Hot Potassium Carbonate” processes). However, these processes involve high temperatures and, especially, high inlet gas pressures to overcome solvent rate limitations – not feasible conditions for post-combustion flue gas scrubbing. At low CO_2 partial pressures, a catalyst is needed for potassium carbonate-based aqueous solvents to provide efficient CO_2 absorption within gas-liquid contactors of a viably small size. The current project used carbonic anhydrase enzyme catalyst dissolved in aqueous potassium carbonate-based solvent as the CO_2 absorption solvent.

Enzyme-promoted aqueous K_2CO_3 was selected as the solvent for this bench-scale program due to its high thermal stability, non-toxicity, and very low enthalpy of reaction (27 kJ/mol CO_2,) that allows solvent regeneration to occur at significantly lower temperature compared to benchmark MEA (83 kJ/mol CO_2 [36]). The lower temperature requirement means lower quality steam demand for solvent regeneration, which, together with vacuum regeneration, has the potential to contribute positive impact on gross plant power output. Carbonic anhydrase enzyme helps overcome the inherently slow reaction rates of the K_2CO_3-based solvent, which have previously prohibited its use for CO_2 scrubbing from ambient pressure gas streams.

Many different carbonic anhydrase enzymes are found in living systems [28]. CAs have also been modified by chemical and protein engineering techniques to improve their properties. For flue gas scrubbing applications, particularly suitable CAs would have good thermo-stability and longevity at the process temperature conditions, good tolerance for alkaline pH and high ionic strength conditions, resistance to chemical degradation, oxidation and inactivation by contaminants in the system, and good tolerance of physical stresses caused by pumping, filtration, flowing and other process operations. Figure 6 illustrates an approximate comparison of the short term (15-30 minute) thermo-stability properties of several different carbonic anhydrases that could be suitable for CO_2 scrubbing applications, depending on the specific process conditions. The comparison is only approximate because different researchers use different methods and solvents for their evaluations. Also, many other CA candidates are known and are being discovered, so the main purpose of the figure is to give an indication that certain rather thermostable CA candidates are already known, and these same candidates tend to also exhibit the other properties desired for gas scrubbing applications. Furthermore, strategies such as protein engineering [65], chemical modification and immobilization can be used to improve enzyme properties for use in industrial applications and adapt the physical characteristics of the biocatalyst to the requirements of reactor designs and process steps ([28], [73]). Notable examples are the greater than five month performance robustness demonstrated by Akermin in a pilot trial at the National Carbon Capture Center (NCCC) with a single loading of enzyme immobilized on structured packing in the absorber [74], the demonstration by Capasso *et al.* [75] that a thermostable CA could tolerate exposure to 100°C for 48 hours when immobilized in a polyurethane foam, and the studies by Lu *et al.* [50] demonstrating that CA immobilized by various techniques showed significant retention of enzyme activity compared to the dissolved form of the enzyme. Therefore, whereas in the past, human and bovine carbonic anhydrases were the only available candidates for conducting evaluations, today, the picture is much different.

Another desirable property for CAs used in industrial applications is good tolerance of microbial degradation to facilitate handling and storage. However, it is beneficial to balance this property with the disposal advantage of having a biodegradable material in the waste stream after use. One way to achieve this balance is to include an antimicrobial agent (or preservative) in the enzyme product or process liquids that provides the needed protection during storage and use but has lowered (or even eliminated) efficacy once delivered to the waste stream. Economically, it will be important to produce the enzymes at a scale and cost that meets the techno-economic requirement.

The proprietary microbial carbonic anhydrase supplied by Novozymes for the project was considered from preliminary laboratory testing to have sufficiently good properties to enable completion of the bench-scale testing, and was provided to the project as a developmental prototype to validate these properties and further evaluate what characteristics would be important for an eventual commercial product.

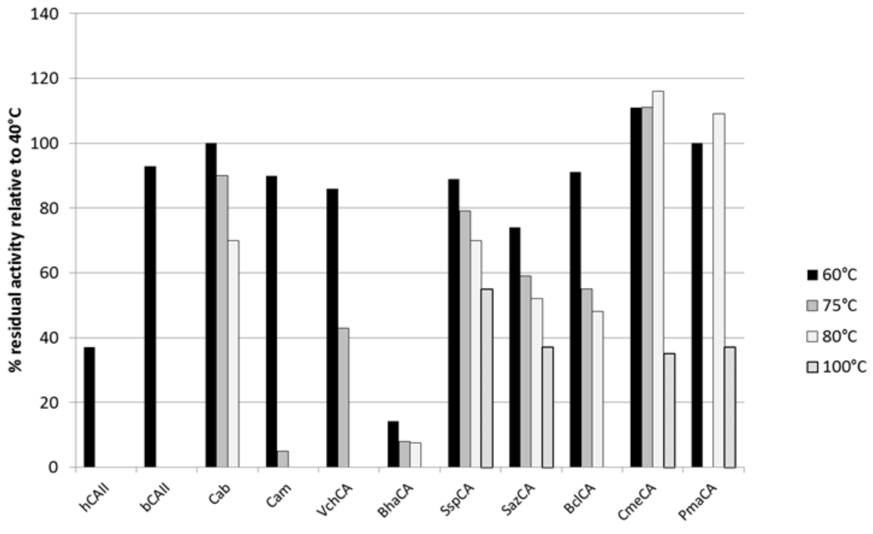


Figure 6. Thermo-stability for several different carbonic anhydrases. Expressed as a percent of their individual stability at 40°C. *Reprinted from Novel Materials for Carbon Dioxide Mitigation Technology, Salmon and House, Chapter 2, Enzyme-catalyzed solvents for* CO_2 *separation, Figure 6, Page 56, Copyright 2015 [28], with permission from Elsevier.*

3.1 Reaction Chemistry

The overall chemical reaction for CO_2 absorption in aqueous K_2CO_3 solvent is presented as Reaction 1. The conversion of sparingly-soluble CO_2 to highly-soluble potassium bicarbonate ($KHCO_3$), which typically is a slow reaction, is accelerated by the presence of carbonic anhydrase enzyme dissolved in the solvent. The reaction reverses in the regeneration section to release CO_2 from the solvent.

$$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2KHCO_3 \qquad \text{(Reaction 1)}$$

Equations describing the enzyme-catalyzed carbonate absorption solvent are as follows:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \qquad \text{(Reaction 2)}$$

$$CO_{2(aq)} + HO^- \leftrightarrow HCO_3^- \qquad \text{(Reaction 3)}$$

$$HCO_3^- + HO^- \leftrightarrow CO_3^= + H_2O \quad (pKa = 10.3) \qquad \text{(Reaction 4)}$$

$$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+ \qquad \text{(Reaction 5)}$$

$$H_2CO_3 + HO^- \leftrightarrow HCO_3^- + H_2O \quad (pKa = 6.4) \qquad \text{(Reaction 6)}$$

$$H_2O \leftrightarrow H^+ + HO^- \qquad \text{(Reaction 7)}$$

For the solvent system in the proposed operating range, Reactions 3 and 5 are responsible for the absorption of CO_2 into the liquid phase as bicarbonate. Carbonic anhydrase catalyzes Reaction 5, with the additional proton (compared with Reaction 3) rapidly absorbed by alkalinity in the solvent. The driving force for the forward reaction of Reactions 3 and 5 is the increased aqueous solubility of bicarbonate compared with CO_2. Note that the specific reactions available for characterization in Aspen Plus® are slightly different than those listed above. A more detailed discussion of those reactions, and the corresponding data fits are shown in Section 7.

3.2 Enzyme Catalytic Mechanism

Carbonic anhydrases (E.C.4.2.1.1 [76]) are a widespread class of metal-containing enzymes found in all domains of life that catalyze the physiologically important reactions of carbon dioxide hydration and the reverse reaction, bicarbonate dehydration, providing rapid approach to equilibrium between dissolved CO_2 and bicarbonate ion in aqueous solutions [77]. The overall enzyme-catalyzed reaction is shown in Reaction 8. Carbon dioxide is the substrate for carbonic anhydrase in the forward reaction (left to right), and bicarbonate is the substrate in the reverse reaction (right to left).

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+ \qquad \text{(Reaction 8)}$$

Carbonic anhydrase enzymes are true catalysts – facilitating, but not consumed by, the interconversion of carbon dioxide and bicarbonate. Under ideal conditions, some carbonic anhydrases exhibit very high catalytic efficiency, on the order of one million molecules of CO_2 converted to bicarbonate per molecule of CA per second [78]. This is up to three orders of magnitude faster than CO_2 reaction with the fastest amine-based solvents [79], however, these ideal catalytic rates are subject to physical limitations in gas scrubbing systems, and enzyme integration with reactor designs that minimize rate-limiting mass transfer is needed to take best advantage of the enzyme's high catalytic efficiency.

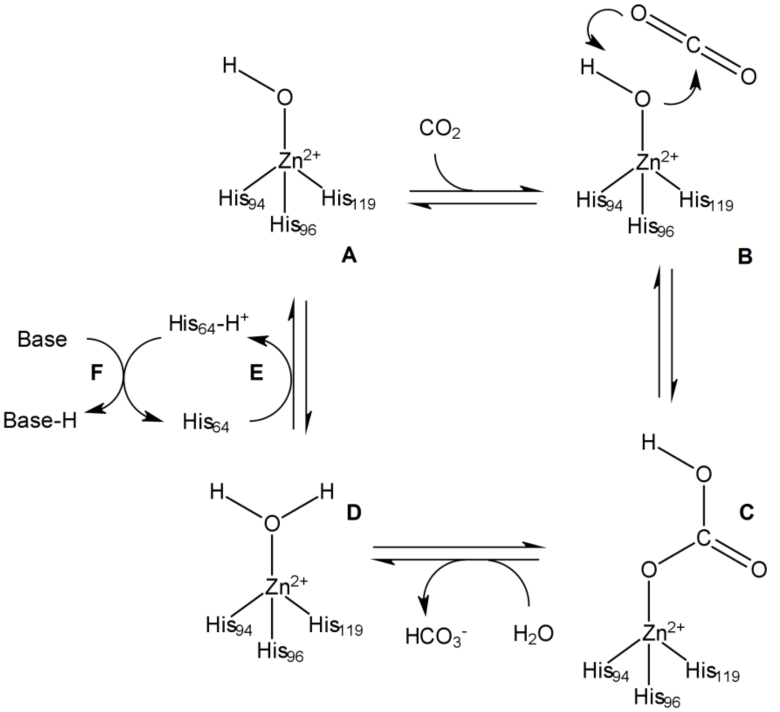


Figure 7. Carbonic anhydrase catalytic mechanism. *Reprinted from Novel Materials for Carbon Dioxide Mitigation Technology, Salmon and House, Chapter 2, Enzyme-catalyzed solvents for CO_2 separation, Figure 3, Page 31, Copyright 2015* [28], *with permission from Elsevier.*

At a mechanistic level, the carbonic anhydrase catalyzed reaction occurs in several steps in the enzyme active site (Figure 7). The catalytic cycle for the forward reaction – conversion of CO_2 to bicarbonate – starts with the enzyme in the catalytically active Zn-hydroxide form (A). Prior to catalysis, carbon dioxide must be present in a hydrophobic pocket near the active Zn-hydroxide. The affinity of CO_2 for this hydrophobic pocket is low (~100 mM) which is consistent with the high turnover number requiring rapid product dissociation [80]. Zn(II)-activated hydroxyl reacts as a nucleophile with the carbonyl carbon of CO_2 (B) generating a zinc-bound bicarbonate (C). A water molecule displaces bicarbonate to form a Zn(II)-water coordination (D). Bicarbonate is released to the reaction media. Zn-water is inactive to further reaction with CO_2 until a proton is removed from the Zn-bound water in a sequence of intramolecular (E) and intermolecular (F) proton transfers to a proton acceptor (Base) in the bulk solvent to regenerate the active (A) form. The abstraction of the proton from Zn-bound water has been well established as the overall rate limiting step [81]. The pH of the solution will decrease as protons are released into the bulk solvent.

3.3 Gas-Liquid Mass Transfer with Chemical Reaction

In order for carbonic anhydrase to catalyze CO_2 absorption in aqueous liquids, CO_2 must reach the enzyme active site. When the enzyme is located as a dissolved molecule in the water phase, carbon dioxide molecules from the gas phase ($CO_{2(g)}$) must physically enter the water phase (Reaction 2) becoming dissolved $CO_{2(aq)}$ which can enter the enzyme active site where it reacts with water to form bicarbonate (Figure 8). Therefore, although the rate for overall Reaction 8 is very fast when catalyzed by CA under ideal conditions (not mass-transfer limited), significant physical barriers can contribute to an overall rate limitation for CA catalyzed reactions in a gas-liquid contactor CO_2 scrubber, where the rate of CO_2 mass transfer between the gas and the liquid and the rate of $CO_{2(aq)}$ diffusion though the liquid can dominate the overall gas absorption process [82].

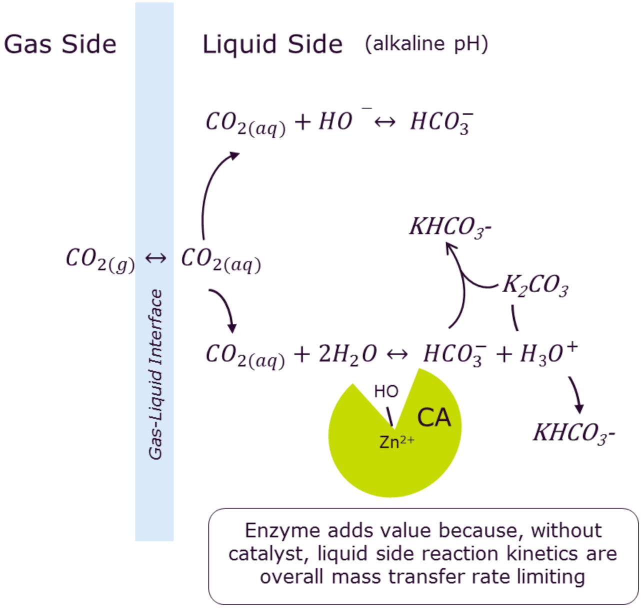


Figure 8. Schematic of CO_2 absorption with chemical reaction.

3.4 Solvent Composition and Properties

The baseline solvent selected at the initiation of the project comprised 20 wt% K_2CO_3, a concentration thought sufficient to foster good CO_2 loading yet avoid bicarbonate insolubility that could arise with higher CO_2 loadings in higher concentrations of K_2CO_3. Stepwise enzyme additions to the baseline solvent in WWC testing identified 3 g/L as the active enzyme concentration beyond which further significant increases in catalytic effect were no longer observed. Thus, 20 wt% K_2CO_3 with 3 g/L enzyme dose formed an initial baseline working solvent, with physical properties presented in the State Point Data Table (Appendix H). Further work during bench unit shakedown and parametric testing sought to improve solvent performance with small increases in K_2CO_3 concentration to optimize the balance between cyclic capacity and bicarbonate solubility, and also to improve solvent economy by decreasing the enzyme concentration. Results from these tests indicated that the optimal enzyme-solvent composition for the 500 hour test in the bench unit would comprise 2.5 g/L enzyme dissolved in aqueous 23.5 wt% K_2CO_3.

Potassium carbonate was purchased from a chemical supply vendor. A developmental carbonic anhydrase enzyme was provided by Novozymes. The working solvent was prepared by first dissolving the target carbonate into a portion of deionized water. The enzyme stock solution provided by Novozymes was added to the K_2CO_3 solution and the final solution mixed thoroughly. The initial carbon loading was performed by circulating the solvent through the absorber with 15% CO_2 (balance N_2) feed gas through the column until the pH of the solution was within the lean working range. Prior to operating the unit, the total inorganic carbon and alkalinity were determined with adjustments made if needed. Solvent was stored in a sealed container at ambient temperature when not in use. Samples were taken daily prior to and after use for measurement of enzyme activity, physical properties, and visual observation of appearance.

The enzyme solution used in this project comprised a cell-free brown aqueous liquid containing dissolved carbonic anhydrase, as shown in Figure 9, A. The enzyme solution was diluted with lean 23.5 wt% K_2CO_3 solution and was then heat-treated to remove components (benign fermentation products) that are less thermal stable than the CA. Heat treatment comprised stirring the diluted enzyme solution at 88°C for 10 – 25 minutes, allowing the liquid to cool to room temperature, and then filtering the solution to remove solids that formed in the liquid during the heat treatment. The purpose of inducing formation of and removing these solids by pre-treatment was to reduce solids accumulation in the bench unit working solvent and reduce fouling of bench unit filters. Pre-treatment conditions were selected so that the CA activity level in the liquid was not significantly affected by the heat treatment. The resulting brown filtered solution containing dissolved CA was the stock solution used to supply the bench unit for initial fill and subsequent replenishment amounts. The stock solution was added to solvent in the bench unit and mixed to comprise the working solvent (2.5 g/L active enzyme in 23.5 wt% carbonate). Preparing the working solvent in this way did not change the nominal alkalinity or carbon loading of the solution.

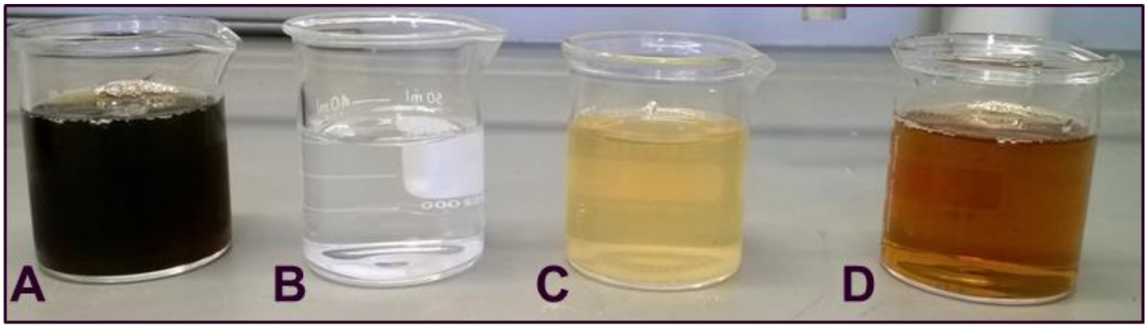


Figure 9. Solvent and enzyme solution photographs. (A) Enzyme liquid concentrate, (B) lean K_2CO_3 solution, (C) bench unit working solvent comprising 2.5 g/L active enzyme in 23.5 wt% carbonate, and (D) stock solution used to supply the bench-unit.

3.5 Solvent Vapor Liquid Equilibrium (VLE)

Vapor liquid equilibrium (VLE) data for aqueous potassium carbonate systems at temperatures above 70°C were published by Tosh *et al.* [83], and more recently were measured by Lu *et al.* [50] at 70°C to compare with the Tosh data and at 50°C to expand the data set to lower temperatures across a range of carbonate-to-bicarbonate (CTB) conversion for CO_2 absorbed in aqueous 20 wt% potassium carbonate. The studies by Lu *et al.* [50] also evaluated the impact of additives such as inorganic salts and glycols to reduce the water vapor saturation pressure, with a view towards reducing the amount of heat contributed to water vaporization in the stripper. With 20 wt% of potassium acetate or potassium formate present, the water vapor pressure over potassium carbonate solution was found to decrease by 20%, and the beneficial effect extended across the range of CTB conversions measured for the generation of VLE curves. The tested additives were also found to increase the solubility of CO_2 into the potassium carbonate solutions, apparently by virtue of an increased buffer capacity effect, to favor CO_2 absorption. Ethylene glycol addition gave a similar effect that was more pronounced at 50°C, consistent with its behavior as a physical solvent for CO_2.

Figure 10 shows a plot of published Tosh [83] data used in the Aspen Plus® model for K_2CO_3. This data is for 20 wt% K_2CO_3. Two Aspen Plus® models were run to spot check the predictions versus the original Tosh data. As shown in Figure 10, the data spot checks coincide with the original Tosh data.

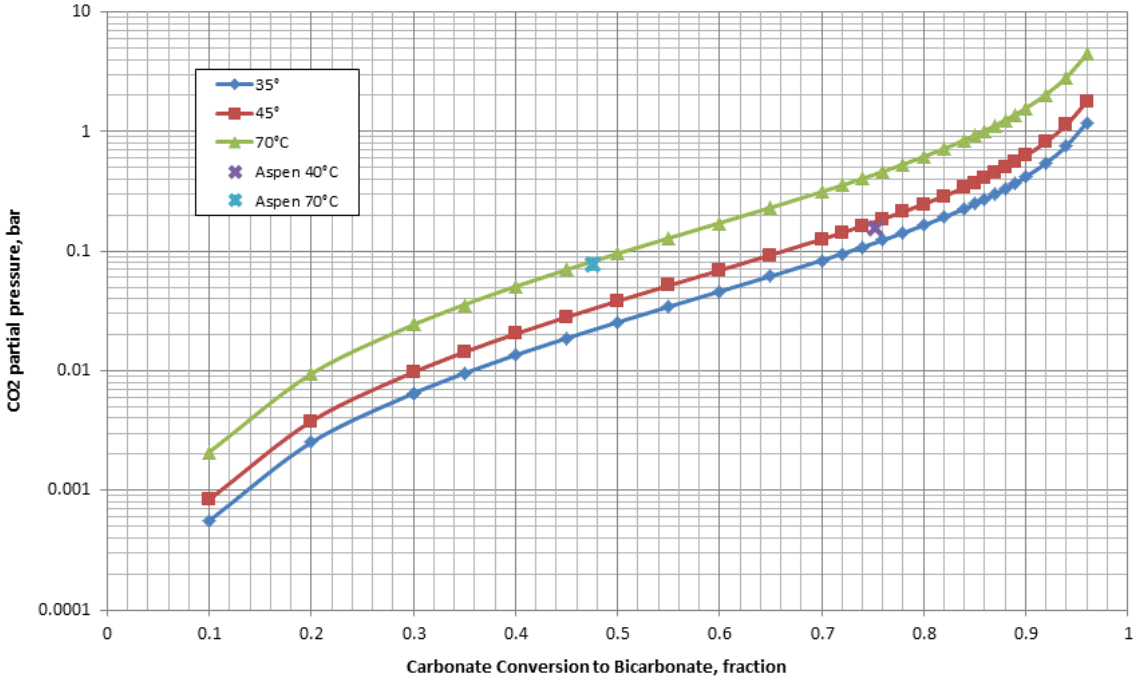


Figure 10. Tosh VLE data versus spot checks with individual Aspen Plus® runs.

3.6 Solvent Working Capacity and pH Range

According to Reaction 1, the theoretical maximum CO_2 loading in a solution of K_2CO_3 is 1 mole of CO_2 per one mole of K_2CO_3. However, the actual attainable working capacity under steady state scrubber conditions will be lower than this due to limits on the respective absorption and desorption driving forces and the corresponding vapor-liquid equilibrium. Therefore, the working capacity of the solution is a reflection of how much K_2CO_3 has been converted to $KHCO_3$ (called carbonate-to-bicarbonate, CTB, conversion) upon the addition of CO_2 under steady-state process conditions. In preliminary testing, a rich loading of 61% CTB conversion (carbon loading = 2.78 mol CO_2/kg solution; alkalinity = 3.45 mol alkalinity/kg solution) was obtained using 128 kPa (10 psig and 75% CO_2) inlet CO_2 partial pressure in the bench-scale absorber for an un-catalyzed K_2CO_3 solution. Using 6 x 6 mm ceramic rashig ring packing in the 3 inch diameter stripper column, and with a reboiler solution temperature of 103°C and steady-state vapor temperature of 91 to 93°C, a lean solution with 42% CTB conversion (carbon loading = 2.49 mol CO_2/kg solution; alkalinity = 3.51 mol alkalinity/kg solution) was achieved. In order to confirm that sufficient steam was being produced to strip the CO_2, the water condensate rate was determined and found to correspond to around 30 LPM of steam. Based on the partial pressures of CO_2 and steam at the top of the stripper and the liquid volumetric flow rate (to maintain 90% capture mass balance), less than 10 LPM of steam should be required. Therefore, the steam rate was considered to be sufficient and the stripper column was subsequently increased in packing height from 1 to 1.8 m to improve gas-liquid contact for separation. This modification was completed before operational limits testing. For bench-scale testing, the targeted steady state lean and rich CO_2 loadings (Appendix H) were 0.3 mol CO_2/mol K_2CO_3 (30% CTB conversion) and 0.67 mol CO_2/mol K_2CO_3 (67% CTB conversion). However, in practice, a lower working capacity of 0.2 mol CO_2/mol $K_2CO_{3,}$ corresponding to ~0.3 mol CO_2/kg solution (or 0.013 kg CO_2/kg solvent), was observed during Parametric Test #1 with 3 g/L enzyme.

The bench-scale system was equipped with capability for on-line pH measurement as an approximate means of monitoring CO_2 loading during testing, and an off-line correlation between pH and CO_2 loading was established using test solutions prepared and tested at different carbon loadings and temperatures. A nominal 20 wt % aq. K_2CO_3 solution (3.1 mol alkalinity/kg solution, actual) was prepared. The solution was CO_2 loaded by sparging with CO_2. At regular time intervals, carbon loaded samples were drawn and measured for pH (at 3 temperatures), alkalinity and carbon loading. The alkalinity of the samples was determined from equivalence point titrations with standardized sulphuric acid solutions. The carbon loadings were determined according to a method adapted from Goyet and Snover [84] using phosphoric acid to liberate CO_2 from the samples. Details of the alkalinity and carbon loadings tests are provided by Matin et al. [85]. The CTB conversion was calculated according to Equation 1.

$$CTB\ conversion = \frac{measured\ carbon\ loading - (alkalinity)0.5}{(alkalinity)0.5} \qquad \text{(Equation 1)}$$

The temperature range selected gave flexibility of ±5°C around the bench-scale absorber operating target temperature (40°C). The measured data were used to correlate pH versus CTB conversion using the linear regressions shown in Figure 11. The pH range shown in Figure 11 is indicative of the solvent pH range observed during bench-scale operating. Ultimately, although pH was useful as an on-line system monitoring tool, CTB conversion in the solvent was determined analytically according to Equation 1.

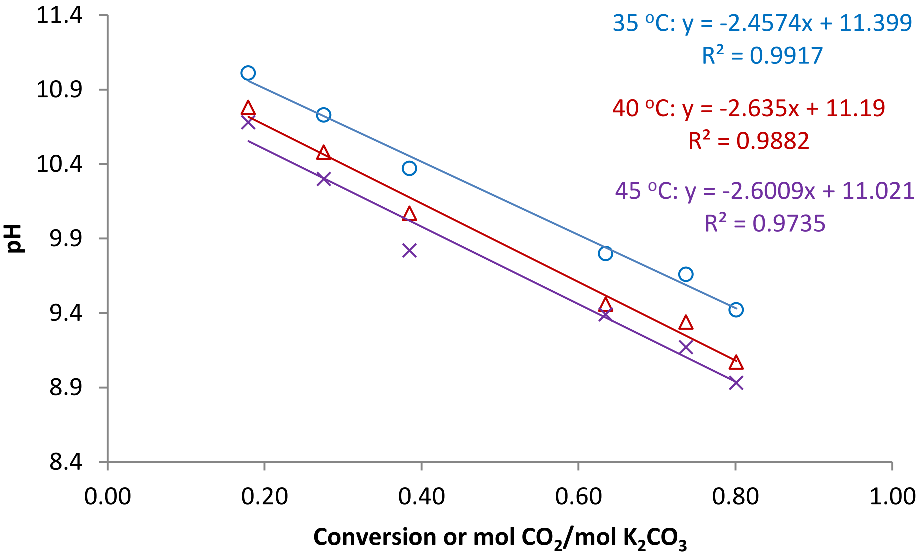


Figure 11. CTB conversion impact on measured pH at different temperatures.

3.7 Initial Solvent Reaction Kinetic Measurements (*absorption conditions only*)

While the cost, low environmental impact, lack of degradation, and regeneration energy for a potassium carbonate based solvent system provide compelling advantages over a primary or secondary amine solution, the low absorption mass transfer rate make the process challenging. This directly impacts the absorber capital which represents 30% of the overall CO_2 capture process cost as estimated by NETL for a monoethanolamine (MEA) based system [22]. Thus, it is critical to show the enzyme performance enhancement in promoting CO_2 capture.

The CO_2 hydration rate promotion by carbonic anhydrase provided by Novozymes was evaluated using a Wetted Wall Column (WWC) at the UK-CAER. The WWC is an in-house apparatus for overall mass transfer coefficient (K_g) determination of a gas-liquid absorption process. Using the WWC, a known amount of carbonic anhydrase enzyme was added to the 20 wt% K_2CO_3 solvent to investigate the effect of enzyme concentration on the overall mass transfer coefficient of CO_2 in the solvent. From Figure 12 it is clear that there is a sharp increase, 5.6 times higher, in K_g with 2 g/L of enzyme compared to the non-catalyzed case. Furthermore, the mass transfer continues slightly to rise as catalyst concentration is increased from 2 to 4 g/L of enzyme, with no further increase observed beyond a 4 g/L dose. The relative rate increase between consecutive concentrations becomes much less pronounced as enzyme concentrations increase, leading to a typical “plateau” effect that commonly occurs in enzyme dose-response measurements when the amount of substrate (in this case CO_2) available to the enzyme becomes limiting.

In a subsequent study the effect of temperature on mass transfer coefficients of enzyme promoted K_2CO_3 were measured. As shown in Figure 13, temperature had limited impact on mass transfer over the absorber temperature range of 30-50 °C, indicating the robust catalytic effect of enzyme across a wide and applicable absorber temperature range.

A 30 wt% MEA solution was previously measured to have a mass transfer coefficient of 1 mmol/m^2/s/kPa at 0.4 C/N carbon loading and 40 ^{o}C; and the baseline enzyme/K_2CO_3 solvent was measured to support a mass transfer rate 50% higher than the benchmark 30 wt% MEA at enzyme concentrations >2 g/L, which was a success criterium for the project.

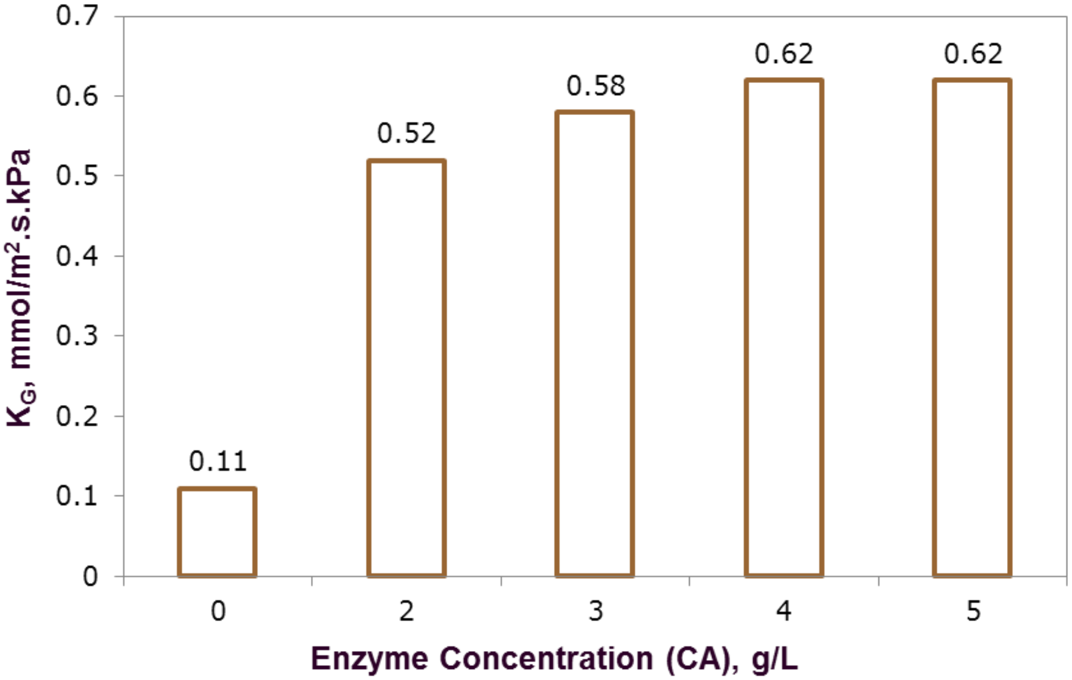


Figure 12. Effect of enzyme concentration on overall mass transfer coefficient. Test conditions used were: aq. 20 wt% K_2CO_3 solvent; liquid flow rate = 180 ml/min; total gas flow rate = 6 LPM; temperature = 40 °C.

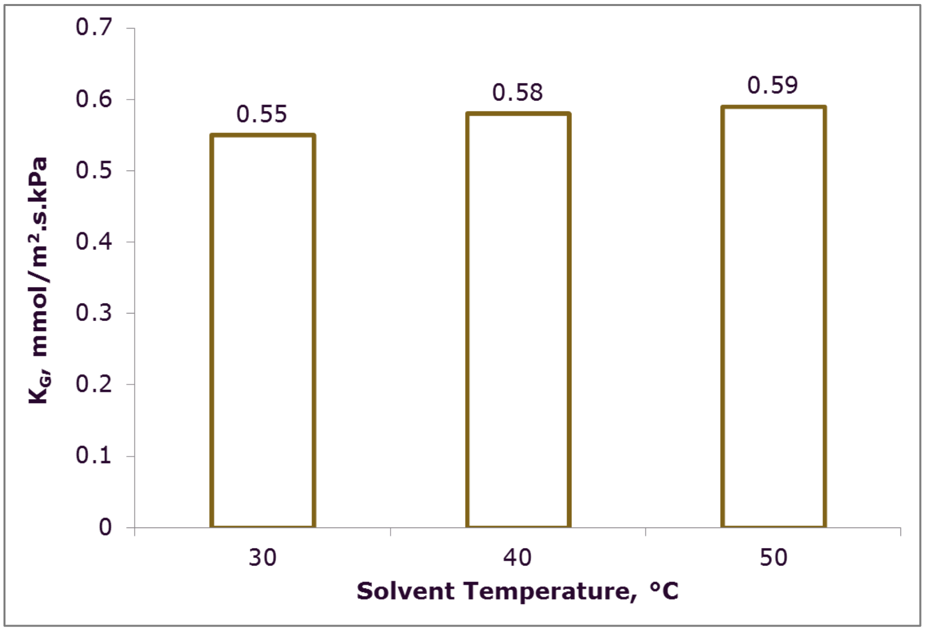


Figure 13. Effect of temperature on overall mass transfer coefficient. Test conditions used were: aq. 20 wt% K_2CO_3 solvent; liquid flow rate = 180 ml/min; total gas flow rate = 6 LPM; enzyme concentration = 3 g/L.

3.8 Solvent Contaminant Resistance

No provision was made for experimental evaluation of aqueous K_2CO_3-based solvent contaminant resistance, because studies and publications by Akermin, Inc. [66] and the University of Illinois [50] previously demonstrated the robustness of enzyme-promoted K_2CO_3 solvents to typical flue gas contaminants at lab scale.

3.9 Solvent Corrosiveness

No provision was made for experimental evaluation of the corrosiveness of the working solvent towards materials of construction, because the degree of corrosiveness is expected to be low and have no impact on the operation of the bench-scale system.

3.10 Solvent Safety & Sustainability

A preliminary assessment of solvent chemical safety and environmental impact was included as part of the EH&S assessment (Section 9).

4 ULTRASONICS APPROACH FOR DESORPTION ENERGY REDUCTION

As previously stated, enzyme-enhanced potassium carbonate CO_2 capture offers theoretically lower energy performance compared to primary amines. Nevertheless, due to limitations on enzyme longevity at high stripping temperatures, lower stripping temperatures are required if enzyme is recirculated in the system, through both the absorber and stripper. Vacuum-assisted stripping is one means of enabling lower desorption temperatures. Another concept explored during this project involved ultrasonic regeneration. A simplified schematic of the envisioned process is shown in Figure 3.

The principle behind ultrasonic regeneration is based on bubble formation in, and release from, the CO_2-loaded solution. Ultrasonic acoustic waves produce alternating high-pressure (compression) and low-pressure (rarefaction) cycles (Figure 14). Bubbles produced during the low-pressure rarefaction stage have a high surface area and behave like a vacuum to draw dissolved gas out of the liquid and into the gas bubble as the gas bubble expands ("Expanding Bubble" graphic). For an aqueous K_2CO_3-based CO_2-loaded solution, the composition of gas inside the formed bubbles will be a mixture of CO_2 and H_2O. The bubbles can grow in size and, due to their low density, will rise upwards in the liquid to release entrapped gas into the headspace. Re-dissolution of bubbles – such as is caused by a long travel path through the liquid – works against the release of gas to the headspace. As bubbles shrink during compression ("Shrinking Bubble" graphic), the pressure inside the bubble increases, causing CO_2 to be absorbed by the surrounding liquid. An important feature of ultrasonic regeneration is to cause the expanded bubbles to release gas to the headspace prior to compression. The bench-scale regenerator design took this into consideration by using the upward flow of solvent through the regenerator to push the gas/liquid mixture generated in the ultrasonic zone upwards to the gas/liquid separation zone to maximize gas release and minimize gas re-dissolution (Table 5).

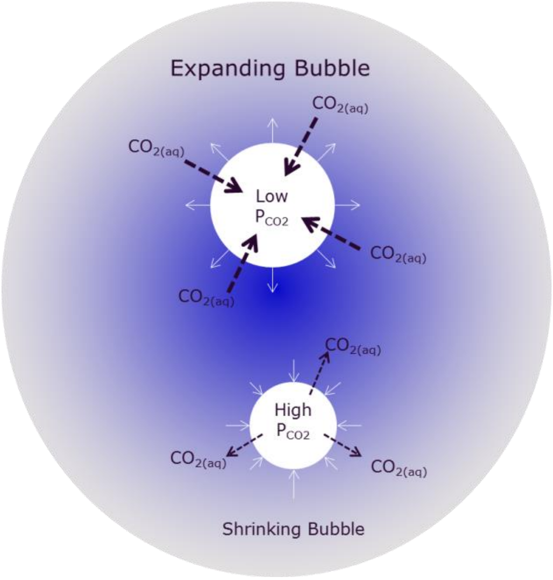


Figure 14. Schematic of gas bubble compression and rarefaction induced by ultrasonics.

Table 5. Rationale for Application of Ultrasonics to CO_2 Regeneration

Rectified Diffusion Mechanism [86]	Proposed approach for solvent regeneration
Bubbles expand and shrink in an ultrasonic field • Expanding bubbles = lower pressure inside the bubble & higher bubble surface area • Shrinking bubbles = higher pressure/ lower surface area Rectified diffusion results when expanding bubbles allow for a biased transfer of dissolved gas into the bubble from solution	Create a population of seed bubbles • Grow the bubbles via rectified diffusion • Frequency optimization likely required Rapid formation and removal of bubbles; aimed at limiting enzyme residence time in the regenerator and minimizing gas re-dissolution Leverage enzyme-based rate enhancements to stabilize and grow bubble formation

4.1 Ultrasonic Regeneration Background

For regeneration to be effective in the 70-80°C temperature range, a driving force in addition to thermal energy must be applied. While combining a vacuum swing component to a standard thermal swing desorption can be effective, the added compression needed on the separated CO_2 stream may limit the energy benefit. Therefore, it was proposed to harness ultrasound-driven rectified diffusion to increase the pressure at which CO_2 desorbs from the solution, offering an improvement in desorber performance at moderate temperatures with little to no need for vacuum. During rectified diffusion the growth of the bubble occurs because, as the bubble oscillates in the ultrasound field, rates of mass transport into the bubble during expansion are higher than rates of mass transport out of the bubble during compression. This effect occurs in part because the surface area of the bubble wall is greater during expansion resulting in a net increase in the amount of gas in the bubble ([87] , [88], [89], [86], [90], [91]), and small bubbles above a threshold size grow over time, despite not being favored by equilibrium.

During rectified diffusion, bubble growth stops when a size is reached where mass transport into and out of the bubble are in equilibrium. If, after bubble growth, the ultrasonic excitation is removed, the bubble rises due to buoyancy, while simultaneously dissolving back into the solution. However, if inertial forces are applied by rapidly spinning the fluid to obtain gas-liquid separation following ultrasound application, it is theoretically possible to extract CO_2 at a pressure higher than the equilibrium partial pressure expressed by the bulk liquid. Alternatively, maintaining ultrasonic excitation during bubble rise/coalescence may also assist CO_2 separation. Achieving adequate gas removal may require multiple stages of ultrasound excitation followed by separation. Predicting that the ultrasonic power requirements are sufficiently low, the benefits could significantly improve overall energy efficiency of the process.

Ultrasonic or acoustic energy has been used to enhance industrial processing for more than 40 years [92]. The use of acoustic energy to influence chemical reactions is known in the scientific community as sonochemistry, where sound frequencies from the audible range into the ultrasonic range (400 Hz to 1 MHz and higher) are employed in modifying specific chemical reactions to generate greater quantitative yields with a corresponding increase in the rates of the reactions under investigation [93]. Current industrial examples of ultrasonic applications for enhanced degassing of various liquid media include carbonated beverages, high-temperature melting materials ([94], [95]), and enhancing bioreactor fermentations to reduce CO_2 in ethanol production [96], as well as high-powered (>1 W/cm2) ultrasonic approaches for degassing liquid food products, induction of oxidation/reduction reactions, and other processes [97].

High power ultrasound has only recently become an efficient tool for other large scale commercial applications, such as emulsification, homogenization, extraction, crystallization, dewatering, low temperature pasteurization, degassing, defoaming, activation and inactivation of enzymes, particle size reduction and viscosity alteration. This can be attributed to improved equipment design and higher efficiencies of large scale continuous flow-through systems. High power ultrasonics is not an off-the-shelf technology and needs to be developed and scaled up for each application. Several processes that take place in the presence of cells or enzymes are activated by ultrasonic waves. High intensity ultrasound can break cells or denature enzymes; however, low intensity ultrasound can improve mass transfer of reagents and products through the boundary layer or through the cellular wall and membrane. Matsuura et al. [98] showed an increase in the fermentation rate of sake, beer and wine when relatively low intensity ultrasonic energy was applied during the fermentation process. The mechanism proposed is that the ultrasound drives off CO_2 (produced during the fermentation process) which normally inhibits fermentation [99].

4.2 Batch Mode Ultrasonics Testing Approach

PNNL led the laboratory-scale sonication testing in a static configuration to determine the operating conditions necessary for enhancing CO_2 release from the solvent via rectified diffusion. Utilizing an existing temperature-controlled reaction vessel, equipped with an ultrasonic horn to add ultrasonic energy at a specific frequency to the loaded K_2CO_3 solution, parametric assessments of ultrasonic energy, sonication time, burst sequence, solvent CO_2 loading, solvent temperature, head-space pressure, and CA enzyme concentration were carried out to identify the optimal operating envelope for the ultrasonic regenerator. The goal with this system was to quantify the regeneration effect of ultrasonics at atmospheric headspace pressures, independent of bulk temperature, and determine if it is on par with vacuum stripping at the same temperature.

4.3 Batch Mode Ultrasonics Results

A laboratory “Batch Ultrasonic Test System” was constructed at PNNL so that the impact of ultrasonic energy could be quantified on solvent CO_2 release, while maintaining a constant temperature. A schematic (Figure 15) and photograph (Figure 16) of the batch-mode experimental configuration is shown in the figures. In the Figure 16 configuration, the ultrasonic horn is oriented upwards, which was found to be beneficial for the release of CO_2 from K_2CO_3 solvent that was loaded near to saturation. In earlier configurations (Figure 15), the ultrasonic horn was oriented downward, and, although significant bubble generation was observed at the tip of the horn, limited detectable CO_2 gas release above the bulk liquid level was attributed to bubble re-dissolution during the long bubble travel path to the surface.

Multiple tests were performed on the batch ultrasonic test system. The tests focused on quantifying the release of CO_2 from a loaded K_2CO_3 solution via ultrasonic energy addition, while holding the bulk solvent temperature at 70°C. The batch system was temperature-controlled to allow introducing ultrasonic power while maintaining temperature to within 2 °C.

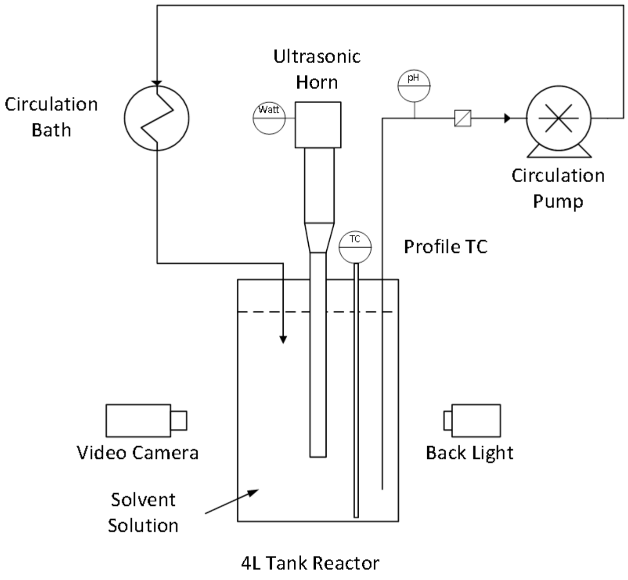
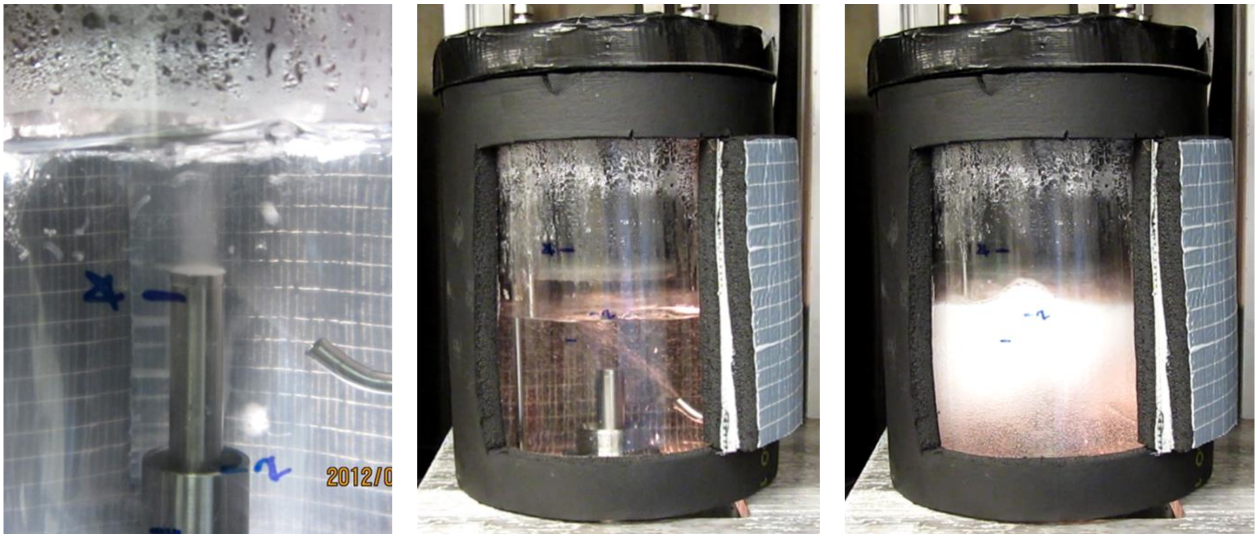


Figure 15. Schematic of PNNL batch-mode ultrasonic desorption system.



Pure Water at 70^{o}C
With Sonication

Loaded Solvent at 70^{o}C
No Sonication

Loaded Solvent at 70^{o}C
With Sonication

Figure 16. Visible agitation and bubble formation during batch mode ultrasonics testing.

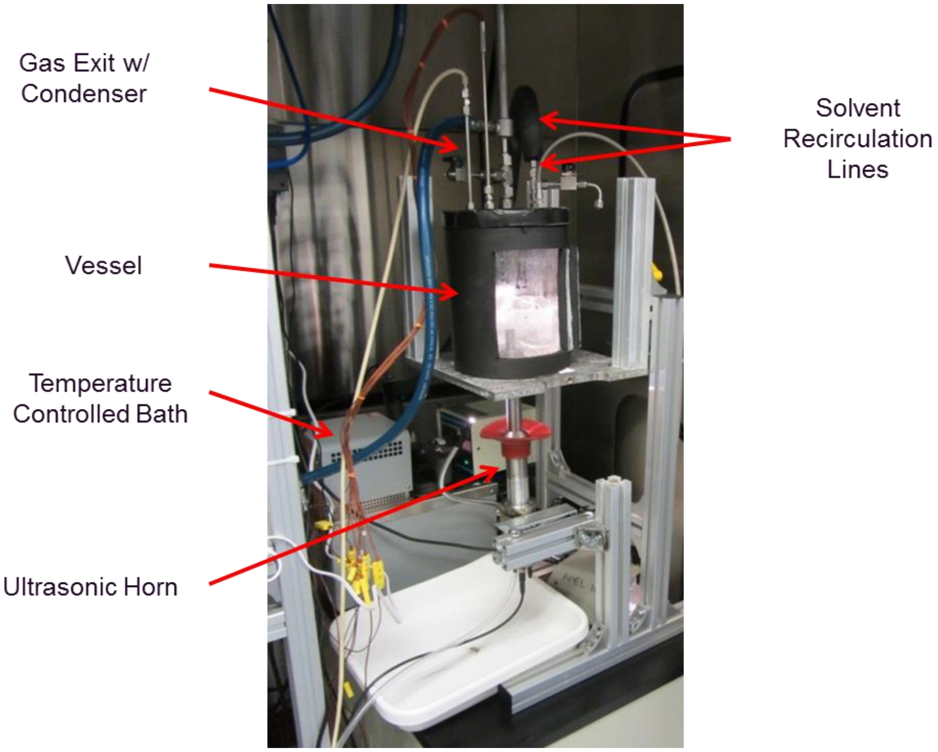


Figure 17. PNNL’s laboratory batch ultrasonic test system.

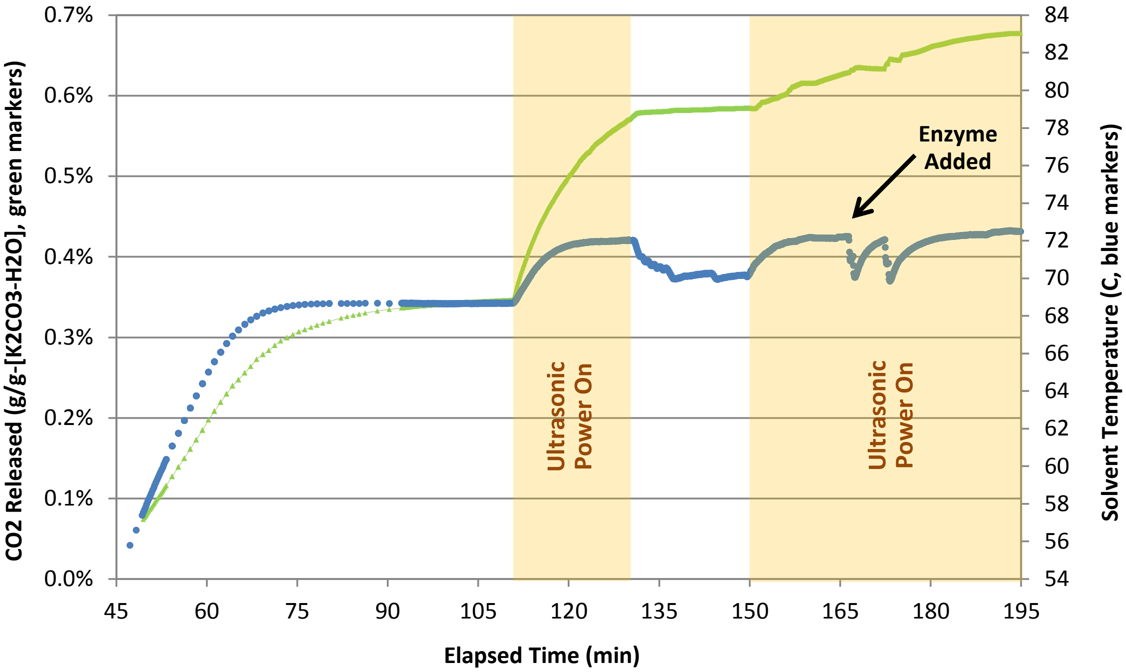


Figure 18. Evidence of ultrasonic energy enhancement of CO_2 release independent of temperature. The amount of CO_2 released (green line) increased independently of applied temperature (blue line) when ultrasonics was applied (yellow-shaded zones).

Tests on the Batch Ultrasonic Test System provided visual (Figures 16 and 17) and measurable (Figure 18) evidence of ultrasonic energy enhancement of CO_2 release, that appeared to be independent of temperature, and provided a basis for initial energy estimation for a full scale CO_2 regeneration system. Figure 16 shows vigorous agitation and bubbling was observed when ultrasonic power was applied to CO_2-loaded 20% K_2CO_3 solution at 70^{o}C, whereas pure water with ultrasonic power applied showed minimal bubbling emerging in a vertical column from the top of the inverted ultrasonic horn (silver cylinder centered in the photograph). CO_2-loaded solvent at 70°C showed minimal bubbles in the liquid, considered to be caused only by the flow of recirculating fluid entering the reaction chamber from a small stainless steel tube visible in the lower right of the reaction chamber.

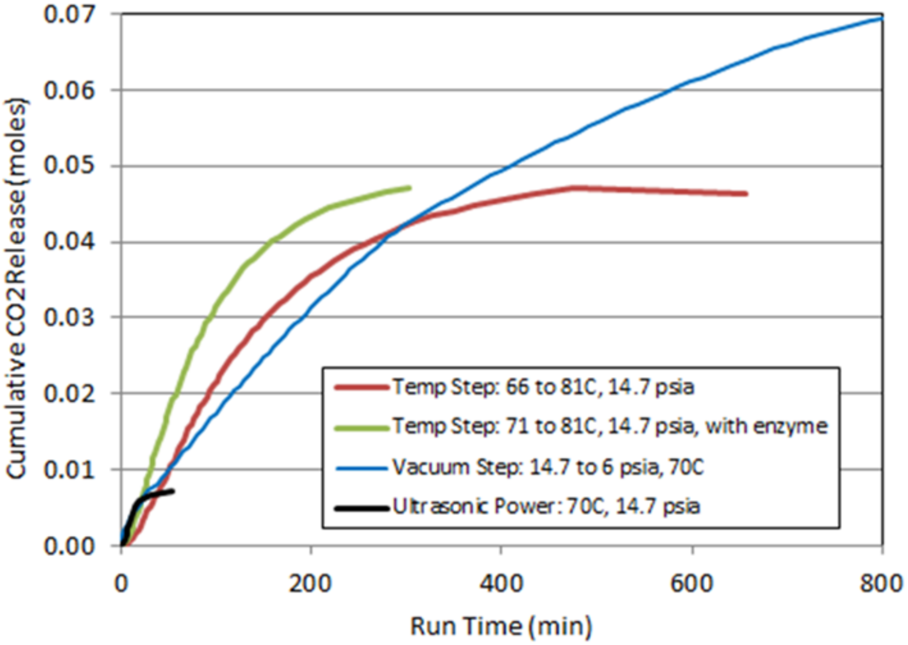


Figure 19. Batch mode comparison of thermal, vacuum and ultrasonic CO_2 release.

Additional batch testing was performed with temperature and bulk vacuum increases only so that the results could be compared with the ultrasonic measurements. These tests were performed in a 1-L Parr reactor filled with 500 mL of solvent. The results from the different batch mode tests are compiled in Figure 19, presented as cumulative CO_2 release versus run time. All tests were carried out using CO_2-loaded aq. 20 wt% K_2CO_3. For the temperature step tests, the initial carbonate (K_2CO_3) to bicarbonate ($KHCO_3$) conversion was ~82%, and for the vacuum and ultrasonic tests, the initial conversion was 72%. Enzyme was only added to one of the temperature increase tests shown in Figure 19. Similar initial CO_2 release rates (initial parts of curves) were observed in all cases with an apparent higher rate in the presence of enzyme (green curve versus red curve), suggesting a contribution from enzyme in overcoming potential kinetic limitations. The total CO_2 release for the ultrasonic solvent regeneration test at atmospheric pressure was low compared to the vacuum (blue) and thermal (red and green) regeneration tests. CO_2 re-dissolution into the large volume of solvent present in these tests was suspected to be a main contributor to the low performance.

Although the extent of CO_2 release had not met the target, these initial observations using the laboratory ultrasonic horn demonstrated that beneficial CO_2 release effects are achievable using ultrasonics, and provided benchmark data for the work during Budget Period 2 to maximize the extent of these benefits by replacing the laboratory horn configuration with the flow-through configuration.

The demonstrated batch testing ultrasonic energy was 4.9 kJe/kg solvent, or 10.3 kJe/mol of CO_2 released. Based on this measurement, a full-scale CO_2 regeneration system was estimated to be possible with an ultrasonic energy requirement of 1.5 kJe/kg solvent, equating to just over 11 MWe of parasitic power for the ultrasonic system in the 550 MWe reference system. This estimate was partially justified by the fact that large-scale ultrasonic ship ballast water treatment systems draw 0.24 to 0.79 kJe/kg of water [100].

4.4 Continuous Flow Ultrasonics Testing Approach

A major issue with the batch ultrasonic testing system was the re-dissolution of CO_2 from bubbles that were formed in the bulk solvent before they could be removed. As a result, a continuous flow-through sonication configuration was pursued. The system was sized for potential retrofit to the bench-scale process at UK-CAER, primarily via the non-intrusive flow-through type ultrasonic regeneration unit (Figure 20). PNNL designed, assembled and operated the flow-through ultrasonic regeneration system (Figure 21) using borrowed components from an available sonication system to conduct preliminary evaluations of CO_2 release before committing the project to purchase dedicated equipment at high cost.

The prototype ultrasonic reactor components included: piezoelectric transducer, waveguide, customized clamps to adapt to a single-wall conduit of 1 inch in diameter, reactor tubing and flanges in the form of a spool piece, and the appropriate power supply unit. As planned in the original proposal, cyclonic separation was incorporated at the exit of the prototype ultrasonic device as means to rapidly remove formed CO_2 bubbles before they could re-dissolve. The flow-through system was expected to allow for improved bubble disengagement and more efficient transmission of electrical power to the ultrasonic energy in the solution compared to the batch mode system. The entire unit was assembled and instrumented to operate in a semi-continuous flow-through mode.

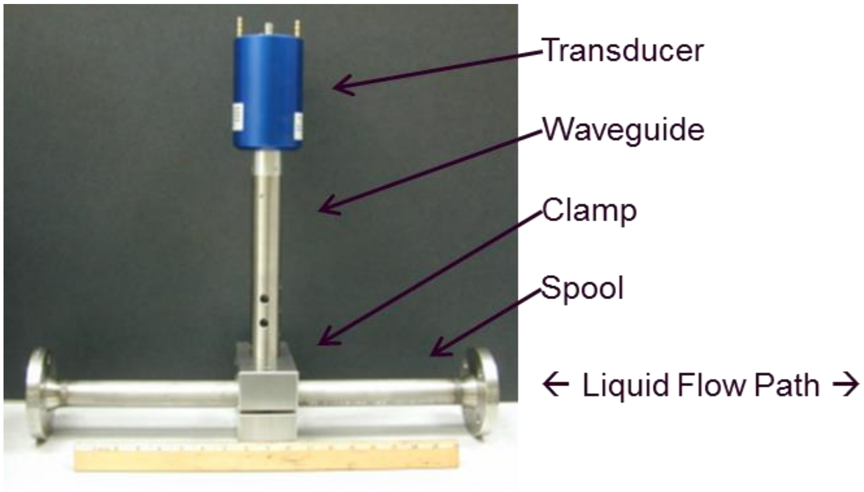


Figure 20. Photograph of a commercial flow-through sonication system comprised of a transducer/waveguide assembly, clamp and spool piece.

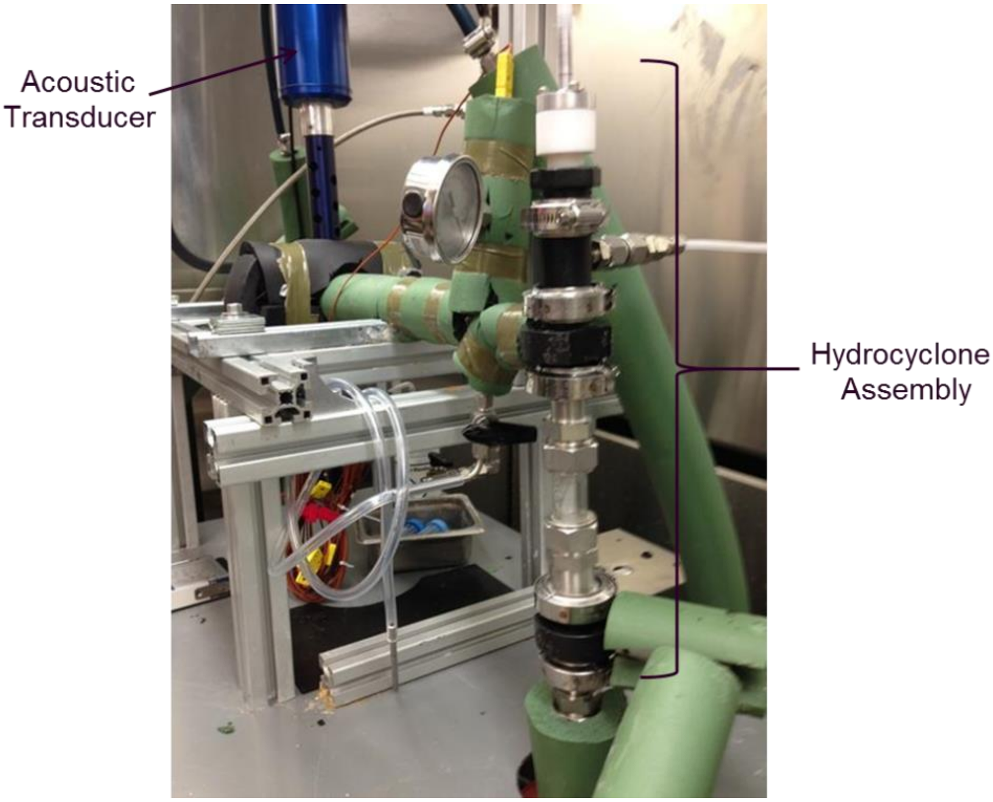


Figure 21. Photograph of the flow-through ultrasonic system. The sonicator assembly is identified by the blue unit labeled acoustic transducer in the background. The foreground equipment is the hydrocyclone gas-liquid separator assembly.

The flow-through system was based on the solvent being pumped from a common reservoir, where it returned after gas release. The volume of the reservoir was large enough (for most tests) to assure only small changes in CO_2 loading with time. The solvent leaving the reservoir was heated by pumping it through a coil immersed in a heated bath. The solvent then flowed into the tube sonicator. The sonicator exited into a 1-inch hydrocyclone for rapid bubble disengagement. A mixer was added to the hydrocyclone to create centrifugal action at low flows. A secondary ultrasonic "horn" was positioned at the bottom of the hydrocyclone as an alternate means of adding ultrasonic energy. Gas was pulled from the top of the hydrocyclone, through a condenser, via a slight vacuum, to encourage disengaged bubbles to exit the hydrocyclone instead of the reservoir. Gas flowrates were quantified via a positive displacement flow meter on the exit of the vacuum pump.

4.5 Continuous Flow Ultrasonics Test Results

Parametric testing was conducted on the flow-through system. Key variables included: solvent flow rate (0.3 to 2.1 lpm), hydrocyclone mixer speed, hydrocyclone configuration (up or down), temperature, enzyme (present or not present), ultrasonic source (tube sonicator or horn), solvent preparation (prepared from salts or sparged with CO_2), and vacuum.

Figure 22 shows as plot of data taken from one of the flow-through tests. The dotted red line is temperature at entry to ultrasonic spool. The solid red line is temperature at exit of ultrasonic spool. A solvent flowrate of 0.3 lpm was used, with a hydrocyclone mixer speed that helped release bubbles despite the low centrifugal force. A slight vacuum (several inches of water) was pulled on the gas at the top of the hydrocyclone to assure gas flow through the flow meter. The hydrocyclone was in the ‘up’ configuration, where the liquid was added from the bottom. Finally, both the horn and tube (“clamp on”) sonicator were operated. The cumulative gas release (dotted blue line) shown in Figure 22 was constant in three separate regions. The first region was during horn sonication only (175 to 200 min). The second region was with both the horn and tube (“clamp on”) sonicators operating (200 to 230 min). The third region was with both sonication units operating and with enzyme added to the solution (230 to 275 min). Clearly, the most significant gas release was in the second region. This gas release equates to 0.0011 moles of CO_2 per minute. The period after enzyme addition was expected to have a higher CO_2 release, but was lower in observation. The suspected reason for this reduction was a significant amount of foam generation in the hydrocyclone, which may have reduced the ability for gas to be released. The left hand photo in Figure 22 is representative of sonication prior to enzyme addition. Bubbles were being released at a measureable rate and they popped once reaching the liquid-gas interface. After enzyme addition (right-hand photo) there appeared to be more bubble generation but the visual observation may have been confounded by the foam layer that formed. The foam layer may have also caused the observed decrease in overall CO_2 release by impeding bubble popping before re-dissolution. Note that no antifoam additions were used in the testing. Addition of antifoam to minimize the foam layer as a way to help promote gas release from the liquid is one feature that should be further investigated.

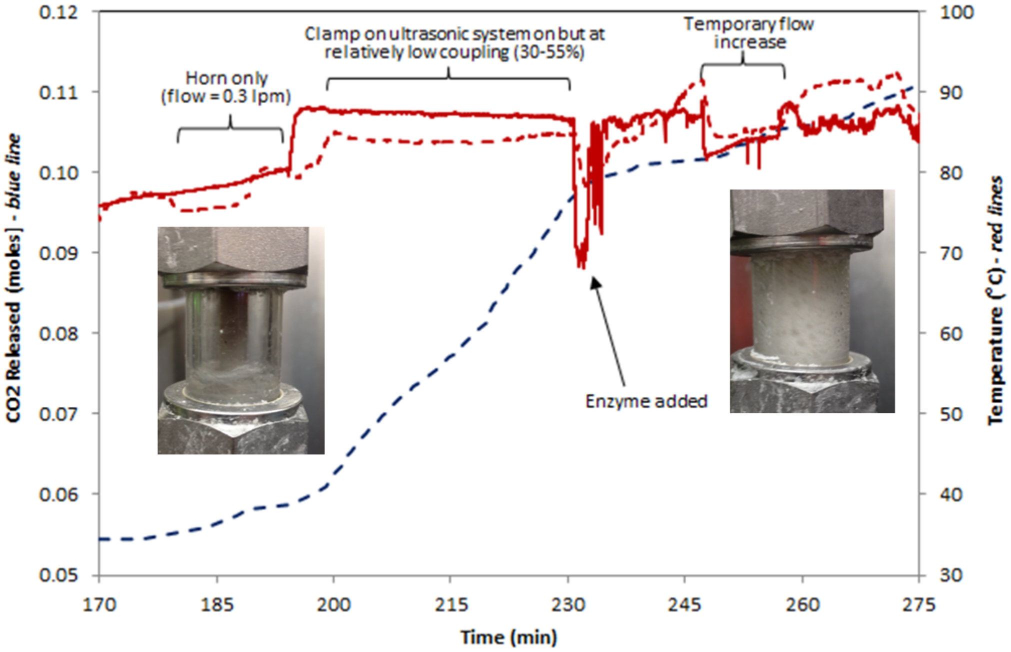


Figure 22. Flow-through ultrasonics test using solvent loaded with CO_2 via sparging an aq. 20 wt% K_2CO_3 solvent to a 72% conversion of K_2CO_3 to $KHCO_3$ for the inlet liquid composition. The dashed red line is the temperature into the tube sonicator and the solid line is the corresponding outlet temperature. The system utilized a hydrocyclone separator.

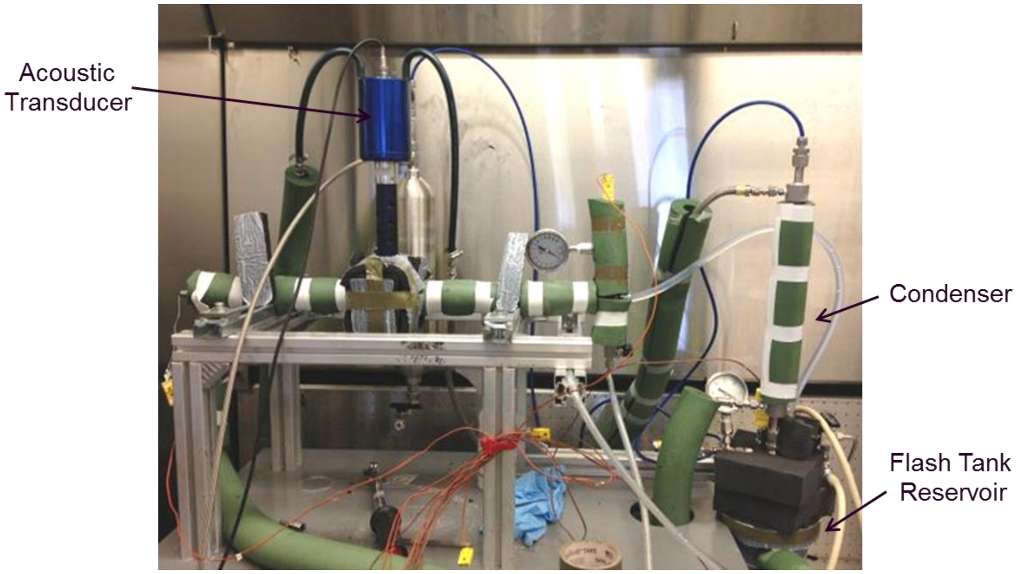


Figure 23. Flow-through ultrasonic system configured with a flash tank reservoir in lieu of the hydrocyclone gas-liquid separator.

Additional flow-through testing was performed using a flash tank reservoir in lieu of the hydrocyclone separator. The purpose of the tests with the flash tank configuration was to obtain flow-through test data with acoustic energy and vacuum using the same flow loop configuration. The flash tank reservoir flow loop configuration is shown in Figure 23.

Figure 24 shows plots of flow-through system testing for more direct comparison of vacuum and ultrasonics. The red lines correspond with the vacuum-only test and the blue lines correspond with the ultrasound-only test. The solid lines represent cumulative CO_2 release and the dashed lines represent solvent temperature. The solvent was prepared by dissolving appropriate amounts of potassium carbonate and potassium bicarbonate salts in water to give the equivalent of a 20 wt% K_2CO_3 solution with a CO_2 loading level of 77% K_2CO_3 converted to $KHCO_3$. The solutions were processed through the unit under an identical solvent flow condition of 0.9 lpm and starting temperature (70°C). The system utilized recirculation from a modified holding tank (to allow the vacuum operation), with approximately 1.1 liters of total solution. Based on the flow rate for the tests, a relatively high number of tank turnovers was experienced. The initial slope of the curves in Figure 24 suggest that the CO_2 release rates were similar between the two tests. However, the ultrasonic test experienced a significant temperature increase (more than 10°C) which had to be accounted for in the release comparisons. The change in the slope of the solid blue line at approximately 25 minutes corresponds with a change in the relative acoustic power level (from 85-90% to 45-50%).

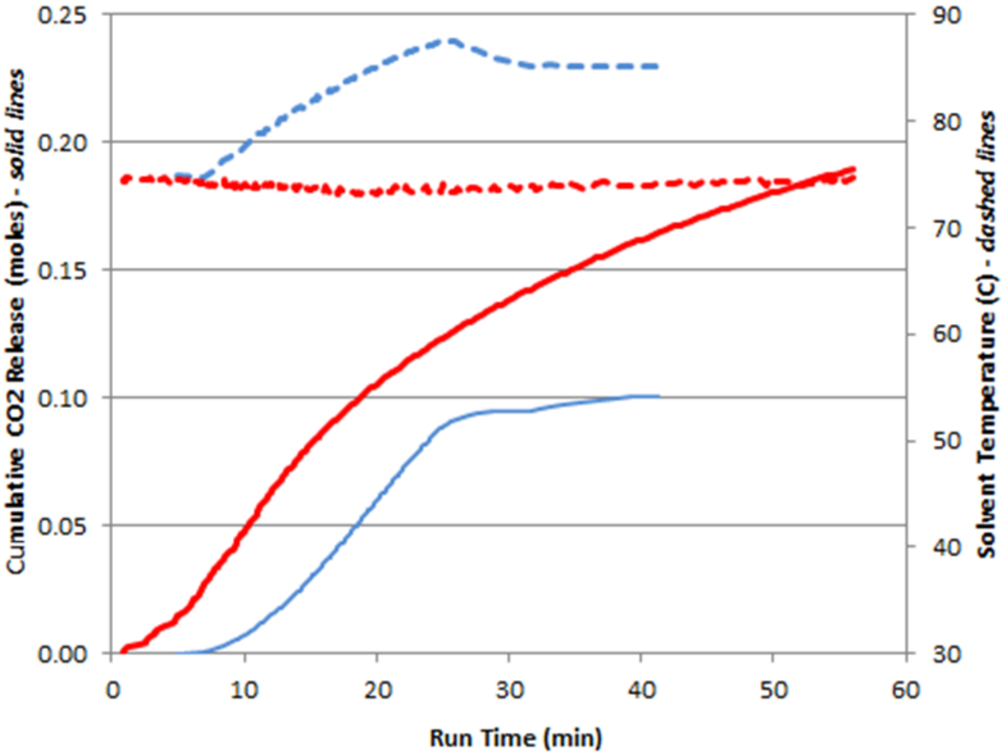


Figure 24. Flow-through ultrasonics test using solvent prepared from (bi-)carbonate salts To give a 20wt% (K_2CO_3 basis) solvent with 77% equivalent K_2CO_3 converted to $KHCO_3$ (prepared using the respective salts). Liquid flow rate was 0.9 lpm. The red lines are at 0.4 atm pressure (no ultrasonics) and the blue lines are from the tube sonicator (no vacuum). No enzyme was used in these tests.

Table 6 shows a comparison of the testing results from batch and flow-through reactors, as well as comparison to equilibrium projections for temperature and vacuum changes only and comparison versus the 70°C/ 6 psia vacuum stripping target. The analysis of the data shown in Figure 24 obtained using the flash tank flow loop configuration shown in Figure 23 is listed as “Vacuum (salt soln)” and “Ultrasonic (salt soln).” The test “Ultrasonic (sparged soln)” was performed using the hydrocyclone flow loop configuration shown in Figure 21. The PARR reactor results include the vacuum testing as well as temperature step testing (Figures 25 and 26). A key comparison in the table is the CO_2 release rates between the various tests. The maximum release rates for the flow-through tests were simply derived from the slopes of the corresponding CO_2 release curves. For the batch tests the initial slope of CO_2 release curve was used to determine the maximum release rates. The total CO_2 releases were also calculated for the batch and flow through tests. These were compared to equilibrium estimates based on the observed temperature and pressure changes (second to last column). Equilibrium CO_2 release estimates were also made in Aspen Plus® based on the starting solutions achieving the 70°C/ 6 psia project target (last column).

Table 6. Comparison of CO_2 Release from Batch and Flow-through Testing

	Initial CO2 Loading	**Start Temp (C)**	**End Temp (C)**	**Solvent Flow Rate (lpm)**	**Total Solvent Volume in System (L)**	**Max CO2 Release Rate (mol/min)**	**Instantaneous CO2 Release Rate (mol/L)**	**Total CO2 Release (mol/L)**	**Equilib CO2 Release from Temp/ Vac Change (moles/L)**	**CO2 Release Reqd to Hit 70C 6psia Equilibrium Target (moles/L)**
Flow-through Testing										
Vacuum (salt soln)	77%	75	75	0.9	1.1	0.00715	0.008	0.173	0.409	0.360
Ultrasonic (salt soln)	77%	75	87	0.9	1.1	0.00625	0.007	0.089	0.169	0.360
Ultrasonic (sparged soln)	72%	80	86	0.3	7.2	0.00108	0.004	0.004	0.032	0.275
Batch Ultrasonic Testing										
Test #1 (sparged soln)	84%	68	72	NA	2.2	0.00852		0.060	0.057	0.482
Test #2 (salt soln)	72%	70	70	NA	2.2	0.00033		0.003	0.000	0.285
PARR Testing (salt solutions)										
Vacuum step - no enzyme	72%	70	70	NA	0.6	0.00018		0.155	0.285	0.285
Temp step - no enzyme	90%	40	52	NA	0.6	0.00009		0.016	0.000	
Temp step - no enzyme	90%	52	66	NA	0.6	0.00006		0.021	0.071	
Temp step - no enzyme	82%	66	81	NA	0.6	0.00023		0.084	0.166	
Temp step - w/ enzyme	90%	41	61	NA	0.6	0.00018		0.018	0.000	
Temp step - w/ enzyme	90%	61	71	NA	0.6	0.00013		0.027	0.151	
Temp step - w/ enzyme	81%	71	81	NA	0.6	0.00037		0.086	0.159	
Temp step - w/ enzyme	71%	81	88	NA	0.6	0.00041		0.093	0.112	

The last four columns for the flow-through testing in Table 6 are critical to understanding the performance of the ultrasonic system. The first test – vacuum only – shows a total release for the test of 0.173 mol/L, which is approximately half of the equilibrium release projections. However, multiple turnovers of the solvent holding tank occurred before the total CO_2 release was achieved. The maximum instantaneous CO_2 release rate was only 0.008 mol/L, or approximately 2% of the equilibrium projection.

The equivalent ultrasonic test (second row) produced a total CO_2 release of 0.089 mol/L. However, the solvent temperature increase incurred during this test could account for all of the observed increase (equilibrium projection due to observed temperature only is 0.169 mol/L). The second ultrasonics flow-through test (third row) shows an even lower total CO_2 release (0.004 mol/L), likely due to the lower initial CO_2 loading in the solvent.

The instantaneous CO_2 release rates for the ultrasonic flow through tests are also important to point out. These rates, 0.007 and 0.004 mol/L, respectively, are similar to the observed instantaneous rate from the vacuum test (0.008 mol/L). This suggests that there may be a similar rate limitation between the two processes. Unfortunately, the opportunity with ultrasonics is based on achieving higher CO_2 release rates than achievable with vacuum, such that multiple trays or sonicators would not be required. The flow through test results did not support this goal.

In order to provide further insights into potential rate limitations, the batch system data is provided (Figures 25 and 26). A key observation for the PARR testing is that introduction of enzyme appears to have increased the release rates (mol/min basis) at a given temperature. This supports rate limitations at temperatures as high as 80°C. Nevertheless, the observed maximum CO_2 release rates were still quite low – between 9 x 10^{-5} and 41 x 10^{-5} mol/min. The total CO_2 releases from those experiments were close (within 20% to 80%) to the approximate equilibrium projections.

Despite potentially higher CO_2 release rates with the ultrasonic tests (Figure 19), the total CO_2 release was not significant compared to a once-through projection to achieve equivalent performance with 70°C/ 6 psia vacuum stripping (less than 2% for one test and 25% for the other, but with multiple reservoir tank turnovers). Furthermore, the observed increases in temperature for the ultrasonic flow-through tests could more than account for the observed CO_2 release, which could have masked any effect of the targeted rectified diffusion.

Figure 27 presents a visual compilation of results from the batch and flow-through ultrasonics and vacuum testing, wherein experimentally observed CO_2 release is plotted in relation to the projected CO_2 release at equilibrium, represented by the dashed line. The targeted level of ultrasonics-induced CO_2 release needed to generate sufficiently lean solvent for reasonable solvent cyclic capacity, is shown by the yellow-shaded oval, which represents the Aspen Plus® simulated conditions for 70 °C and 6 psia vacuum stripping.

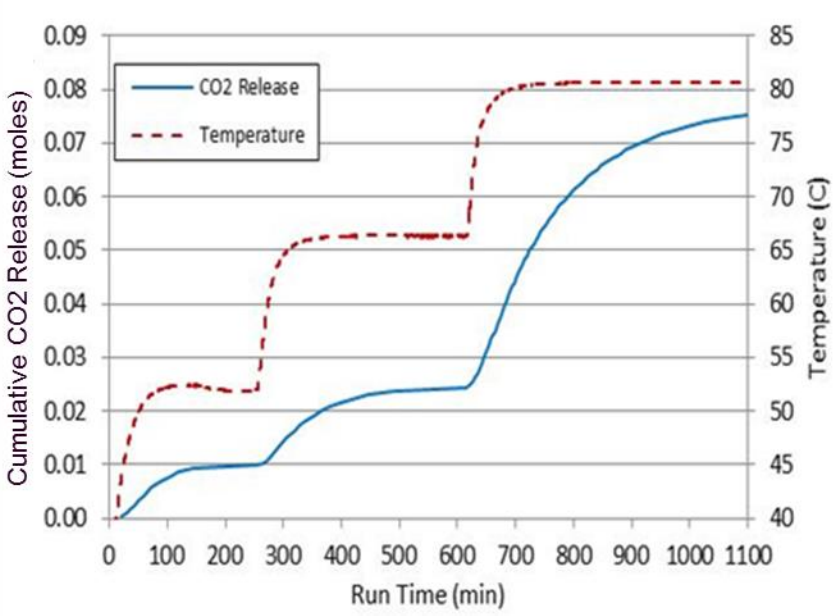


Figure 25. CO_2 release rates as a function of temperature change – *no enzyme present.*

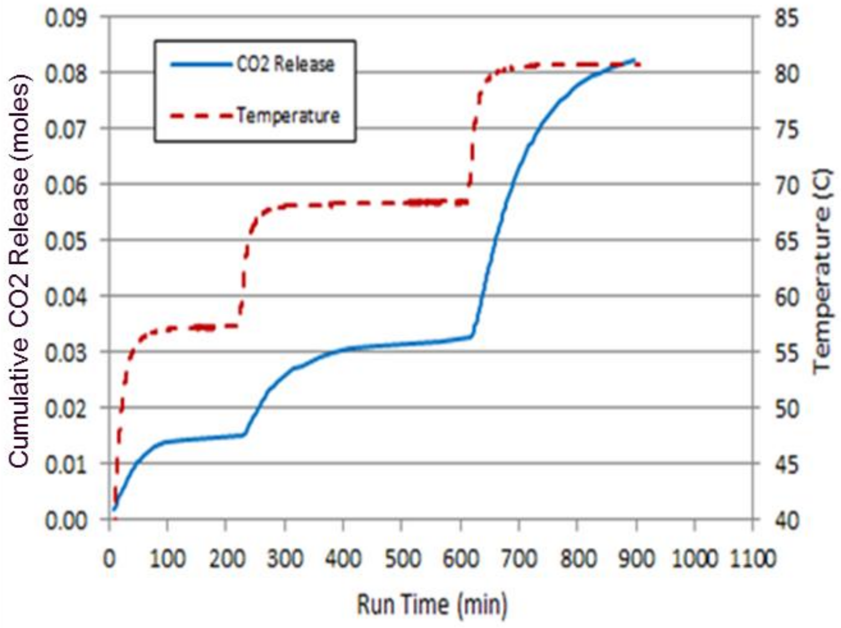


Figure 26. CO_2 release rates as a function of temperature change – *with enzyme present*.

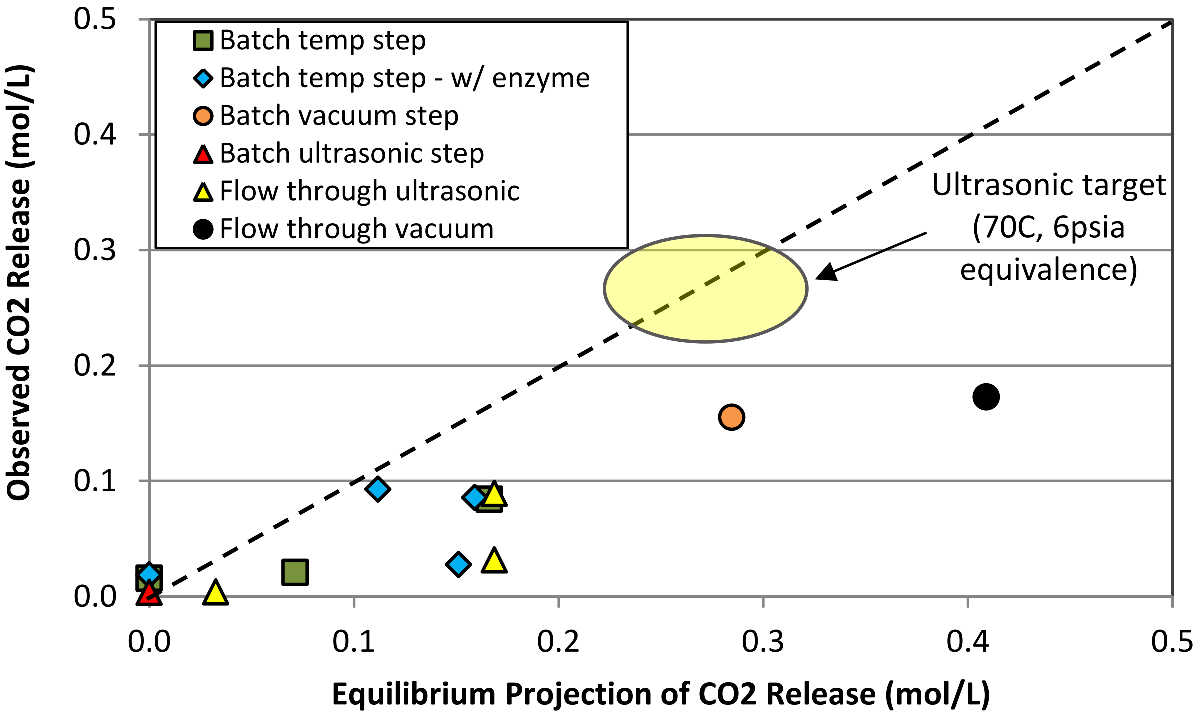


Figure 27. Summary of regeneration testing results.

The results show that all observed CO_2 release values were below equilibrium projections. Therefore, none of the tests, including the vacuum tests, achieved the simulation-predicted target (based on equilibrium assumptions). Kinetic limitations were also suspected because multiple passes (5+) were required for significant CO_2 release from both vacuum and ultrasonic flow through tests. Overall, CO_2 released during the ultrasonic flow through tests were within temperature-driven projections, meaning they could be explained by temperature increases alone.

4.6 Challenges Identified for Use of Ultrasonics

One of the initial project goals was to demonstrate the feasibility of ultrasonics as a novel low energy regeneration approach. A key technical challenge was the need to validate the actual performance of the ultrasonic regeneration technology and its capability to provide the lean solvent composition required by the process. Indications of ultrasonic regeneration benefit were observed in lab scale batch-mode tests. However, whether the extent of lean loading required could be achieved within a short time period was still a question. Therefore, a prototype bench-scale ultrasonics flow through reactor was designed, constructed and tested. Construction and testing of the prototype unit was a risk-mitigation approach not originally accounted for in the project tasks or budget, yet was accomplished in such a way that conclusions were reached early and within the framework of the overall project. During testing of the prototype, special attention was paid to separately account for temperature-dependent CO_2 release and CO_2 release that could be attributed to the ultrasonic effect known as rectified diffusion. Although several different configurations of the prototype ultrasonic regenerator were evaluated, including novel incorporation of a hydrocyclone to enhance gas-liquid separation, the magnitude of measured CO_2 release was within the range of temperature-dependent release, therefore, the separate benefit of ultrasonics could not be verified.

As a result, work on the ultrasonics approach was discontinued in favor of conducting the bench-scale testing using the low temperature vacuum regeneration approach. Vacuum regeneration was the reference case for ultrasonics and was an alternative case presented in the Preliminary Technoeconomic Feasibility Assessment, however comprehensive data on an integrated system with low temperature vacuum regeneration was lacking. The vacuum approach aimed at understanding the corresponding kinetic behavior and system performance with soluble enzyme. This information could address the limiting performance observed in the original ultrasonics measurements since the targeted operating temperatures are similar.

4.7 Recommendations for Further Work with Ultrasonics

An important consideration for further work with ultrasonics would be to better understand the potential exposure of operators to ultrasonic frequencies, and engineering mitigations to address excessive exposure levels. Threshold Limit Values® for airborne ultrasound have been adopted by the Occupational Safety and Health Administration (Appendix D). Improvements in ultrasonic effectiveness could potentially be achieved using alternate ultrasonic frequencies and solvent compositions favoring enzyme-based kinetic increases without foam production. Alternative acoustic or cavitation transmission geometries could also be explored, both for CO_2 desorption and absorption, such as controlled flow cavitation [48] or resonant acoustic mixing [47] technologies. These technologies could be especially effective when applied together with carbonic anhydrase immobilized as or on nanoparticles or microparticles to provide efficient mixing in the liquid to help overcome liquid-phase mass transfer limitations and take advantage of the CO_2 absorption enhancement that can occur at the gas-liquid interface when the size of the particles helps transport the biocatalyst into and out of the liquid film reaction zone ([101], [60], [49]). Because the majority of the acoustic energy can be directed into the liquid, it would be relevant to investigate acoustic geometries adapted to integrate together with conventional gas-liquid mass transfer systems [36], such as membrane, bubble-tank, jet, spray, packed and tray type contactors, as well as develop hybrid systems or even completely new designs. In laboratory-based stopped-flow experiments where a key feature of the apparatus is ‘instantaneous’ mixing, very high CO_2 absorption and desorption rates are achievable in the presence of carbonic anhydrase [78] which argues in favor of gas scrubbing designs that maximize mixing. Furthermore, ultrasonics could provide a means for rapid, localized solution heating that could potentially enable stripper redesign to limit solvent exposure time at high temperature and minimize thermal degradation of solvent components.

5 VACUUM APPROACH FOR DESORPTION ENERGY REDUCTION

Carbonic anhydrase enzyme accelerates inter-conversion between dissolved CO_2 and bicarbonate ion, which is the rate-limiting step for absorption and desorption in solutions that rely on ionic complexation of CO_2. Utilization of vacuum during the regeneration stage increases the overall driving force for the solvent regeneration reaction at moderate temperatures when using potassium carbonate-based solvents. Although it was recognized that application of vacuum would have a corresponding compression penalty downstream of the CO_2 capture unit, due to the use of low-enthalpy solvents, which could require very low pressure steam during the regeneration cycle, based on the Preliminary Techno-economic Assessment [69], the technology was projected to require 43% less parasitic power from a coal-fired power plant compared to the NETL Case 10 MEA scrubbing technology (Table 7).

Table 7. Preliminary TEA Summary of Projected Efficiency and Relative Parasitic Load

Case	Efficiency (HHV)	Parasitic Load for Capture vs. MEA
Case 9 (no capture)	36.80%	
Case 10 (MEA)	24.99%	100%
K_2CO_2/enzyme – vac strip, LP steam	24.34%	105%
K_2CO_3/enzyme – vac strip, VLP steam @ 8psia	**29.97%**	**57%**
K_2CO_2/enzyme – ultrasonic strip, LP steam	26.63%	85%
K_2CO_3/enzyme – ultrasonic strip, VLP steam @ 8psia	31.41%	45%

An important element of this projection was the potential ability of enzyme to help overcome rate limitations that may exist at low regeneration temperature conditions, as well as verify the rate enhancement benefits of enzyme in the absorber.

6 BENCH-SCALE UNIT CONSTRUCTION, OPERATION AND TESTING

The bench-scale integrated carbon capture test unit formed the backbone of this project's evaluation of the enzyme enhanced potassium carbonate solvent process for post-combustion capture. As such, careful design considerations, and several iterative changes were invested during bench unit construction. The unit was put through a series of shakedown tests that included operational extremes with and without enzyme. With evidence of reproducible operation, unit parametric testing commenced, followed by a cumulative 500 h test that comprised 75 run days. Throughout unit operation, online and offline data collection was used to understand various aspects of the solvent process, including: (i) understand bench unit operational parameters and effects on the process, (ii) characterize enzyme effects on the system, and effects of the system on the enzyme, (iii) translate experimental results to an Aspen Plus® modeling approach, (iv) inform the environmental, health and safety assessment of unit operation, and (v) build a foundation for a large scale technical and economic assessment of the proposed enzyme enhanced potassium carbonate solvent process for post-combustion capture. Although further work during scale-up studies is required to reduce uncertainties in projecting full-scale capture from a bench-scale system, the bench-unit provided valuable learnings and insights to future assessments of this innovative technology.

6.1 Bench-scale Unit Construction

UK-CAER constructed a bench-scale integrated carbon capture test unit for the enzyme enhanced potassium carbonate solvent evaluation. In order to observe the flow hydraulic pattern, a transparent chlorinated polyvinyl chloride (CPVC) column was procured and fabricated with a ID of 7.6 cm (3 in), a packing height of approximately 2 m (3.3 ft), and a maximum total column height of 2.6 m. The absorber packing material consisted of 6x6 mm Raschig rings. The absorber was sized to treat a desired 30 SLPM of simulated flue gas containing ~15% CO_2 balanced with N_2. A 7.6 cm (3 in) ID stainless steel stripper with a 2 m (3.3 ft) height of raschig ring 6x6 mm packing, and a condenser for solvent recovery and reduced vacumm pump power demand, were integrated with the absorber. As the solvent system was designed for vacuum stripping, a vacuum system including a vacuum pump and vacuum regulator (to maintain the desired vacuum) was installed. A heater and a chiller were installed for solvent solution temperature control. A hot oil system provided the necessary heat for solvent regeneration. Two high pressure liquid pumps were connected to the scrubber and the stripper. The pumps were designed to minimize cavitation created under vacuum stripping conditions. Two in-line flow meters were installed to monitor the volumetric solvent flow rates in and out of the stripper. A picture of the integrated bench-scale test system consisting of the absorber column and vacuum stripping column with connecting ancillary process equipment is shown in Figure 28. A simplified process and instrumentation diagram (P&ID), indicating the locations of measurement points, is shown in Figure 29 (a detailed P&ID is shown in Appendix A).

The system was instrumented to allow comprehensive data gathering on temperature profile along the absorber and stripper column and to calculate mass transfer flux. A National Instruments Labview system was installed to enable process control and data acquisition. There are over 30 sampling points including 14 for temperature, five for flow rate, two for pH, three for pressure, and two for inlet/outlet gas concentration at various locations with each parameter being logged by the National Instruments Labview system. With the inlet and outlet CO_2 concentrations, CO_2 capture efficiency is calculated using Equation 2.

$$Capture\ Efficiency = \frac{inlet\ CO_2\ mole\ flow\ rate - outlet\ CO_2\ mole\ flow\ rate}{inlet\ CO_2\ mole\ flow\ rate} \qquad \text{(Equation 2)}$$

The reboiler duty is calculated from heat capacity, hot oil flow rate, hot oil density, hot oil inlet/outlet temperatures using the heat balance Equation 3.

$$Reboiler\ Duty = C_p Q \rho (T_{hot\ oil\ inlet} - T_{hot\ oil\ outlet}) \qquad \text{(Equation 3)}$$

Auxiliary power for vacuum pump is measured by an electric meter and logged for energy consumption analysis.

Figure 28. Integrated bench-scale test system.

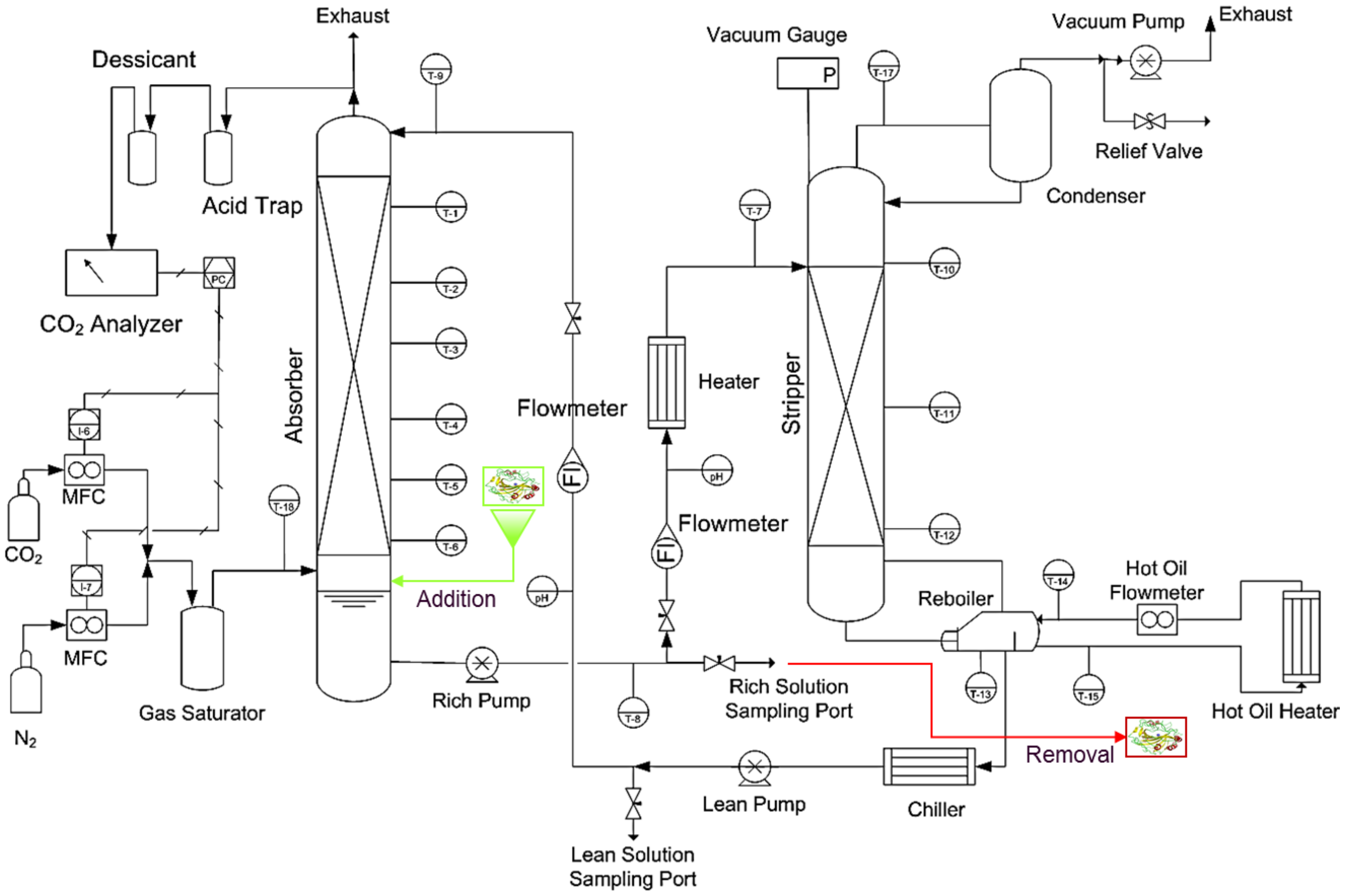


Figure 29. Simplified Process and Instrumentation Diagram (P&ID) of bench-scale unit, with locations for enzyme/solvent addition (green arrow) and removal (red arrow) indicated to carry out replenishment.

Table 8. Bench Unit Experimental Conditions and Corresponding Measurement Methods

Experimental Condition	Measurement Method
Liquid Flow Rate, mL/min	Liquid flow meter to measure volumetric flow rates
Ab.Gas IN. TC, ^{o}C	Thermocouple to measure gas inlet temperature
BP.TC, ^{o}C	Thermocouple to measure reboiler bath temperature
Lean.TC, ^{o}C	Thermocouple to measure lean solvent temperature
Inlet Conc.CO_2_%	CO_2 analyzer to measure gas inlet concentration
Outlet Conc.CO_2_%	CO_2 analyzer to measure gas outlet concentration
MFC.CO_2_LPM	Mass flow controller to control CO_2 inlet flow rate
MFC.N_2_LPM	Mass flow controller to control N_2 inlet flow rate
Total Gas Flow, LPM	Total inlet gas flow rate
Oil.Flowrate, LPM	Hot oil flow meter to measure hot oil volumetric flow rates
REBOUT.TC, ^{o}C	Thermocouple to measure hot oil outlet temperature
REBIN.TC, ^{o}C	Thermocouple to measure hot oil inlet temperature
Q, Reboiler, KW	Reboiler duty calculated from Equation 3
Vacuum Pump, Watts	Energy meter to measure vacuum pump work
Corrected Vacuum Pump from bleed valve, kW	Corrected pump work from a bleed valve
Estimated heat loss (kW)	Estimated heat loss from system temperature, ambient temperature, and material heat conductivity
Antifoam Dosing (vol%)	Antifoam dosing in volumetric percentage of total solvent volume
CO_2 In, mol/s	CO_2 inlet molar flow rate calculated from MFC.CO_2_LPM
CO_2 out, mol/s	CO_2 inlet molar flow rate calculated from MFC.N_2_LPM and Outlet Conc.CO_2_%
Capture Efficiency (%)	Capture efficiency calculated from CO_2 In and CO_2 Out
Energy Demand (kJ/mol CO_2 captured)	Calculated from (Reboiler Duty + Vacuum Energy – Estimated Heat Loss)/moles CO_2 captured
Stripper Pressure, kPa(a)	Pressure sensor to measure stripper top pressure

6.2 Bench-scale Unit Operation and Testing

Commissioning and shakedown testing was performed on unit operations and on the integrated bench-scale system as a whole. The bench-scale unit operations were individually tested, as appropriate, prior to integration to confirm proper performance, whereupon the unit operations were conjoined for subsequent integrated bench-scale testing. Integrated shakedown testing was conducted, within the constraints of equipment capability, across a broad range of parameters to demonstrate equipment performance reproducibility. The impact of key process variables such as absorber temperature, liquid/gas ratio, overall liquid and gas mass flow rates, pH, enzyme presence and CO_2 inlet temperatures and pressures on the CO_2 absorption rate, solvent CO_2 loading, and enzyme activity were evaluated to ensure stable and reproducible system performance across testing limits and enable assessment of the regeneration energy requirement. The bench unit treated 30 SLPM of synthetic gas that approximated flue gas (~15% CO_2).

Unit parametric testing included initial testing to determine the necessary enzyme makeup rate based on combined consideration of changes in unit CO_2 capture efficiency, and changes in enzyme activity determined in an offline enzyme activity assay. With enzyme makeup rate determined, parametric testing commenced, incorporating the most promising integration of stripper pressure, solvent, and absorber temperature to the bench-scale CO_2 capture system to carry out thorough parametric testing of key variables (enzyme dose, liquid flow rate and heating source supply temperature) and monitoring of outputs to identify the optimal operating envelope for the long-term test program. Sub-optimal stripping conditions (absent enzyme) were deliberately included in the test plan to explore the potential for stripping rate enhancement provided by enzyme.

The long-term test comprised 500 hours of total run time at steady-state condition, which equated to ~7 hours per weekday (to limit project costs), resulting in 75 run days. The input test conditions for the long duration testing were based on the performance mapping developed in parametric testing. Enzyme dosing together with solvent was carried out to maintain enzyme loading and solvent alkalinity. A run period absent enzyme dosing was included to determine the enzyme activity loss rate over time. Throughout the long-term test, samples were collected to investigate changes to solvent physical properties, and the absorption and stripper columns were monitored for problems, such as foaming and precipitation. The energy demand of the vacuum pump was also monitored, along with the impacts of stripper operation on the CA enzyme.

6.2.1 Shakedown Tests

Upon finishing the construction of the unit, UK-CAER conducted a shakedown evaluation on the integrated system to ensure system operability, stability, and ability to achieve the overall targets. During shakedown process, calibration and functionality of installed instrument, including thermocouple, pressure gauges, flow meters, pH meters, and mass flow controllers, were conducted for QA/QC purposes. The shakedown work was conducted in two steps. The first step was to establish preliminary system performance, experimental stability, and unit operability, using mock fluid (water) and nitrogen, followed by target solvent, simulated gas and vacuum. Enzyme provided by Novozymes was later introduced to the system in the second step to identify any potential operational issues due to enzyme in solution. Heat transfer studies on preheater, reboiler, and lean chiller were performed using water at typical process flow rate of 300 ml/min and temperature of 40 °C to ascertain required heating and cooling duties could be supplied to meet desired set-points with necessary modifications and adjustments made as desired.

6.2.2 Operation Limits

The purpose of the limit tests was to establish operating boundary (upper and low limit) for reproducible system performance at selected conditions and implement any needed hardware modifications to ensure the conditions required for parametric testing can be reliably achieved. During this phase of testing, the reboiler was modified to increase solvent residence time and maximize its efficiency. This modification was completed before carrying out operation limits and parametric tests. The operation limit of each of the factors considered for the parametric test plan was identified. The maximum liquid flow rate was physically limited at 700 ml/min by the liquid pump head and the heater and chiller duty. The minimum stripper pressure was limited at 0.3 atm by the vacuum pump head. Minimum absorber feed temperature was limited at 30 °C by the chiller duty. The maximum concentration of potassium carbonate was limited by the bicarbonate and carbonate solubility. The minimum and maximum concentration of enzyme was recommended by Novozymes according to results from WWC testing, wherein 3 g/L enzyme dose was identified as a maximum concentration, and 2x and 10x lower doses were selected to encompass a suitable dose-response range. The system performance at these limits was tested in three sets of experiments: (1) testing of liquid flow rate, stripper pressure, and absorber temperature; (2) testing of enzyme concentrations of 0.3, 1.5 g/L and 3 g/L; (3) testing of potassium carbonate concentration. From the tests, it was found that the pumps, mass flow controller for simulating flue gas, heater, and chiller were capable of delivering stable and accurate outputs at the tested extreme conditions. Detailed system operation results are tabulated in Appendix B. As shown in Section 8.1, system performance with >90% capture was achieved using the higher enzyme dose and lower absorber temperature conditions. Certain instability in the stripper due to foaming was observed at the stripping side, which is discussed in detail in Section 6.3.1. The foaming was mitigated by introducing an appropriate anti-foam agent. Solvent loading at 23.5 wt% K_2CO_3 was superior to 20 wt% for improved cyclic capacity, and the former concentration was selected for use in further testing. Although some risk of bicarbonate precipitation in rich solvent was present during solvent storage, it was not a concern during unit operation.

6.2.3 Parametric Tests

Following the shakedown tests and limitation tests, UK-CAER conducted a parametric evaluation on the integrated system to identify operation parameters to achieve target of 90% capture with enzyme. The impact of key process variables, including absorber temperature, liquid circulation rate (liquid/gas ratio), enzyme concentration on the CO_2 absorption rate and lean solvent CO_2 loading was evaluated to ensure that the target of 90% capture efficiency is achievable. The test results were used to support kinetic modeling development conducted by PNNL. The parametric tests were carried out in two phases as described below.

6.2.4 Parametric Testing Phase I

The overall target of parametric test Phase I was to reach 90% capture efficiency by determining the enzyme dosing / replenishment rate. Operation conditions was initially set at 500 mL/min liquid flow rate, 0.35 atm vacuum stripping, 40 °C absorber temperature, and 85 °C reboiler heating source temperature suggested from the limitation tests.

6.2.4.1 Parametric Test Baseline Establishment

Prior to the parametric test, baseline was validated in two identical runs with uncatalyzed 23.5 wt% K_2CO_3 solvent (no enzyme) at vacuum stripping condition of 0.4 atm, the gas flow rate of 30 LPM, solvent flow rate of 300 ml/min, and 40 °C solvent temperature in the absorber. System performance of each run is listed below in Table 9 which is the reference case without enzyme for next parametric study. In order to accommodate the thermal stability of enzyme, the reboiler temperature is limited to less than 80^oC. Due to the extreme low kinetic of CO_2 hydration step without the presence of enzyme, the capture efficiency was considerably low (~18%). The energy demand is one order of magnitude higher than alkanolamines due to the low cyclic capacity and high water evaporation in the stripper.

Table 9. Phase I Testing of 23.5 wt% K_2CO_3 with Vacuum Stripping (no enzyme)

Test Condition	Run 1	Run 2
Liquid Flow Rate, mL/min	300	300
Ab.Gas IN. TC, ^oC	40	40
BP.TC, ^oC	78.5	78.8
Lean.TC, ^oC	41	40
Outlet Conc.CO_2_%	12.4	12.5
MFC.CO_2_LPM	4.45	4.45
MFC.N_2_LPM	25.6	25.6
Q, Reboiler, KW	0.88	0.87
Vacuum Pump Energy Meter, kW	0.02	0.02
Estimated heat loss (kW)	0.09	0.09
Antifoam Dosing (vol%)	0	0
CO_2 In, mol/s	3.3	3.3
CO_2 out, mol/s	2.7	2.7
Capture Efficiency (%)	19	18
Energy Demand (kJ/mol CO_2 captured)	1302	1311
Stripper Pressure, kPa(a)	40	40

6.2.4.2 Determination of Enzyme Dosing and Preliminary Replenishment Rate

Work continued in Phase I of parametric testing with the objective of reaching ~90% capture efficiency by assessing operational enzyme dosing / replenishment rate and solvent composition. The operational enzyme dosing has been determined to be 2.5 g/L to reach 85% capture efficiency from several consecutive runs with incremental enzyme dosing from 1g/L with operating conditions at 500 mL/min liquid flow rate, 0.35 atm vacuum stripping, 40 °C absorber temperature, and 90 °C reboiler heating temperature. The performance of the system at the conditions above is tabulated in Table 10.

Table 10. Phase I Testing of 23.5 wt% K_2CO_3 with 2.5 g/L Enzyme and Vacuum Stripping

Test Condition	Value
Liquid Flow Rate, mL/min	500
Ab.Gas IN. TC, ^oC	39.1
BP.TC, ^oC	75.9
Lean.TC, ^oC	40.1
Inlet Conc.CO_2_%	14.8
Outlet Conc.CO_2_%	2.64
MFC.CO_2_LPM	4.45
MFC.N_2_LPM	25.6
Total Gas Flow_LPM	30.0
Oil.Flowrate, LPM	10.1
REBOUT.TC, ^oC	86.6
REBIN.TC, ^oC	90.0
Q, Reboiler, KW	0.88
Vacuum Pump, Watts	176
Corrected Vacuum Pump from bleed valve, kW	0.08
Estimated heat loss (kW)	0.09
Antifoam Dosing (vol%)	0.04
CO_2 In, mol/s	3.31
CO_2 out, mol/s	0.52
Capture Efficiency (%)	84.4
Energy Demand (kJ/mol CO_2 captured)	310
Stripper Pressure, kPa(a)	35.7

To ensure the results from parametric tests are not confounded by enzyme degradation, the replenishment rate was preliminarily assessed through a five-run evaluation (Figure 30). From the first two runs, a 15% drop in capture efficiency was observed. Therefore, a replenishment rate of 15% of total enzyme in system was estimated and applied to the subsequent two runs, which boosted the performance back to 85% capture efficiency. A reduced replenishment rate of 10% was attempted on the fifth run, which led to a 10% drop in performance. Based on the tests above, a replenishment rate of 20% per run was determined for the phase 2 parametric test before a more precise enzyme degradation rate was established from long-term tests.

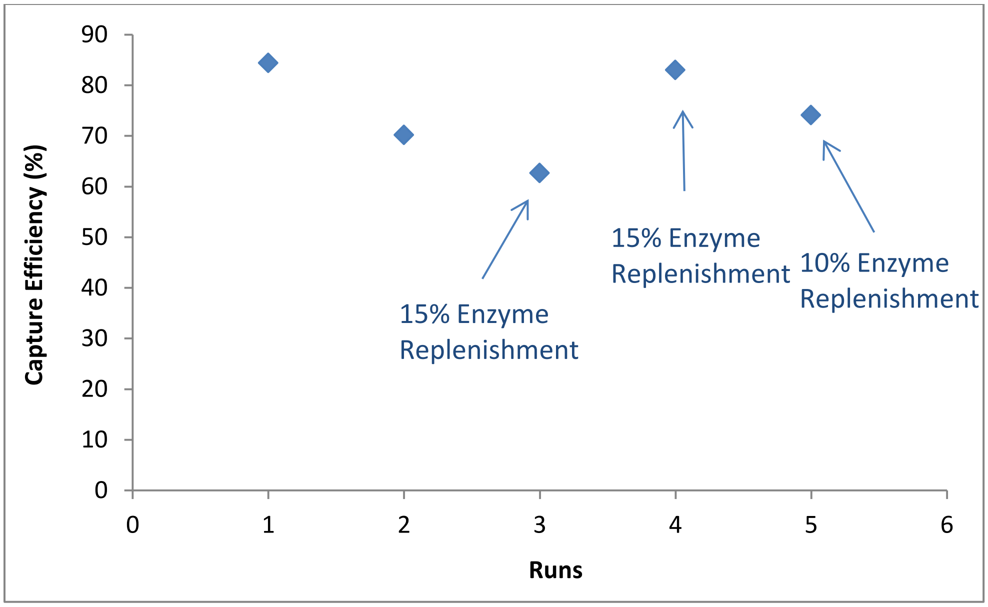


Figure 30. Tests of enzyme replenishment rate.

6.2.4.3 Determination of Solvent Composition

One observation from the previous tests in Phase I is that it was difficult to reach the DOE's target of 90% capture efficiency due to relative high CO_2 partial pressure in the lean solvent that is determined by regeneration temperature. The choice of regeneration temperature was initially made based on the Aspen Plus® prediction for achieving the necessary lean solvent loading under vacuum conditions, provided there was no kinetic limitation. Having a lower temperature in the stripper was also desirable due to limited enzyme thermal stability. Novozymes proposed an alternative solvent composition comprising 23.5 wt% K_2CO_3 plus 4 wt% sodium tetraborate decahydrate (borax) which was expected to have lower CO_2 partial pressure than that of potassium carbonate at similar carbon loading in the lean solvent. Three repeating runs using the carbonate-borax combination solvent with 2.5 g/L enzyme were performed and are presented in Table 11. Compared to the results from 23.5 wt% K_2CO_3 with 2.5 g/L run at same operating condition in Table 10, no major improvement in cyclic capacity was observed for the carbonate-borax combination solvent. Consequently, a 23.5 wt% potassium carbonate solvent composition was selected for the subsequent parametric and long-term tests.

Table 11. Bench-scale Test Results for 23.5 wt% K_2CO_3 plus 4 wt% Sodium Tetraborate Decahydrate (borax) and 2.5 g/L Enzyme

Test Condition	Run 1	Run 2	Run 3
Liquid Flow Rate, mL/min	500	500	500
Ab.Gas IN. TC, ^oC	41.1	40.7	40.9
BP.TC, ^oC	76.3	76.2	76.3
Lean.TC, ^oC	40.6	39.2	39.0
Inlet Conc.CO_2_%	14.8	14.8	14.7
Outlet Conc.CO_2_%	2.61	3.08	2.62
MFC.CO_2_LPM	4.45	4.45	4.46
MFC.N_2_LPM	25.6	25.6	25.6
Total Gas Flow_LPM	30.0	30.0	30.0
Oil.Flowrate, LPM	10.1	10.1	10.1
REBOUT.TC, ^oC	86.8	86.8	86.6
REBIN.TC, ^oC	90.1	90.1	90.0
Q, Reboiler, KW	0.89	0.88	0.91
Vacuum Pump, Watts	174	174	173
Corrected Vacuum Pump from bleed valve, kW	0.08	0.08	0.08
Estimated heat loss (kW)	0.09	0.09	0.09
Antifoam Dosing (vol%)	0.04	0.04	0.04
CO_2 In, mol/s	3.31	3.31	3.31
CO_2 out, mol/s	0.51	0.60	0.51
Capture Efficiency (%)	84.6	81.8	84.5
Energy Demand (kJ/mol CO_2 captured)	313	318	320
Stripper Pressure, kPaA	37.1	36.3	36.8
Rich Carbon Loading (mol CO_2/kg)	2.22	2.23	2.22
Lean Carbon Loading (mol CO_2/kg)	1.98	2.07	2.02

6.2.5 Parametric Testing Phase II

The overall target of Phase II was to accommodate the demands for both enhancing capture efficiency by adjusting operating parameters for possible 90% CO_2 capture and providing experimental results for process regression and modeling performed at PNNL (Section 7).

A matrix of key operation test parameters, including enzyme concentration, liquid flow rate, reboiler duty (adjusted by hot oil inlet temperature), and absorber temperature, using a fractional factorial design are listed in Table 12. The detailed test results are tabulated in Appendix B.

Table 12. Bench-scale Phase 2 Parametric Test Matrix

Run	Enz. conc. (g/L)	Flow rate (ml/min)	Hot oil inlet (°C)	Absorber (°C)	Vacuum at stripper top (atm)
1	2.5	500	95	40	0.35
2	2.5	600	95	40	0.35
3	2.5	400	95	40	0.35
4	2.5	300	90	40	0.35
5	4	500	90	40	0.35
6	4	300	90	40	0.35
7	1	500	90	40	0.35
8	1	300	90	40	0.35
9	0	500	90	40	0.35
10	0	500	95	40	0.35

6.2.5.1 Effect of Enzyme Concentration

In reviewing the testing results from the parametric test Phase II, enzyme dosing shows a major and positive impact factor on capture efficiency at concentrations below 2.5 g/L, which is consistent with the mass transfer tests conducted in WWC. However, CO_2 capture improvement reaches a plateau beyond the dosing rate of 2.5. A main reason for the plateau at higher enzyme dose is considered to be due to the reduced driving force at absorber top with the increasing of kinetics. As shown in Figure 31, the driving force dropped to less than 1 kPa at enzyme dosing above 2.5 g/L, beyond which the capture is limited by equilibrium instead of kinetics.

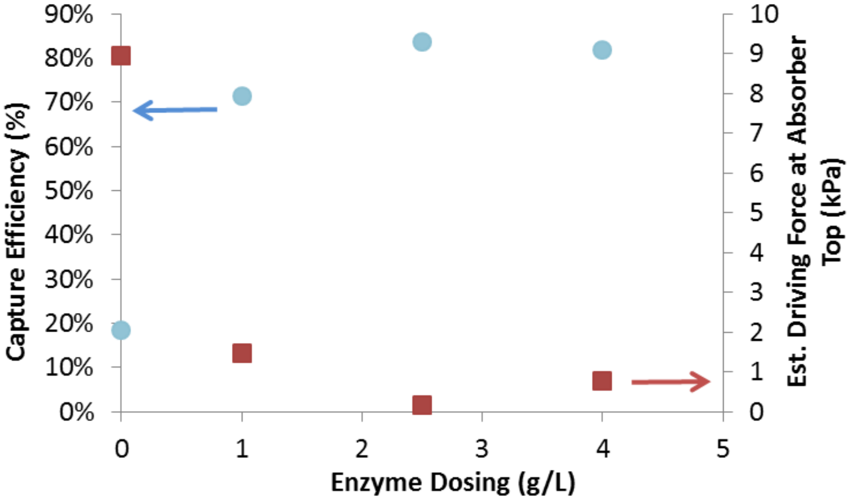


Figure 31. Enzyme impact on bench-scale CO_2 capture efficiency and driving force. CO_2 capture efficiency (circles) and driving force (squares) for enzyme concentrations of 0, 1, 2.5, and 4 g/L at 500 ml/min.

6.2.5.2 Effect of Absorber Temperature

Based on the analysis above, capture efficiency was considered to be limited by driving force in which the CO_2 pressure has approached the solvent's CO_2 equilibrium pressure at the absorber top when enzyme concentration increased above 2.5 g/L. It was expected that the capture efficiency could be increased by reducing absorber temperature which reduces solvent equilibrium partial pressure of CO_2 at given carbon loading and increases driving force at anticipated gaseous CO_2 concentration. Comparison of 30 °C and 40 °C absorber temperatures in Table 13 shows that, with similar lean condition, the capture efficiency increased from 84% to 88% by decreasing 10 degrees in temperature. A further increase to 90% capture would have required either an even lower absorber temperature or a leaner solvent with lower partial pressure of CO_2. Although a higher capture efficiency was measured at 30°C, the project team decided to proceed with 40°C because this: (1) represents a more application-relevant temperature, (2) reduces risk of bicarbonate precipitation in rich solvent as temperatures decrease, and (3) minimizes challenges of cooling flue gas when cooling water temperature is high.

Table 13. Effect of absorber temperature on capture efficiency

Absorber Temperature	Capture Efficiency
40 °C	84%
30 °C	88%

6.2.5.3 Effect of Solvent Circulation Rate and Enzyme Concentration on Stripping

Figure 32 shows the lean solvent conversions from the tests with different enzyme concentrations and liquid circulation rate. Solvent CTB conversion was calculated from the measured carbon loading and the measured alkalinity according to Equation 1. It was observed that change in enzyme concentration, which represents solvent kinetic rate, or change in solvent liquid flow, which represents the residence time in stripper, had relatively limited impact on percent lean conversion. This is primarily due to fact that desorption in the stripper and reboiler is limited by the driving force, and was also partially attributed to the oversize stripper design of the bench-scale unit (Section 3.6). Therefore, for the purposes of bench-scale testing, the capture efficiencies for the three cases did not vary in a significant way from each other.

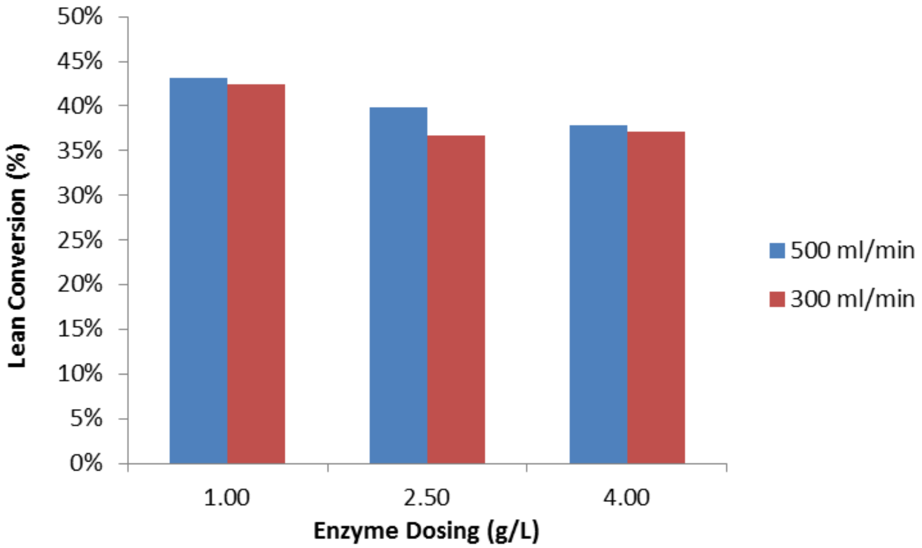


Figure 32. Lean conversions with different flow rates (300 and 500 ml/min) at three different enzyme concentrations.

Based on the results from Phase II parametric tests, the optimal operating condition for long term testing was selected based on parametric test #1, which included a 40°C absorber, 95°C reboiler heating source temperature, 0.35 atm stripper top pressure, and 2.5 g/L enzyme dosing yielding an 88.5 to 89.5% capture efficiency. A baseline test without enzyme using the same process conditions was performed in parametric test #10 as a long term test reference. In addition, results generated during this phase of testing were used to demonstrate an experimental link between the measured performance of the bench-scale system and the kinetic-based stripping simulation developed by PNNL (Section 7).

6.2.6 Long-term Testing

The condition for the long term run was selected to be 40°C absorber, 95°C reboiler heating source temperature, 0.35 atm stripper top pressure, 500ml liquid flow rate, and 2.5 g/L enzyme dosing which yielded a capture efficiency close to the 90% NETL target in the parametric tests while taking into consideration the limitations of enzyme thermal stability. CO_2 capture efficiency during the cumulative 500 h test is presented in Figure 33. Energy demand for the bench-scale system was monitored during the 500 h test. Results are presented in Figure 34 along with the corresponding CO_2 capture efficiency. Points are also included to show results for the system operating with potassium carbonate solvent alone, without enzyme. Note that energy demand is presented on a logarithmic scale because when enzyme is not present in the system, the energy demand for potassium carbonate solvent to capture even a very limited amount (19%) of CO_2 is very high (1600 kJ/mol CO_2 captured), compared to the average energy demand during the period of enzyme replenishment (313 kJ/mol CO_2 captured) that delivered an average 84% CO_2 capture efficiency.

Due to a higher reboiler heating surface temperature (95°C) than the conditions tested in parametric test Phase I, an active enzyme replenishment rate of 20% was selected for starting the long-term test. During the long-term test, further refinement of the replenishment rate was tested by decreasing the replenishment rate to 10%, as suggested by Novozymes, to observe the performance response. Upon reducing the replenishment rate at 300 h, an initial slight performance drop was observed as shown in Figure 33. However, the capture efficiency was maintained at 80% during the subsequent 10% replenishment test time. The 20% replenishment rate was resumed at 360 h to determine whether the decrease in CO_2 capture efficiency to 80% over the period with 10% enzyme replenishment would return to a higher CO_2 capture efficiency. However, no major increase in CO_2 capture efficiency was observed after resuming the increased replenishment. Although it is possible that the active enzyme concentration in the solution during this time was above the target concentration of 2.5 g/L, results presented in Section 8 (Figure 51) indicate that active enzyme concentration in the unit did not exceed the target 2.5 g/L concentration. Also, prior WWC tests (Figure 12) showed that CO_2 absorption rate is much less sensitive to active enzyme concentration at concentrations above 2.5 g/L, where the prototype enzyme dose-response reaches a “plateau” region. Thus, the stable performance observed with 10% enzyme replenishment between 300 and 360 h indicates this may have been an adequate replenishment rate.

To better understand the enzyme degradation rate and impact on CO_2 capture performance, the replenishment of active enzyme was stopped at the 450 h mark. A steady drop in CO_2 capture efficiency was observed over time. Enzyme activity in collected solvent samples was analyzed by Novozymes, confirming that enzyme inactivation occurred during the course of the no-replenishment run. A detailed discussion of enzyme stability analysis, degradation rate, and impact on CO_2 capture performance is presented in Section 8.

Instability in CO_2 capture efficiency, fluctuating between 75-90%, was observed at around the 425 h mark. The fluctuation was diagnosed to be caused by accumulation of solids from enzyme degradation on packing and heating tubes, reaching a point where it significantly impacted the mass transfer and heat transfer. To solve the problem, the entire solvent inventory was withdrawn and preserved from the unit. The unit was rinsed with water and potassium carbonate solution to remove the deposition. Stable system operation was resumed after the cleaning and reintroduction of the retained solvent. Further discussion of solids deposition is included below.

6.3 Engineering and Operational Challenges and Mitigations

Several operational challenges were encountered during operation of the bench-scale unit, including foaming and formation and accumulation of solids. Uncontrolled foaming had a negative effect on desorption efficiency. The accumulation of solids in the system raised concerns about potential for unintended enzyme immobilization to absorber and stripper packing, accumulation of solids on the reboiler tubes leading to inefficient heat transfer, and accumulation of suspended solids in the absorption solvent leading to filter fouling and concerns about reduced solvent performance. Routine antifoam addition was implemented to control foaming and both installation of filters and a cleaning procedure were implemented to control solids accumulation in the system and to maintain and restore system performance.

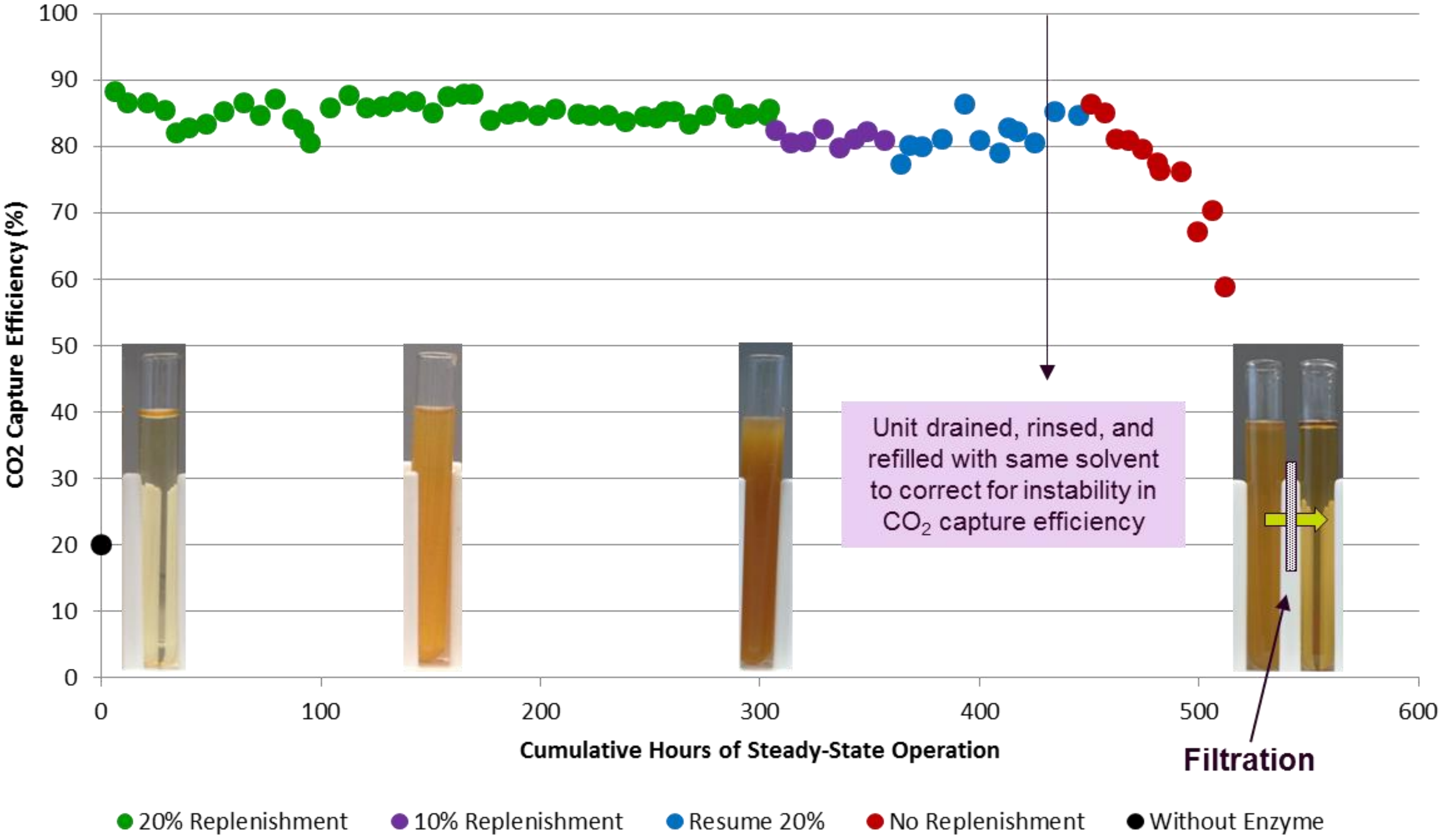


Figure 33. CO_2 capture efficiency during 500 hour testing.

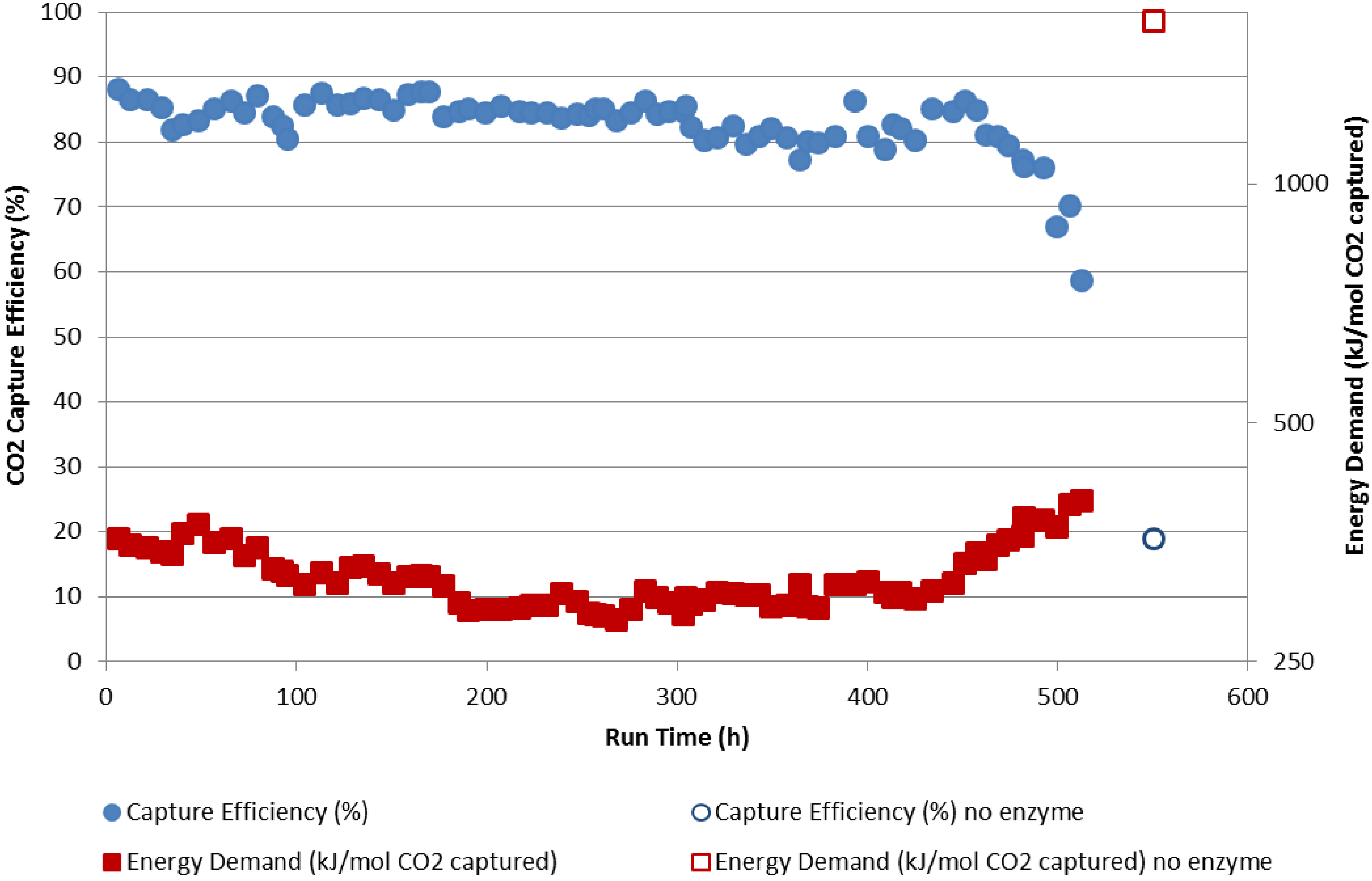


Figure 34. Energy demand during 500 hour testing.

6.3.1 Foaming and Desorption Observations

In preliminary tests with enzyme present, high levels of foaming that caused solvent overflow into the overhead condenser was detected in the stripper. The foaming also led to increased and fluctuating pressure drop and temperature differences across the stripper column. Specifically, the temperature difference between the top and bottom of stripper gradually increased while the pressure drop across the stripper increased significantly beyond the working range of the differential pressure gauge (> 10 inches, water column).

One of the examples is illustrated in Figure 35, showing the stripper top and bottom temperature deviation during the first 280 minutes of a test. During the same period of time, the pressure drop across the stripper was observed to increase beyond the gauge's measurement limit. An amount of 0.02 vol% of antifoam was introduced to the system at the 280 minute time point. After the addition of antifoam, the temperature profile stabilized and the pressure drop decreased back to below 10" water column. Such an observation confirms that the formation of foam would cause increased pressure drop and decreased water vapor flow rate. It also suggests that antifoam has to be introduced to the system on a routine basis to mitigate this foaming problem.

To further investigate the problem, several types of antifoam agents under both simulated and actual bench unit conditions were tested and it was determined that a mineral based antifoam agent had suitable antifoaming performance among the ones tested. A dosing of 0.02 vol% of the antifoam every 4 hours of run time was determined to be sufficient to maintain stable runs during the long-term tests.

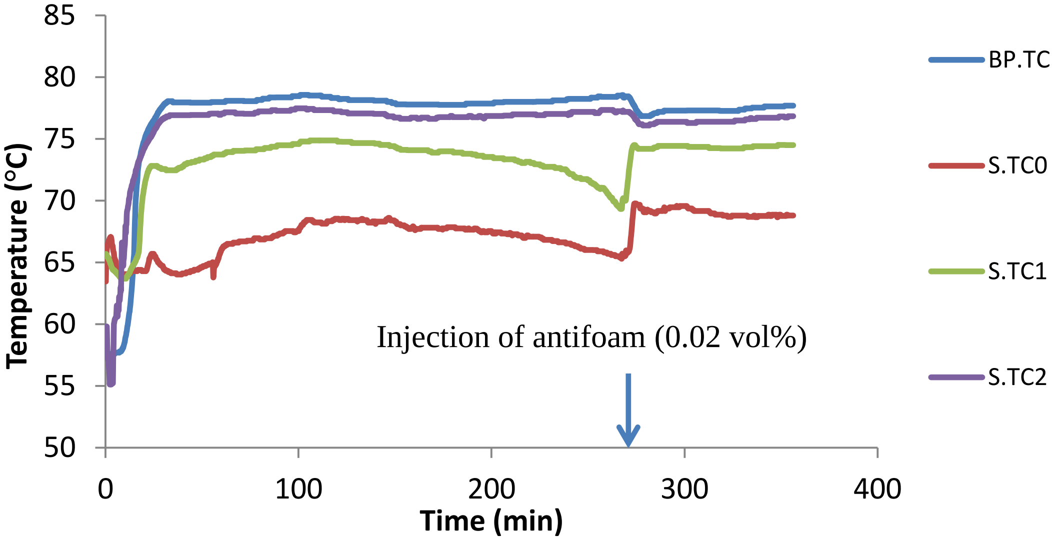


Figure 35. Stripper temperature profile versus time during the first day run with 1.5 g/L enzyme. The location of four temperature measurement points are schematically shown in Figure 36.

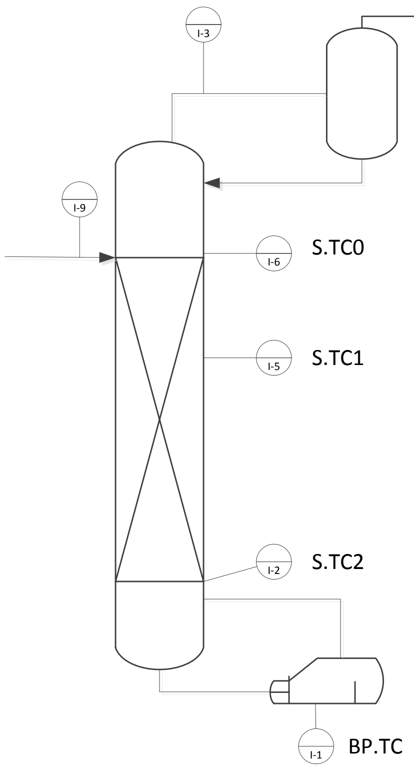


Figure 36. Schematic of temperature measurement points on stripper.

Notably, during lab-scale testing of different antifoams in a bubble-tank set up to run in desorption mode (Figure 37), combinations of CO_2-rich K_2CO_3-based solvent plus enzyme plus antifoam exhibited faster initial rates of CO_2 release compared to the CO_2-rich K_2CO_3 solution alone, and exhibited significantly faster rates of CO_2 release compared to K_2CO_3-based solvent plus antifoam (absent enzyme). A temperature-time profile was measured and superimposed on the CO_2 desorption results presented in Figure 37, confirming that increasing temperature promotes CO_2 release. When enzyme was not present, antifoam addition had the effect of depressing the CO_2 desorption, potentially by impeding mass transfer from the liquid to the gas phase. Such an impediment was not observed for antifoam addition to enzyme containing solutions – instead, enhanced CO_2 desorption was observed. In these cases enhancement was observed, irrespective of the presence or absence of foam. Therefore, antifoam agents may serve to localize enzyme molecules to the gas-liquid interface thereby assisting in the desorption kinetic enhancement. In a further observation, after a 15 minute incubation, the average pH change (final pH minus initial) for solutions containing enzyme and antifoam was 0.85 units versus 0.38 in the absence of enzyme, providing additional evidence of enzyme enhancement of CO_2 desorption. Such observations support that providing high surface area in the stripper could enhance desorption rate, and multistage stripping with staged pressure and temperature conditions could also be beneficial to take advantage of the apparent rate enhancement.

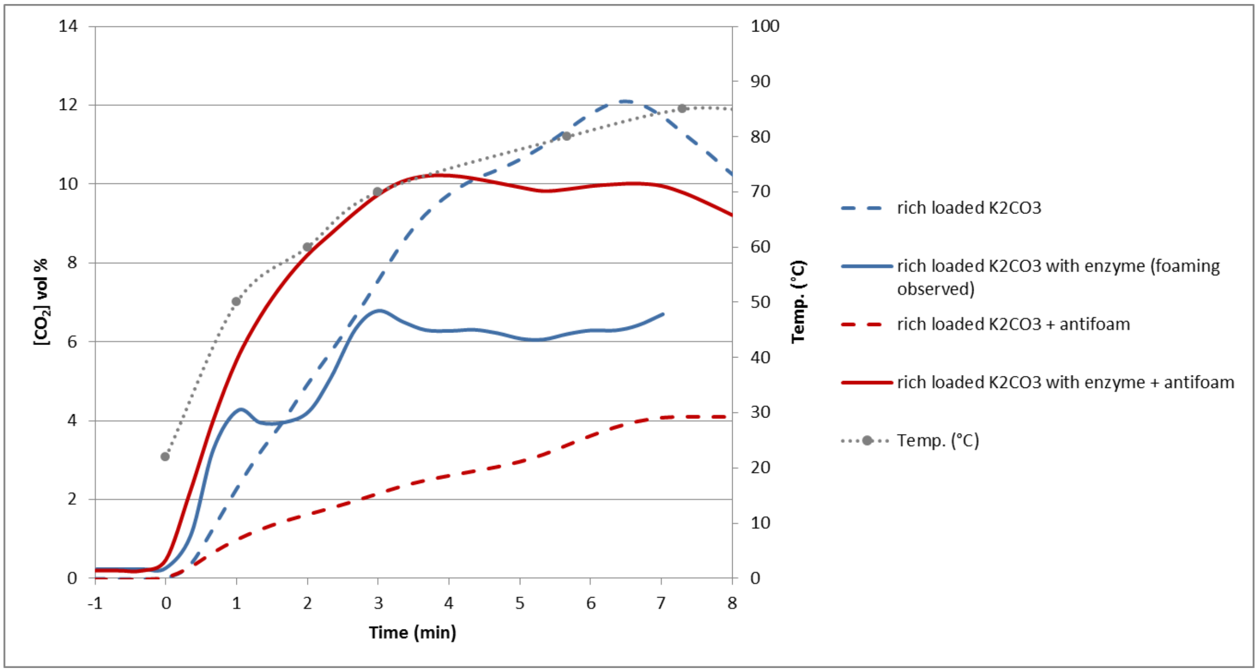


Figure 37. CO$_2$ desorption from rich working solvent in bubble tank reactor.

6.3.2 Formation and Accumulation of Solids

Two polypropylene filters (80 mesh) were placed at liquid line downstream of chiller to remove suspended solid materials formed during the process. At the end of each run day, a layer of pale brown solid material was observed on the in-line filter (Figure 38.A). In addition to these filter-trapped solids, floating solids were also observed in the system after a rest period (Figure 38.B), and also after allowing liquid samples taken from the system to rest (Figure 38.C). These floating solids readily mix back into the liquid, imparting turbidity. Thus, a combination of filterable and non-filterable/floating solids was generated during system operation. Using samples collected from the bench unit and shipped from UK-CAER to Novozymes, measurements were made to quantify solids produced during system operation. These measurements were used to assist in determining solid waste emissions for the full plant feasibility assessment. The rate of total insoluble solids generated during bench unit operation was estimated to be 23 g insoluble wet solids per L solvent inventory per average 7 h run day. This estimation was derived by combining the maximum wet solids retained on a filter during the 500 h run (~3 g wet solids per L inventory) with the average amount of floating solids (20 g wet solids per L inventory) measured in 16 samples dispersed across the time course, beginning at 200 h. With the continued replenishment of enzyme to the system, solid deposition was also observed on absorber packing, leading to the speculation that deposition also occurred on the stripper packing and reboiler surface. Such deposition on packing and reboiler surfaces is difficult to remove unless a complete system rinsing is carried out. The deposition on reboiler heating tubes may decrease the heat transfer performance of the reboiler, evidenced by the decreased reboiler duty during the course of long-term tests.

The wet solids are believed to comprise water, potassium carbonate and bicarbonate, enzyme protein, antifoam, and some contribution of fermentation derived solids carried over from enzyme manufacturing in the stock solution used to supply the unit. The presence of water was evident from weight loss measurements on drying, the presence of carbonate/bicarbonate salts was evident from observations of colorless crystals associated with dried solids, and also inferred due to the presence of water which would contain dissolved salts. The presence of enzyme protein and other protein carried over from fermentation was evident from protein assays (SDS-PAGE, for example). The probable presence of antifoam was evident from visual observation of the floating layer, and also inferred from the fact that the antifoam itself floats in an aqueous solution over time and that it could have hydrophobic affinity for denatured enzyme. The presence of fermentation residuals was at least partially attributed to the brown color carried over from the stock enzyme solution. It is to be noted that these physical observations pertain to the specific prototype enzyme used, and evaluations with other types and formulations of enzyme would probably lead to different results.

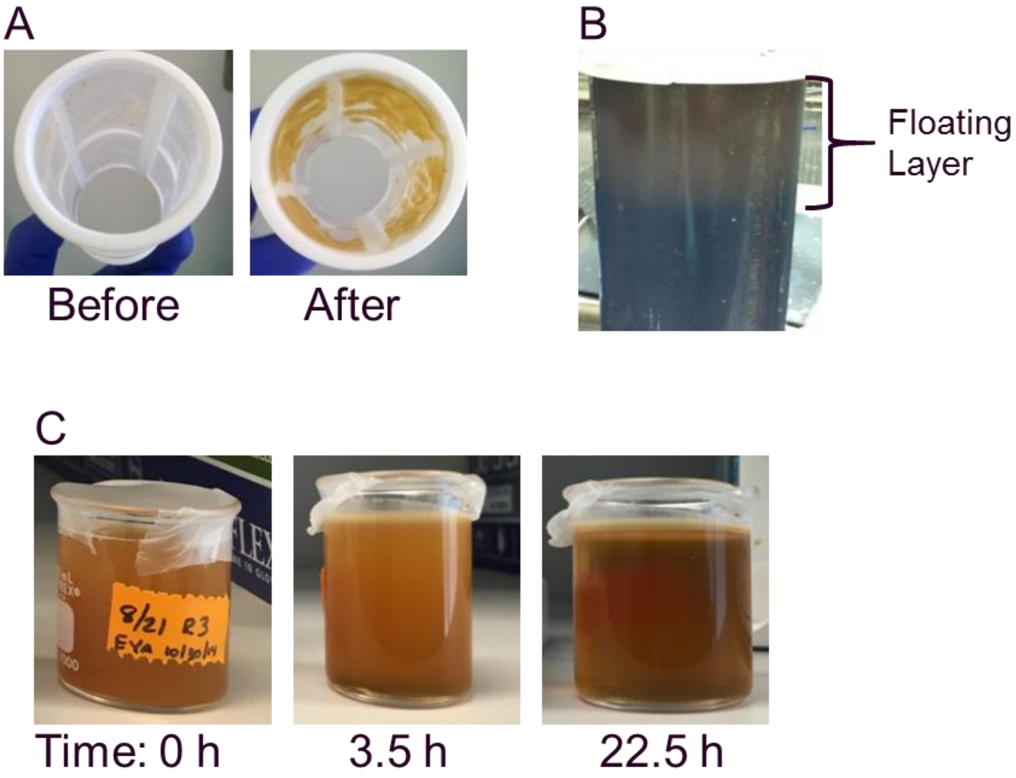


Figure 38. Photographs of filtered and floating solids from bench unit solvent. Image A shows a clean filter (before) and shows solids collected on the filter (after) during bench unit operation. Image B shows a floating layer of solids in the rich reservoir of the bench unit after a rest period. Image C shows time lapse photographs of solids floating to the liquid surface in a sample taken from the bench unit, where time 0 hours shows the solvent initially as a turbid mixture, and upon standing (3.5 h) the solids float towards the liquid surface, where after 22.5 h the bulk of the liquid is clarified.

6.3.3 Unit Cleaning

In order to dissolve the solid deposition on packing and reboiler and deactivate any enzyme left in the system, a cleaning procedure was developed. The procedure includes: (1) a dissolving step which uses 0.1 N KOH at 60°C which was proved to effectively dissolve the solid deposition in the system, and (2) a rinsing step which use DI water to remove KOH and residual process solution out of the system. The cleaning procedure was confirmed to be effective on the bench unit by comparing a baseline run (without enzyme) before and after a series of tests with enzyme.

6.3.4 Cavitation Prevention

One of the challenges in vacuum stripping is the potential cavitation on the pump that pumps lean solvent from reboiler to absorber. At the stripper operating pressure (~0.35 atm) and the carbon loading from reboiler, the static pressure on the suction side of the pump is low enough to cause CO_2 and water evaporation, which dramatically reduces the pump performance and potentially damages the pump. To solve the problem, the pressure at suction side was increased by about 10 feet of water column by positioning the lean pump at a lower elevation (ground floor of the high bay). In terms of pump selection, a rotary pump which is preferable in preventing cavitation than a centrifuge pump was selected to be the lean pump in this project.

6.4 Single Run Bench-scale Test Using MEA

Although not included in the original project plan or budget, an opportunity arose during a gap in project activities to carry out a bench-scale test run using aqueous 30 wt% MEA. Bearing in mind that the bench-scale system was not designed to run optimally with MEA, the test was conducted to give a relative reference for the CO_2 capture and energy requirement performance of the bench-scale system as an indicator for the performance of MEA solvent compared to enzyme-enhanced potassium carbonate solvent. The results are presented in Table 14. At equal liquid flow rate (300 ml/min), inlet gas flow (30 SLPM) and temperature (40°C) conditions, the reboiler duty observed on the bench-scale unit with MEA (0.85 kW) is higher than the CA-promoted K_2CO_3 Parametric Test #6 (0.78 kW), however the CO_2 capture rate with MEA was also higher (94% for MEA versus 84% for Parametric Test #6) leading to a lower regeneration energy demand for the MEA test (262 kJ/mol CO_2 captured) compared to the energy demand (275 kJ/mol CO_2 captured) observed for Parametric Test #6 (Table C.4). In the case of CA-promoted K_2CO_3, the regeneration energy demand metric includes reboiler duty and the energy demand for vacuum generation. Predictive models indicate that regeneration energy demand should be lower for the lower enthalpy K_2CO_3-based solvent, however it was beyond the scope of the current project to conduct further side-by-side testing to explore this discrepancy. Such testing is recommended.

Table 14. Bench-scale Test Results for 30 wt% MEA

Test Condition	Value
Liquid Flow Rate, mL/min	300
Ab.Gas IN. TC, ^{o}C	41.31
BP.TC, ^{o}C	103.56
Lean.TC, ^{o}C	39.40
Inlet Conc.CO_2_%	14.80
Outlet Conc.CO_2_%	1.02
Total Gas Flow_LPM	29.81
Q, Reboiler, KW	0.85
Vacuum Pump, Watts	N/A
Corrected Vacuum Pump from bleed valve, kW	N/A
Estimated heat loss (kW)	0.09
Antifoam Dosing (vol%)	N/A
CO_2 In, mol/s	3.09
CO_2 out, mol/s	0.20
Capture Efficiency (%)	93.63
Energy Demand (kJ/mol CO_2 captured)	262.41
Stripper Pressure, kPa(a)	122.48

N/A = not applicable

7 KINETIC ESTIMATES FOR ENZYME-CATALYZED AQUEOUS K_2CO_3 SORPTION OF CO_2

While the primary reactions associated with aqueous-based potassium carbonate sorption of CO_2 have been listed previously, the following reactions are available in Aspen Plus® to characterize carbonate-bicarbonate reactions in aqueous systems:

$$2H_2O \leftrightarrow H_3O^+ + HO^- \qquad \text{(Reaction 9)}$$

$$CO_{2(aq)} + HO^- \leftrightarrow HCO_3^- \qquad \text{(Reaction 3)}$$

$$HCO_3^- \rightarrow CO_{2(aq)} + HO^- \qquad \text{(Reaction 10)}$$

$$HCO_3^- + H_2O \rightarrow CO_3^= + H_3O^+ \qquad \text{(Reaction 11)}$$

Note that the best reaction to represent enzyme-based absorption acceleration is Reaction 8 (Section 3.2). However this reaction is not available in Aspen Plus® and was not developed as part of this project. Therefore, of the four reactions available in Aspen Plus®, reactions 3 and 10 are those most likely to be rate limited (at high pH) and, thus, impacted by enzyme catalysts. In order to simulate accelerated bicarbonate formation due to enzyme in the existing Aspen Plus® model, the direct reaction with hydroxide was accelerated by adjusting the activation energy. The following sections describe the establishment of the kinetic parameters associated with these two reactions.

7.1 Aspen Plus® Kinetic Parameters for CO_2+OH^- → HCO_3^- (No enzyme)

The forward kinetic model within Aspen Plus® is referenced to Pinsent [102]. The form of the kinetics model is shown in Equation 4:

$$r = kT^n exp\left(-\frac{E}{RT}\right)\prod_{i=1}^{N} C_i^{a_i} \qquad \text{Equation 4}$$

The concentration basis is molarity and the power n is taken as zero, eliminating that temperature term. The forward and reverse reaction rate parameters in Aspen Plus® are summarized as in Table 15. The reverse reaction rate is stated in the Aspen Plus® documentation to be selected to match the equilibrium model predictions.

Table 15. Aspen Plus® Kinetic Model Parameters

Rxn	Reaction	k	E (cal/mol)
3	$CO_{2(aq)} + HO^- \leftrightarrow HCO_3^-$	4.32 x 10^{13}	13,249
10	$HCO_3^- \rightarrow CO_{2(aq)} + HO^-$	2.38 x 10^{17}	29,451

When the equilibrium and kinetic models agree on the equilibrium prediction, the equilibrium model value for K_{eq} will be equal to the ratio of forward to reverse rate constants. Equations 5 and 6 outline this relationship.

$$k_2[CO_2][OH^-] = k_3[HCO_3^-] \qquad \text{Equation 5}$$

$$\frac{k_2}{k_3} = \frac{[HCO_3^-]}{[CO_2][OH^-]} = K_{eq} \qquad \text{Equation 6}$$

The forward rate constant and activation energy in Table 15 correspond to values reported by Pinsent [102]. However, there was disagreement between the equilibrium end point predicted by the as-found Aspen Plus® values for the kinetic model and the equilibrium-predicted values in Aspen Plus®. A significant amount of investigation into the discrepancy was performed, with the outcome being a conclusion that an unexplained error existed in the as-found Aspen Plus® values for the reverse reaction rate expression. Therefore, the following procedure was conducted to modify the reverse reaction rate expression to bring the equilibrium prediction into agreement with that of the equilibrium model.

First, an equilibrium simulation was run to produce concentrations and values of the equilibrium constant over a narrow range of interest. This simulation was comprised of a 10-stage equilibrium absorber with 300 ml/min of 19.2% carbonate-to-bicarbonate conversion lean feed at 40.5°C, 1.23 atm, being contacted counter currently with 30 slpm (ref 21.1°C) at 40.3°C inlet gas temperature, 1.23 atm inlet gas pressure, and containing 0.139 mole fraction CO_2. The molar concentrations of species HCO_3^-, CO_2, and OH^- were obtained from the model and used to determine an apparent equilibrium constant, in molar units, on each stage. The apparent equilibrium constant was then fit against a second order polynomial in temperature over the range of temperatures occurring in the simulation. This plot is shown in Figure 39.

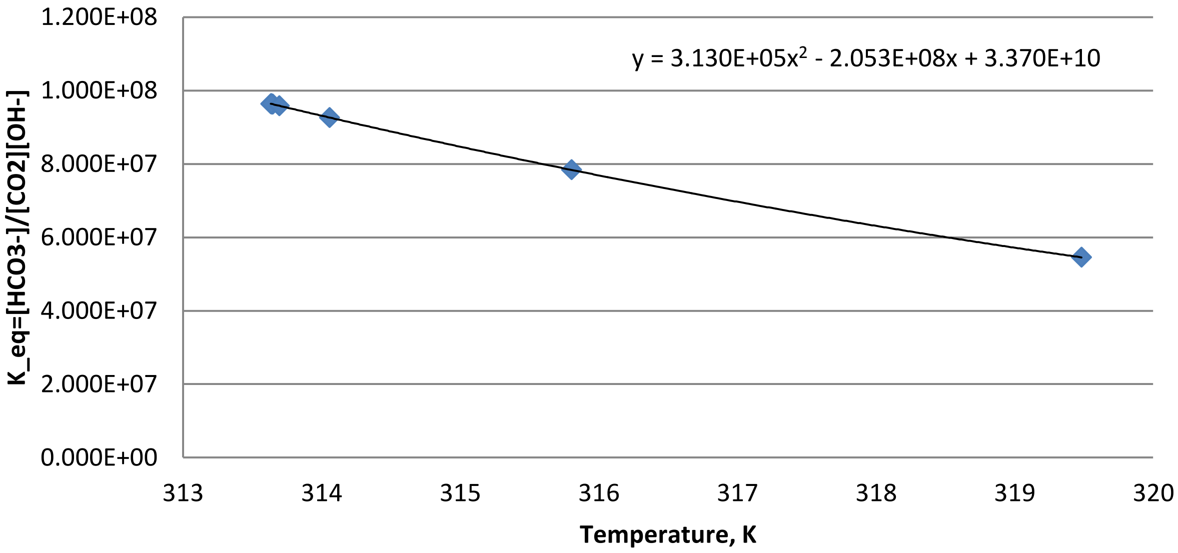


Figure 39. Apparent K_{eq} versus temperature provided by the Aspen Plus® code at conditions of interest.

The correlation for apparent equilibrium constant was then used to calculate a value of K_{eq} at intervals over the temperature range of 40.5°C and 46.3°C. At each temperature, the value of the reverse rate constant needed to match the equilibrium was calculated according to Equation 7.

$$k_{rev} = \frac{k_{fwd}}{K_{eq}} \qquad \text{Equation 7}$$

The resulting values of k_{rev} were then plotted in Figure 40 as $\ln(k_{rev})$ vs 1/T to arrive at an Arrhenius rate expression for the reverse reaction rate. The final reverse reaction rate parameters along with the retained forward rate reaction parameters are summarized in Table 16.

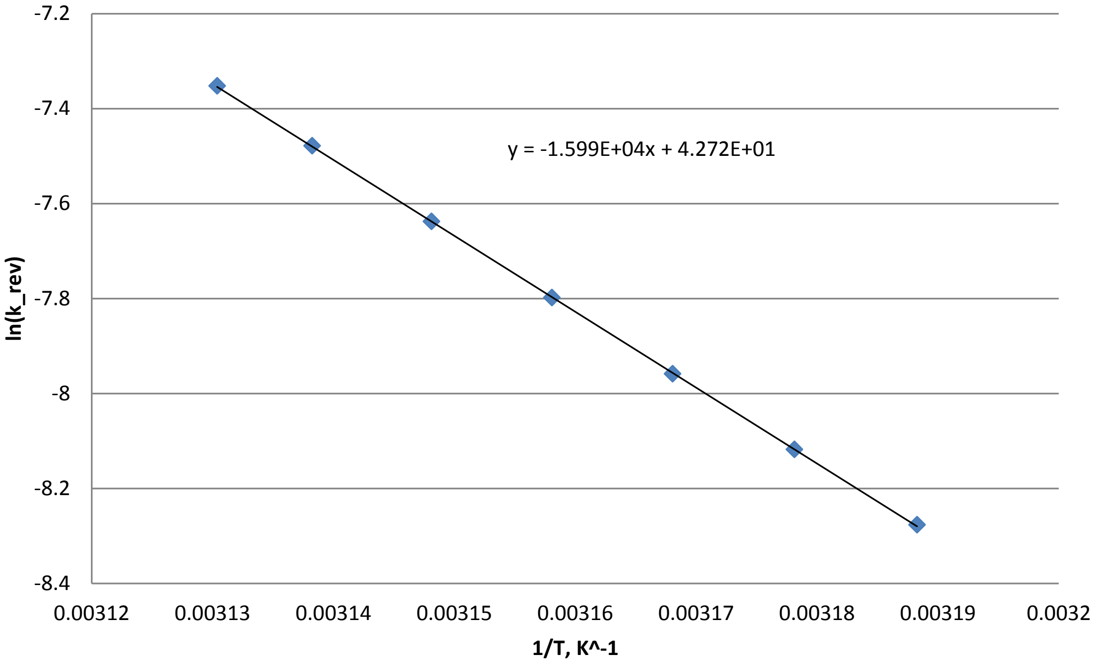


Figure 40. Arrhenius plot for reverse reaction rate. Slope = - E/R, k_3 = exp(42.72).

Table 16. Forward and Reverse Kinetic Parameters for No-Enzyme Conditions

Rxn #	Reaction	k	E (cal/mol)
3	$CO_{2(aq)} + HO^- \leftrightarrow HCO_3^-$	4.32 x 10^{13}	13,249
10	$HCO_3^- \rightarrow CO_{2(aq)} + HO^-$	3.57 x 10^{18}	31,772

7.2 Comparison of Aspen Plus® Predictions and Bench-Scale Results

Bench-scale parametric testing results were compared with Aspen Plus® simulations using the modified kinetic parameters in both the absorber and stripper. The results from this analysis are shown in Table 17. Here, Aspen Plus® model output predictions are highlighted in yellow. Tests with no enzyme and with enzyme were evaluated. The no-enzyme test utilized the revised kinetic parameters described previously. The CO_2 working capacities used to compare the actual and modeling results were taken from the gas-based measurements, shown in the absorber section of Table 17, as these values did not match the same values from the solvent loading measurements in all cases (see the rich and lean CO_2 concentrations in the stripper section of the table). However, the lean CO_2 concentrations from the actual values were used as an Aspen Plus® input.

Table 17. Aspen Plus® Kinetic Parameter Fits from Bench-scale Test Data

	No Enzyme		Enzyme			
	Bench-scale Test	Aspen Prediction	Parametric Test #5	Aspen Prediction	Parametric Test #6	Aspen Prediction
General						
Solute Concentration (K2CO3 equivalent, wt%)	24%	24%	24%	24%	24%	24%
Enzyme Concentration in Solvent (g/L)	0		4		4	
Anitfoam Dosing (vol%)	0		0.04		0.04	
Solvent Recirculation Flow Rate (mL/min)	300	300	500	500	300	300
Absorber						
Dry CO2 Flow Rate into Absorber (lpm)	4.4	4.4	4.5	4.5	4.5	4.5
Dry N2 Flow Rate into Absorber (lpm)	25.6	25.6	25.5	25.5	25.6	25.6
CO2 Gas Conc. into Absorber (vol%, dry)	14.9%	14.7%	14.9%	15.0%	14.9%	14.9%
CO2 Conc. at Gas Exiting Absorber (vol%, dry)	12.4%	12.1%	2.9%	2.8%	2.6%	
CO2 Removed by Solvent in Absorber	18.6%	19.9%	83.1%	83.1%	84.5%	84.3%
Lean Solvent Temperature (entering absorber, °C)	40.5	40.5	40.4	40.5	40.1	40.3
Rich Solvent Temperature (exiting absorber, °C)		41.8		43.5		45.5
Temps along Absorber (°C; top to bottom - first is 35 cm below the packing and 30 cm spacing)	40.3, 39.8, 39.4, 38.9, 38.6, 38.3	40.6, 40.9, 41.1, 41.4, 41.7, 41.8		41.5, 42.2, 43.1, 43.5		41.8, 42.9, 43.8, 44.1
Stripper						
Rich Solvent Temperature (entering stripper, °C)	65.9	65.9	66.0	66.0	66.1	66.0
Stripper Pressure (absolute, top of column, atm)	0.39	0.39	0.34	0.34	0.34	0.34
CO2 Conc. in Lean Solvent (extent of conversion)	24.1%	24.1%	35.7%	35.7%	37.1%	37.1%
CO2 Conc. in Rich Solvent (extent of conversion)	35.4%	29.9%	53.8%	50.7%	57.1%	62.4%
Solvent Temp in Reboiler (°C)	78.5	79.0	76.0	73.6	76.2	74.4
Temperature at Stripper Top (°C)	73.3	74.6	65.2	66.9	65.3	68.1
Reboiler Heat Duty (kWth)	0.88	0.46	0.80	0.64	0.79	0.55
Vacuum Pump Electrical Power (kWe)			NR		NR	
Temps along the Stripper (°C; starting at 10 cm above packing)	73.3, 77.2, 77.7	70.4, 76.7, 78.4, 79.0		62.7, 68.5, 71.2, 73.6		63.9, 69.6, 72.1, 74.4
Fitted Kinetic Parameters						
Forward Reaction (CO_2 + OH^- --> HCO_3^-)						
Pre-exponential factor		4.32E+13		4.32E+13		4.32E+13
Activation Energy, Ef (cal/mol)		13,249		9,400		6,000
Reverse Reaction (HCO_3^- --> CO_2 + OH^-)						
Pre-exponential factor		3.57E+18		3.57E+18		3.57E+18
Activation Energy, Er (cal/mol)		31,772		27,923		24,523

The Aspen Plus® predictions for the no-enzyme case in Table 17 show a good comparison with actual CO_2 removals (within 7%, relative). The CO_2 concentration increase in the solvent was less comparable with actual values (16%, relative). The reboiler heat duty was also significantly different (0.46 kWth predicted, versus 0.88 actual). No heat losses were accounted for in the models. Therefore, from modeling perspective, heat losses were deemed to be the largest contributor to the observed differences.

For the two enzyme cases (two different recirculation flow rates) the forward reaction activation energies were modified until the CO_2 removal predictions matched the actual values. The other predicted values (highlighted in yellow) reasonably matched actual values, with the exception of the lower reboiler heat duties. Note that each of the enzyme cases required different forward-reaction activation energies for the best fit (9,400 and 6,000 cal/mol, respectively, in Table 17). For the purpose of the current study, an averaged value of 7,950 cal/mol was established for subsequent modeling of enzyme-enhanced systems. Using the averaged value, the reverse-reaction activation energy corresponds to 7,950 + 18,523 = 26,473 cal/mol. These values are listed in Table 18. Therefore, a key outcome from the bench-scale results was a complete process data set, with recirculating enzyme, that allowed for kinetic parameters to be fit for both adsorption and desorption.

Table 18. Forward and Reverse Kinetic Parameters for Enzyme Conditions

Rxn #	Reaction	k	E (cal/mol)
3	$CO_{2(aq)} + HO^- \leftrightarrow HCO_3^-$	4.32×10^{13}	7,950
10	$HCO_3^- \rightarrow CO_{2(aq)} + HO^-$	3.57×10^{18}	26,473

7.3 Discussion of the Relationship Between Aspen Plus® Kinetic Fits, Bench-scale and Full Scale Results

Upon consolidating the findings among the bench-scale testing, kinetic parameter fits developed using Aspen Plus® and the full scale simulations, several observations arose related to measured versus predicted reboiler duties, measured versus predicted stripper kinetic effects, and the relationship between absorber height and solvent recirculation relative to NETL Case 10. A discussion of these aspects is presented here.

One observation was that the reboiler duties for the full scale simulation were much lower than the measured bench-scale values. Data from the bench-scale parametric tests were used to develop the catalyzed K_2CO_3 kinetic relationships in Aspen Plus®. The averaged reboiler duty from the bench-scale tests reported in Table 17 was 235 kJ/mol. The Aspen Plus® predictions for simulating bench-scale operation gave reboiler duties that were 20-30% lower than the observed parametric test values. This correspondence was deemed acceptable since no heat losses were included in the models. The reboiler duty (excluding vacuum energy) from the full scale Aspen Plus® projection was 129 kJ/mol, which is much lower than the averaged bench-scale value. However, the liquid-to-gas (L/G) ratio for the bench-scale tests was 50 (on mass basis), versus 27 for the full scale projection. This difference translates into significant differences in sensible heat duty, and, therefore, is the primary driver for the difference between the reboiler duties predicted for the bench-scale unit versus predicted for the full scale system.

Another uncertainty brought up in post analysis was that there was no clear evidence of enzyme-enhanced kinetic effect in the stripper from the bench-scale tests and initial Aspen Plus® models. This was unexpected, because it is known that CA catalyzes the CO_2 release reaction (e.g. Section 6.3.1), and there were predictive indications that a stripper operating with K_2CO_3 solvent could be kinetically limited. For example, when a non-catalyzed K_2CO_3 kinetic stripper simulation was applied to the full scale model, a reboiler duty of 150 kJ/mol was calculated. However, when an equilibrium stripper simulation was applied to the full scale model, a reboiler duty of 128 kJ/mol CO_2 captured was calculated, and a similar reboiler duty of 129 kJ/mol was calculated when the enzyme-catalyzed kinetic stripper simulation was applied to the full scale model, suggesting that enzyme kinetics were required to bring the reboiler duty close to the equilibrium predicted value. It is noted that recirculation and other factors could confound this observation. Nevertheless, the observation could indicate some benefit of catalyzed K_2CO_3 in the stripper.

Analysis of the full scale model was conducted involving running cases with varying absorber height. The results are shown in Table 19, including comparison to NETL Case 10 for MEA. Note that for each absorber height adjustment, the solvent recirculation rate was adjusted to hit the targeted (90%) CO_2 capture rate. The data in the table is consistent with PNNL's prior assessments with catalyzed K_2CO_3, where low absorber heights required significantly higher recirculation rates, resulting in higher L/G, to achieve an equivalent CO_2 capture rate.

Table 19. Aspen Plus® Predictions of CO_2 Capture from Full-Scale Catalyzed K_2CO_3 System versus Absorber Height (inlet gas values equivalent to NETL Case 10 in all cases)

Solvent	Absorber Height (ft)	CO_2 Captured	Solvent Recirculation Rate (lb/hr)	Rich out conversion (from 37.5% lean)	Reboiler Duty (MMBtu/hr)
MEA NETL Case 10	40	89.9%	29,697,000	-----	2,016
Catalyzed K_2CO_3	40	89.3%	70,000,000	62.5%	1,885
	60	90.1%	63,236,000	65.4%	1,778
	80	90.1%	58,213,000	67.9%	1,691
	110	90.0%	55,329,000	69.4%	1,640

Finally, as noted previously, results for bench-scale testing with 30 wt% MEA were contributed to the project by UK-CAER outside of the original project scope. PNNL carried out modeling with that data by applying MEA solvent properties, including kinetics, into the same bench-scale model for catalyzed K_2CO_3. The results of the comparison are shown in Table 20. In this assessment, the MEA predictions are within 15% of the actual bench-scale values (0.12 kW absolute), which is considered to be a reasonable fit considering that no heat losses were included. For the K_2CO_3 case shown the predicted reboiler duty was within 30% of the actual bench-scale value (0.24 kW absolute). While this higher difference with K_2CO_3 was assumed to be due to heat losses in the modeling comparisons, the origin of the difference was not identified in the current study.

Table 20. Bench-scale Test Results for MEA and catalyzed K_2CO_3 Compared to Aspen Plus® Predictions

Test Condition	30% MEA		24% Catalyzed K_2CO_3	
	Bench-scale Results	Aspen Simulation	Bench-scale Results	Aspen Simulation
Liquid Flow Rate, mL/min *	300	300	300	300
Ab.Gas IN. TC, °C *	41.3	41.3	39.5	39.5
BP.TC, °C	103.6	106.7	76.6	75.8
Lean.TC, °C	39.4	40.5	40.3	40.1
Inlet Conc.CO_2, % *	14.8	14.8	14.8	14.8
Total Gas Flow, lpm *	29.8	29.8	30.0	30.0
CO_2 Removed, %	93.6	93.5	84	84.3
Rich.TC2, °C	94.5	94.5	66.2	66.0
Q, Reboiler, kW	0.85	0.73	0.79	0.55
Estimated heat loss (kW)	0.09	0	0.09	0
Stripper Top Pressure, kPaa *	122.5	122.5	34.8	34.2

* Aspen Plus® model inputs indicated with asterisks.

8 EVALUATION OF DISSOLVED ENZYME PERFORMANCE AND ROBUSTNESS

Evaluations of dissolved enzyme performance were measured at UK-CAER on the bench-scale unit. Results from these studies, and the materials and methods used to generate the results, have been described above (Section 6). Results are again summarized here with the intent of facilitating a comparison between online enzyme performance (reflected in bench unit CO_2 capture efficiency) and dissolved enzyme activity measured offline in liquid samples taken from the unit and shipped to Novozymes for analysis. Such a comparison leads one to determine the dissolved enzyme concentration required to achieve a target capture efficiency; and also to determine the rate of active enzyme loss during exposure to bench-unit run conditions, which can then be used to determine the active enzyme replenishment required to maintain a target capture efficiency.

Dissolved enzyme activity was assessed using a pH sensitive colorimetric assay developed during Budget Period 1. The assay adapts the Rickli test tube colorimetric assay [103], commonly attributed to Wilbur and Anderson [104], to a 96-well microtiter plate format operated at 30°C. In brief, a syringe pump coupled to a plate reader (TECAN Infinite M1000) is used to dispense an aliquot of room-temperature CO_2 saturated water into a well containing a solution comprising assay reagent mixed with a dilution of working solvent removed from the bench scale unit. Active enzyme present in the solution will catalyze the hydration of $CO_{2(aq)}$ dispensed into the well, resulting in the formation of protons (as shown in Figure 7) causing a color change in the pH sensitive colorimetric indicator in the reagent. The rate of color change (Δabsorbance/ Δtime) is measured in < 1 s increments by the plate reader, and corrected for the rate of color change caused by working solvent (K_2CO_3) absent enzyme. The corrected rate of color change is analyzed to ensure linearity across the measurement period – thereby ensuring active enzyme was saturated with substrate. If a dilution of working solvent fails to pass the linearity test, a more dilute sample is analyzed. The corrected (enzyme dependent) linear rate of color change is used to determine the concentration of active enzyme in the working solvent. Changes in the active enzyme concentration over time are taken as a measure of enzyme robustness to bench-unit run conditions. Figure 41 shows an example of the change in absorbance versus time data that were used to measure enzyme activity. Note that the change in absorbance with time (as the pH indicator color changes from blue to yellow (or a different color change can occur depending on the particular buffer-indicator pair used [105]) was slower for the "no enzyme" blank sample compared to the five test samples, each containing enzyme. In this example, the five test samples were exposed to ultrasonication for 0, 10, 30, 60 or 140 seconds prior to conducting the activity assay, indicating that exposure to ultrasonics for up to 140 seconds had no significant impact on enzyme activity.

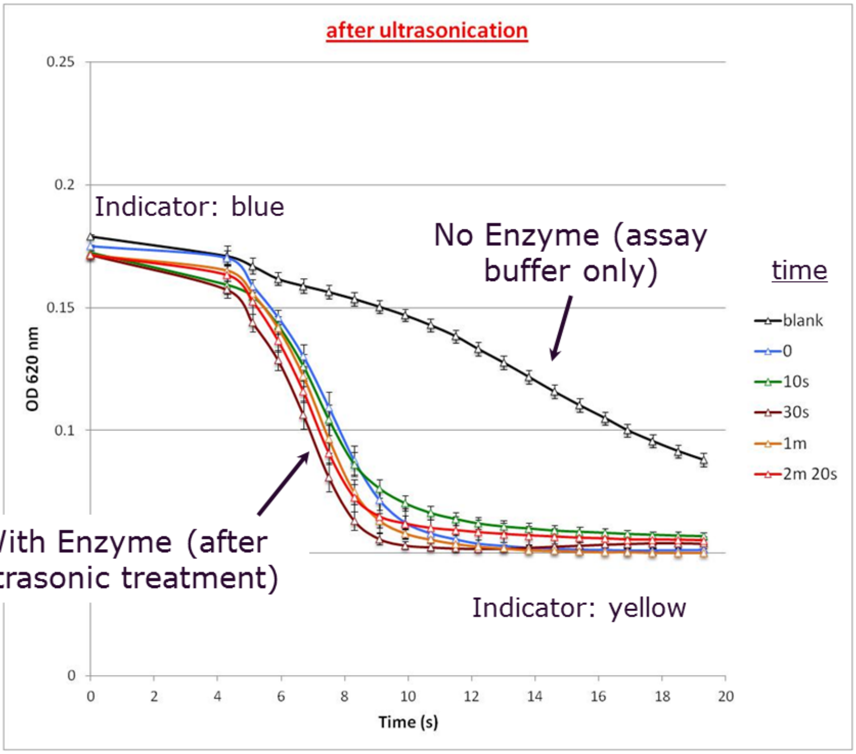


Figure 41. Example of enzyme activity analysis.

In addition to assessments of active enzyme concentration, Sodium Dodecyl Sulfate – Poly-Acrylamide Gel Electrophoresis (SDS-PAGE) was used to detect the physical presence of carbonic anhydrase in select samples taken from the bench-unit. A comparison of the trend linking active enzyme loss with physical presence or absence of enzyme protein may be used to determine inactive enzyme protein accumulation in the system. Because SDS-PAGE allows proteins to differentially migrate in a gel according largely to their molecular size, one can assess whether accumulation results from intact but inactivated molecules, or to protein degradation or aggregation.

Visual observations on select working solvent samples taken from the bench-unit were recorded. Results contributed to understanding the stability of the character of the working solvent during defined exposure conditions in the bench-unit, particularly the effect of run conditions on chromophore containing compounds in the enzyme stock liquid, and the relationship between dissolved protein, and insoluble protein particles.

Throughout the course of investigation samples taken from the rich, lean and reboiler sample ports on the bench-unit were analyzed and compared. No significant differences in either CA activity, SDS-PAGE profile, or visual properties were detected, suggesting solvent inventory in the unit was well mixed, and that samples taken from any port could be considered representative of the whole inventory with regard to these three properties.

Testing throughout this project was also performed to characterize batch-to-batch variation among enzyme solutions, and evaluate enzyme robustness to long-term storage. For storage robustness testing, undiluted enzyme batch samples of the prototype concentrate enzyme solution (Figure 9A) were stored at 25°C below zero, 5°C and ~22°C for 1.5 years, and enzyme activity assessed at periodic intervals, with minimal measureable losses in activity in all conditions. This represents very good storage stability, however, to err on the side of caution, based on these results we practiced (and recommend) refrigerated storage for up to three months, with frozen storage recommended for longer periods of time. Differences in active enzyme concentration across the different prototype concentrate enzyme batches used to support this project were used to adjust dilutions when preparing the bench-unit stock solution (Section 3.4, Figure 9D), and thereby maintain a consistent active enzyme concentration supply for the duration of testing.

8.1 Bench-unit Shakedown and Operational Limits Testing

Bench-unit shakedown and operational limits testing are described above in Sections 6.2.1 and 6.2.2, respectively. During shakedown testing, a single-fill of solvent was used and the entire inventory discarded as needed, and replaced with a fresh fill for subsequent tests. A discontinuous 8-day single fill test, with different run parameters each day (including 90-95°C heating source temperature and 300-625 ml/min liquid flow rate), provided the longest exposure of dissolved enzyme to bench-unit run conditions, and therefore a first assessment of operational enzyme robustness. For this test, the solvent comprised 20 wt% K_2CO_3 equivalent, 0.3 g/L active enzyme and 0.005-0.02 vol% antifoam. Results of CA activity and physical stability during the discontinuous 8-day shakedown run are shown in Figure 42. An approximate 30% loss in active enzyme per ~ 8 h run day was measured, and while the CO_2 capture efficiency fluctuated around the initial value (as expected given the different run conditions per test day), it did not trend directly with the loss of active enzyme (Figure 42.A). The graph in Figure 42.A shows plots of percent CO_2 removal (measured on the bench unit) and normalized percent enzyme activity (measured offline from bench-unit solvent samples) per ~8 h run day. Enzyme was added together with solvent at the start of the 8-day test and was not replenished. The disconnect between enzyme activity loss and maintained CO_2 capture efficiency is likely due to the nonlinear relationship between enzyme activity loss and capture performance, as discussed in Section 8.3. Note that separate studies showed no enzyme activity loss occurs during solvent storage in the unit, but only during unit operation (data not shown). Further investigation of shakedown samples via SDS-PAGE revealed that during operation, physical loss of intact CA is observed, with possible formation of dissolved CA degradation products, and insoluble aggregates (Figure 42.B). SDS-PAGE results are shown for samples taken from the lean (L) and reboiler (R) sample ports on the bench-unit. Dramatic physical loss is observed on run day 5, with gradual loss thereafter. The reason for a dramatic loss event in day 5 is not known, but could potentially be due to a large proportion of enzyme having undergone accumulated physical changes due to repeated high temperature exposure in the reboiler leading to a critical onset of exaggerated aggregation. Observation of the liquid samples showed a gradual increase in turbidity during the run (Figure 42.C). The photograph in Figure 42.C depicts the daily change in visual sample properties from a 3.5 ml aliquot of the working solvent taken from the reboiler sample port at the end of each run day. The tubes show an increase in particles dispersed throughout the solution over time. Note that the narrow opaque layer at the surface of the liquid is an aberration of photography, and not indicative of solids floating at the surface of the liquid.

Subsequent analysis of the turbidity-imparting particles found them to be absent of CA activity and to consist predominantly of protein (data not shown).

During operational limits testing, three active enzyme doses were tested: 0.3, 1.5 and 3 g/L. Each test comprised a single-fill operated for three discontinuous (~ 4.5 h) run days. Key bench-unit run parameters, held constant across the enzyme dose-response tests, were: 700 ml/min solvent flow rate, 30°C absorber, 95°C heating source, and 0.3 atm stripper pressure, yielding a solvent boiling point of 76-80°C. On the initial test day, CO_2 capture efficiencies of 48, 91 and 94% were measured for 0.3, 1.5 and 3 g/L active CA, respectively. The capture efficiency increased ~ 6% across the 3 tests at 0.3 g/L CA, despite a 70% loss of enzyme activity during the same period. At 1.5 and 3 g/L, ~40% loss of enzyme activity was measured, with either a 10% loss in CO_2 capture efficiency, or no loss, respectively (Figure 43). Thus, as observed above with shakedown testing, the rate of enzyme activity loss does not correlate directly with loss in CO_2 capture performance. The rate of enzyme activity loss appears to change with the initial enzyme dose, wherein a higher initial enzyme concentration delays the enzyme degradation rate. The mechanism underlying this observation was not determined, and further work would be required to confirm whether this effect is reproducible, and to understand the underlying mechanism. Despite this, a key conclusion from the operational limits testing is that enzyme promoted K_2CO_3 can achieve >90% CO_2 capture in the bench-unit. Furthermore, the energy demand (kJ/mol CO_2 captured) of the system decreases with increasing enzyme dose (Figure 44), indicating that both CO_2 capture and bench unit operation efficiency is improved with increasing enzyme dose.

Two key learnings related to enzyme use at the close of shakedown and operational limits testing were that: (i) an enzyme-promoted K_2CO_3 process is able to achieve >90% capture in the bench-unit under operational limits testing, with associated reduction in energy demand and (ii) a disconnect exists between active enzyme loss in the solvent and CO_2 capture efficiency in the unit. As the cause for this disconnect was unknown, and could have been due to enzyme assay deficiencies, a decision was made to base active enzyme replenishment on measured CO_2 capture efficiency losses in the unit rather than active enzyme losses measured in the solvent in an enzyme activity assay. For example, in the 0.3 g/L test run in Figure 43, an ~ 25% active enzyme replenishment per day (0.3 g/L × 25% = 0.075 g/L) would be required to adjust for measured enzyme activity loss; however a < 1% replenishment would be required to adjust for measured losses in CO_2 capture efficiency. Thus, during unit parametric testing, where daily enzyme replenishment will be used to correct for enzyme activity loss, the replenishment will be based on unit performance losses measured during a sequence of reproducible runs.

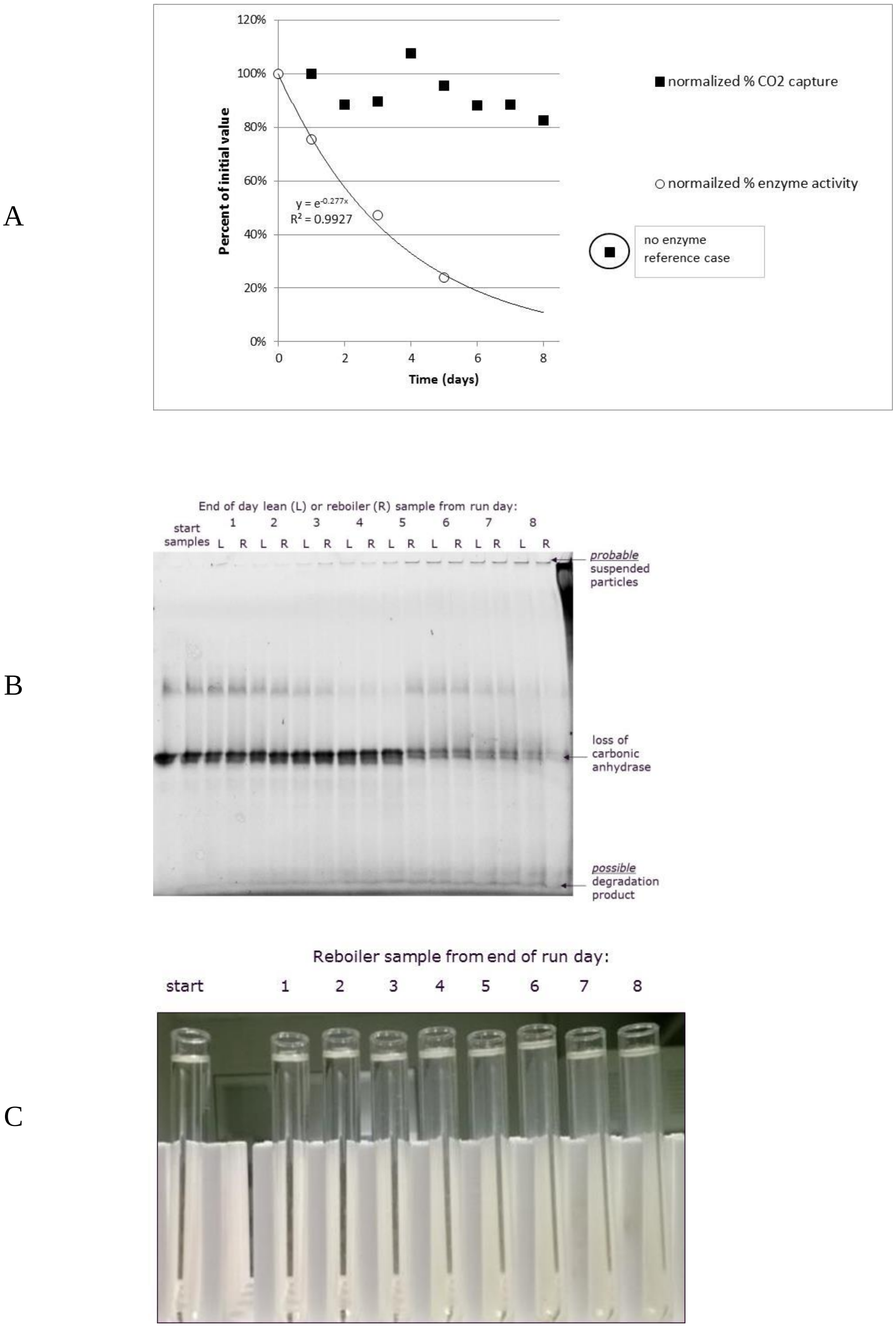


Figure 42. Results of CA activity and physical stability during shakedown testing. At the end of each run day: A) normalized enzyme activity and % CO_2 capture; B) enzyme physical presence in the solvent via SDS-PAGE; and, C) appearance of solvent taken from the reboiler.

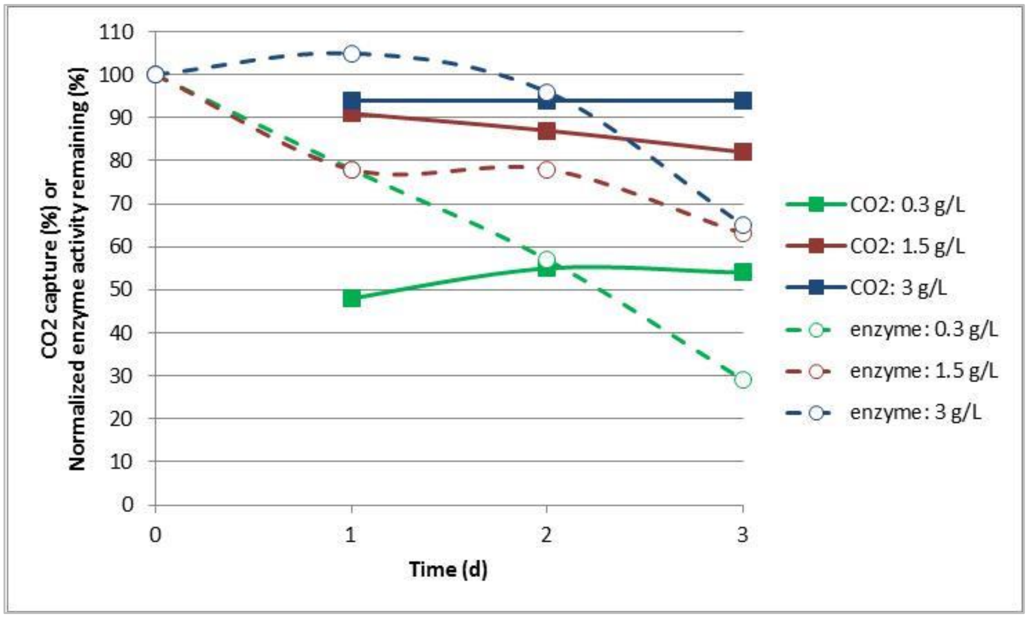


Figure 43. CO_2 capture and enzyme activity during operational limits testing. CO_2 capture efficiency (filled symbols, solid lines) and normalized enzyme activity (open symbols, dashed lines) during operational limits testing with three active enzyme doses. Each test was performed for three discontinuous (~ 4.5 h) run days.

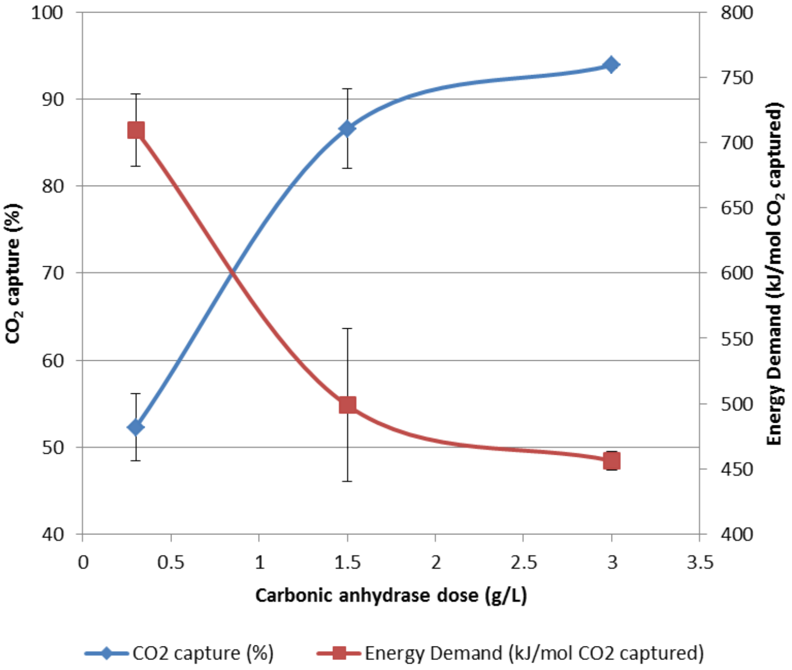


Figure 44. Energy demand and CO_2 capture versus enzyme dose. Data points collected during operational limits testing are the average of three discontinuous (~4.5 h) run days; error bars represent the standard deviation.

8.2 Bench-unit Parametric Testing

Parametric testing was divided into two phases, called Phase 1 and Phase 2. A goal of Phase 1 (Section 6.2.4) testing was to determine the daily enzyme replenishment required to ensure reproducible unit operation across run days with a 2.5 g/L active enzyme dose. Data from a discontinuous five day test in the bench-unit is shown in Figure 30, with the conclusion that a 15% active enzyme replenishment would be used in Phase 2 to correct for enzyme activity loss. However, early in Phase 2 testing, a decision was made to increase the replenishment to 20% of the active enzyme dose, to err on the side of caution and help ensure parametric test results would not be confounded by enzyme degradation.

The program of dissolved enzyme replenishment on the bench-unit was performed as follows: prior to a day's run, an equal volume of solvent inventory (1.07 L) was replaced with a concentrated solution of active enzyme (9 g/L) diluted in a lean 23.5 wt% K_2CO_3 solvent at 37.5% conversion. Thus, a 15 L solvent inventory with 2.5 g/L enzyme dose would contain 37.5 g active enzyme. To account for a 20% active enzyme loss during the prior run day, one would need to add 7.5 g active enzyme (37.5 g × 20% = 7.5 g). In addition, one would need to also account for the active enzyme lost in the volume of inventory removed from the unit (i.e. if 1.07 L removed = 2.5 g initial active enzyme × 80% still active after 20% loss in one run day = 2.14 g active enzyme removed in 1 L). Thus, 9.64 g active enzyme is lost from the system due to enzyme degradation (7.5 g) and solvent removal for replenishment (2.14 g), and 9.63 g active enzyme (9 g/L stock solution × 1.07 L = 9.63 g) is added to account for the loss and maintain 37.5 g/L active enzyme in the 15 L unit inventory. The K_2CO_3 in the solvent is held constant during replenishment due to equal volume removal of working solvent and addition of fresh solvent. Prior to data collection from the unit, the solvent inventory is mixed to allow the fresh enzyme to mix with the bulk solvent.

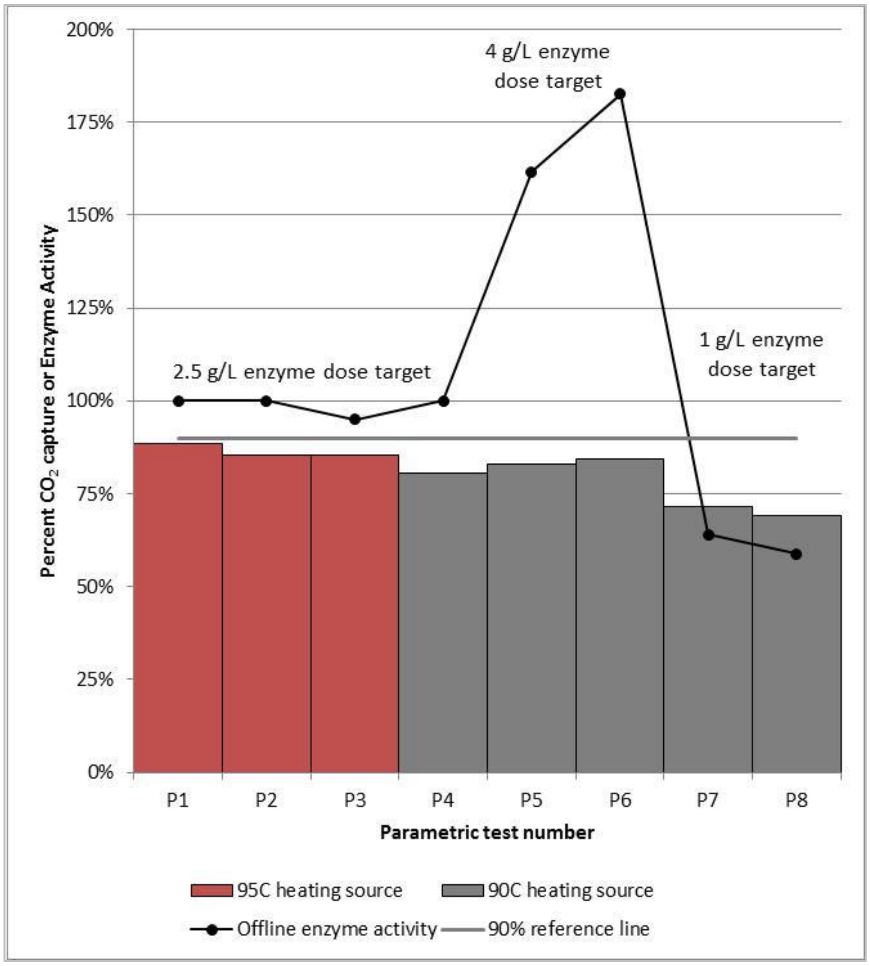


Figure 45. CO_2 capture efficiency and enzyme activity during Phase 2 parametric tests with a 20% active enzyme replenishment program per run day, where filled circles represent enzyme activity, bars represent % CO_2 capture, and the horizontal grey line marks 90% capture.

Results during parametric Phase 2 testing showed no significant difference in CO_2 capture efficiency between replicate runs. Furthermore, the active enzyme replenishment program also negated enzyme activity losses as measured in offline enzyme activity assays (Figure 45). Enzyme dose response testing was one parameter of parametric Phase 2 testing (as described in Section 6.2.5), and enzyme activity assay results show that the measured amount of active enzyme in the system approached the targeted amount. Note that for enzyme dose response testing, the unit solvent was not replaced, but rather the replenishment approach described above was used to achieve the target enzyme dose. The intensity of pale yellow color of the liquid samples also changed concurrent with the enzyme dose, and all samples contained particles imparting turbidity (Figure 46). As a 20% active enzyme replenishment per run day program sufficed to ensure consistent unit operation in the bench-unit during parametric testing, and also appeared to stabilize the active enzyme dose in the system, the same program was implemented for the main part of the 500 h long-term performance test.

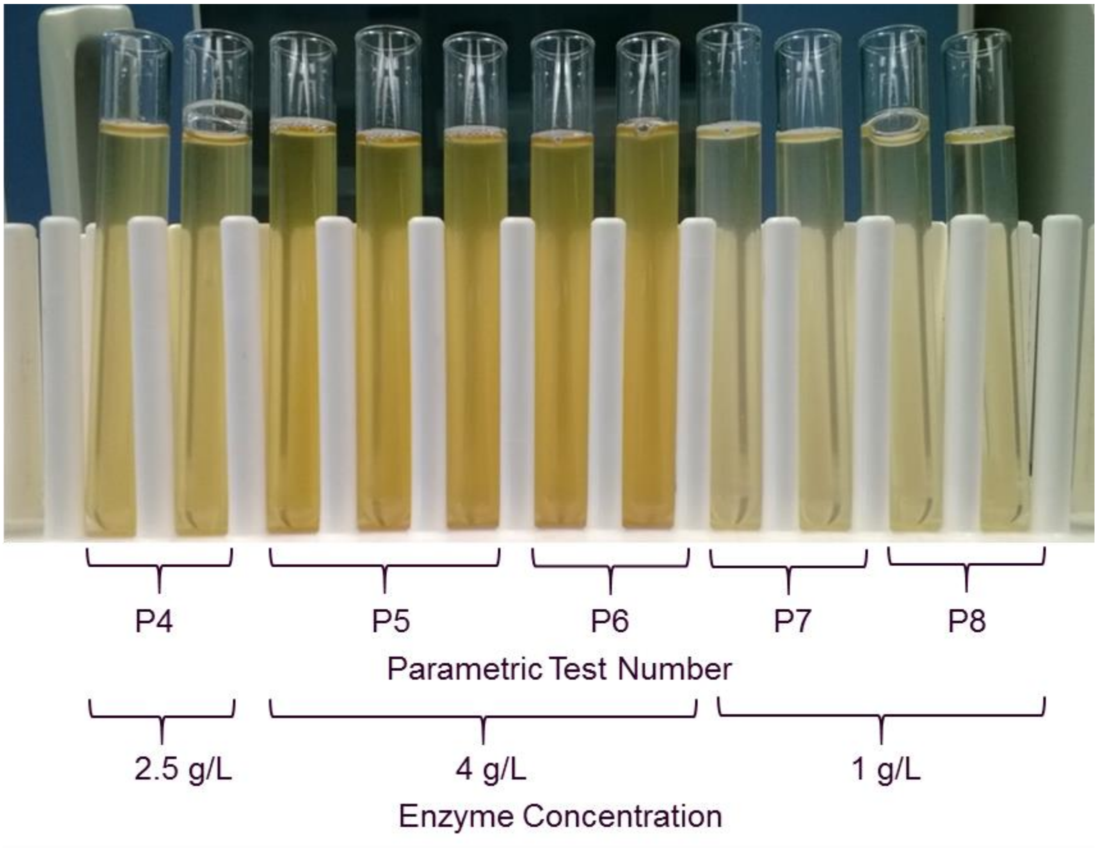


Figure 46. Appearance of solvent during Phase 2 parametric tests. The photograph shows 3.5 ml aliquots of liquid samples taken from the bench unit during parametric tests 4 through 8, with different enzyme concentrations in the solvent.

8.3 Bench-unit Long Term (500 h) Testing

A discontinuous 500 hour long term test (as described in Section 6.2.6) was performed to test bench unit stability and operation with a dissolved carbonic anhydrase promoted K_2CO_3 solvent, implementing a regular regime to replenish enzyme lost through degradation. Enzyme activity analysis was performed on liquid samples from the bench-unit across the duration of the long term test. In general, the CO_2 capture performance measured on the bench-unit correlated with enzyme activity measured in offline enzyme activity analyses for samples taken on the same run day (Figure 47). The first ~ 40 h of the run period experienced a decline in both capture performance and enzyme activity. The reason for this decline is not known, but is hypothesized to be caused by a loss of enzyme in excess of the 20% replenishment requirement due to enzyme deposition to surfaces of the unit. Once these surfaces are “primed” deposition ceases, and stability is obtained. However, not knowing the cause of this initial performance loss during the run, a one-time 90% solvent replacement took place at ~ 50 h runtime mark in an effort to stabilize performance. In retrospect, performance appears to have stabilized prior to the replacement. In order to refine the 20% replenishment program selected for parametric testing, two other replenishment programs were tested during the long term run:10% and no replenishment.

The run period initiating with 10% active enzyme replenishment and continuing to the rinsing of the unit at the ~ 425 h runtime mark (as described in Section 6.2.6) shows less correlation between CO_2 capture efficiency and enzyme activity – perhaps indicating that the decline in capture performance during the period was due to an accumulation of solids on the column packing and heat transfer tubes (as described in Section 6.3.2), rather than a decline in enzyme activity caused by the decreased replenishment, because the offline enzyme activity measured during this period was unchanged relative to the 20% replenishment period, and, although decreased, the CO_2 capture efficiency was also nevertheless stable.

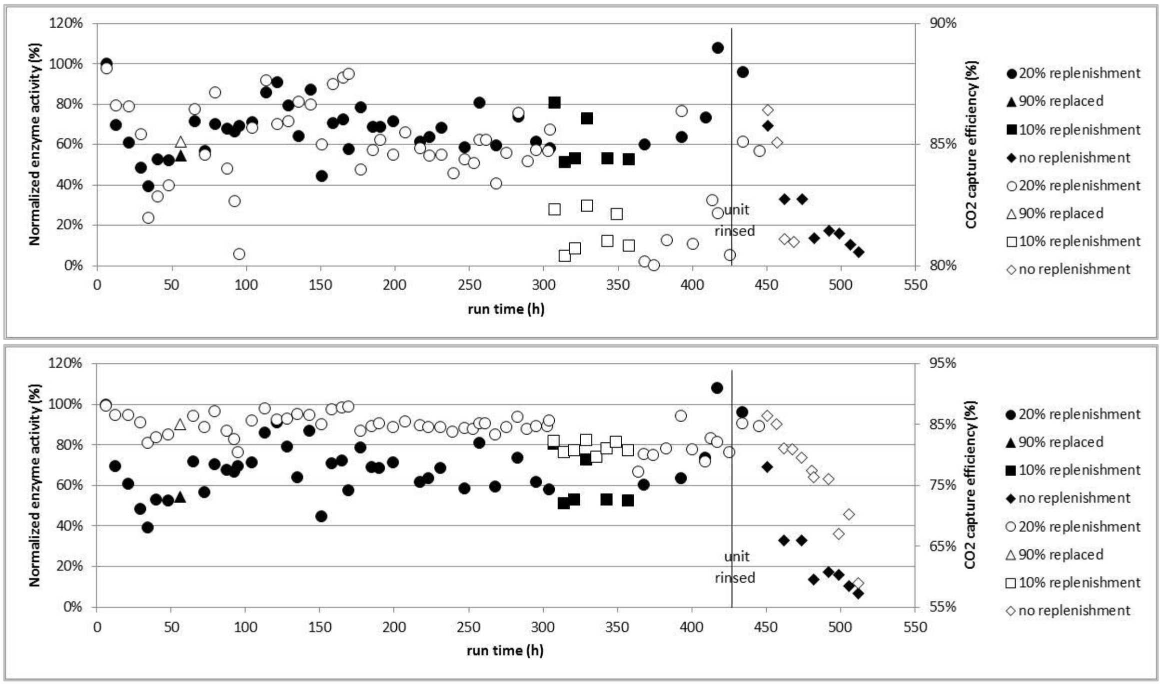


Figure 47. Enzyme activity and CO_2 capture during 500 hour testing. Enzyme activity (closed symbols) and CO_2 capture efficiency (open symbols) during the full 500 hour run; with different symbols denoting the different replenishment programs implemented. The top graph limits the CO_2 capture axis to $\geq$ 80%, to facilitate qualitative evidence of the correlation between capture efficiency and enzyme activity. The bottom graph shows the full range of CO_2 capture performance. The time point at which the unit was rinsed is indicated with a vertical line.

Enzyme activity analysis from samples taken during the period of no replenishment indicates an active enzyme exponential decay rate of 3.5% per hour during unit operation (Figure 48). Thus, the 20% replenishment per ~ 7 h run day that dominated parametric testing and much of the 500 h test was close to the replenishment required for lossless enzyme activity as determined during the period of no replenishment. Evidence of no activity loss during the 10% replenishment period is difficult to explain in light of the empirical decay rate, as no active enzyme was measured to accumulate in the system (Figure 51). The possibility that non-active enzyme components in the technical grade enzyme liquid, or potentially an interactive effect of these with the antifoam agent, contributed to lower CO_2 capture efficiency in the unit during the 10% replenishment period cannot be ruled out, though additional studies would be needed to clarify this, and also whether this behavior was limited to the 10% replenishment period or whether the effect was a cumulative effect that first became apparent during the 10% replenishment period.

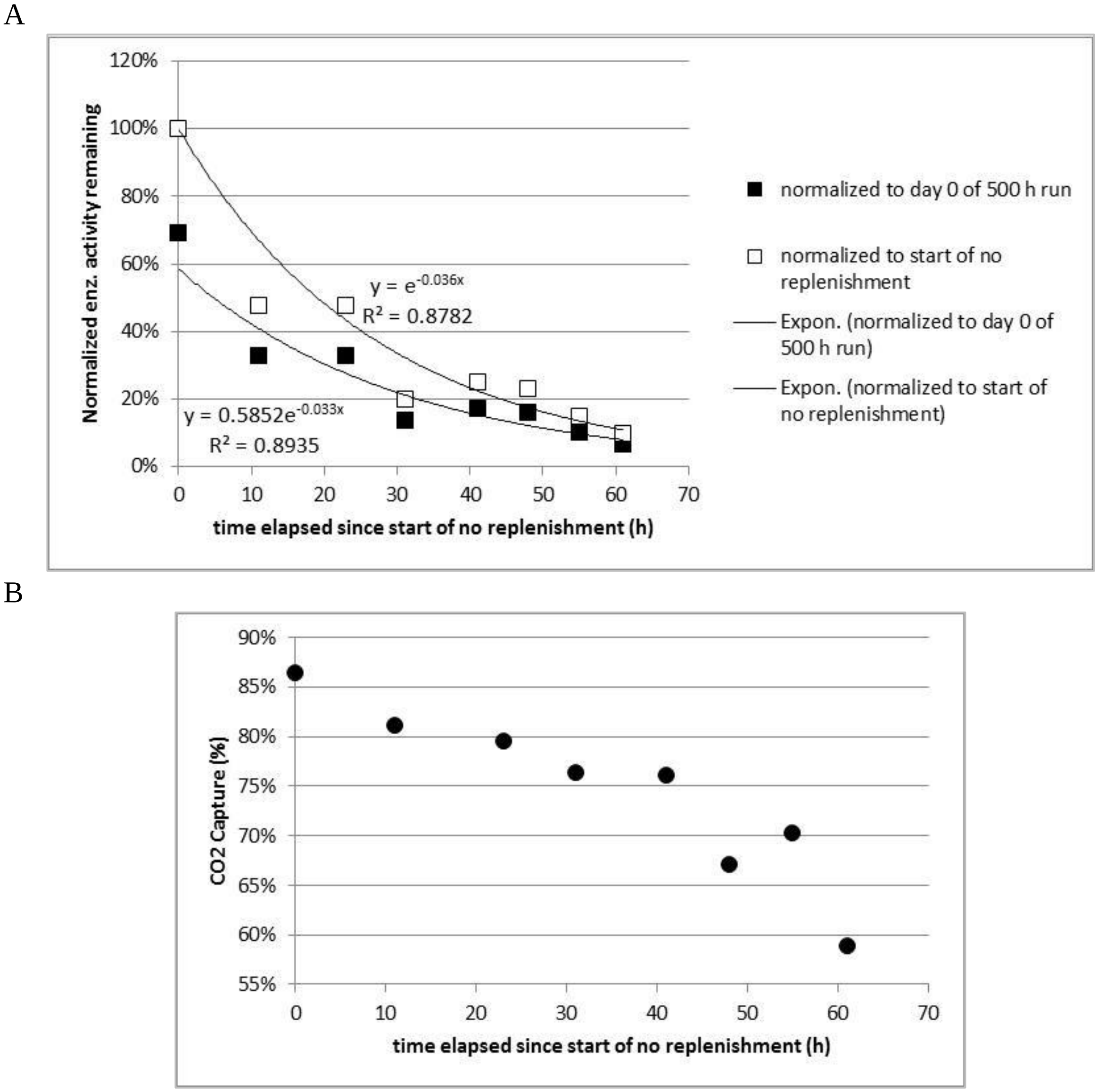


Figure 48. Enzyme activity and CO_2 capture during period of no replenishment (A) data points are normalized to either day 0 of the 500 h run (filled symbols) or to the start of no replenishment (open symbols). (B) shows CO_2 capture efficiency data for the same period of no replenishment.

A plot of CO_2 capture efficiency versus normalized enzyme activity during the period of no replenishment (Figure 49) shows a nonlinear relationship correlates loss of active enzyme and loss of CO_2 capture efficiency; with an ~ 75% loss in active enzyme corresponding to a 10% loss in CO_2 capture efficiency (note that as reference points, CO_2 capture efficiency with no enzyme (from Parametric test 10 (Section 6.2.5) and fresh (100% active) enzyme (Day 0 of the 500 h run) are also shown). This nonlinear relationship likely underlies the results collected during shakedown and operational limits testing where day-to-day CO_2 capture performance varied by only around 5% whereas off-line measurement showed around 20% enzyme activity loss (Figures 42 and 43). The mechanism underlying this nonlinear relationship remains to be determined. This data supports that a moderate loss in active enzyme may not be detrimental to system performance; however, to sustain lossless performance, a higher than targeted replenishment rate was required.

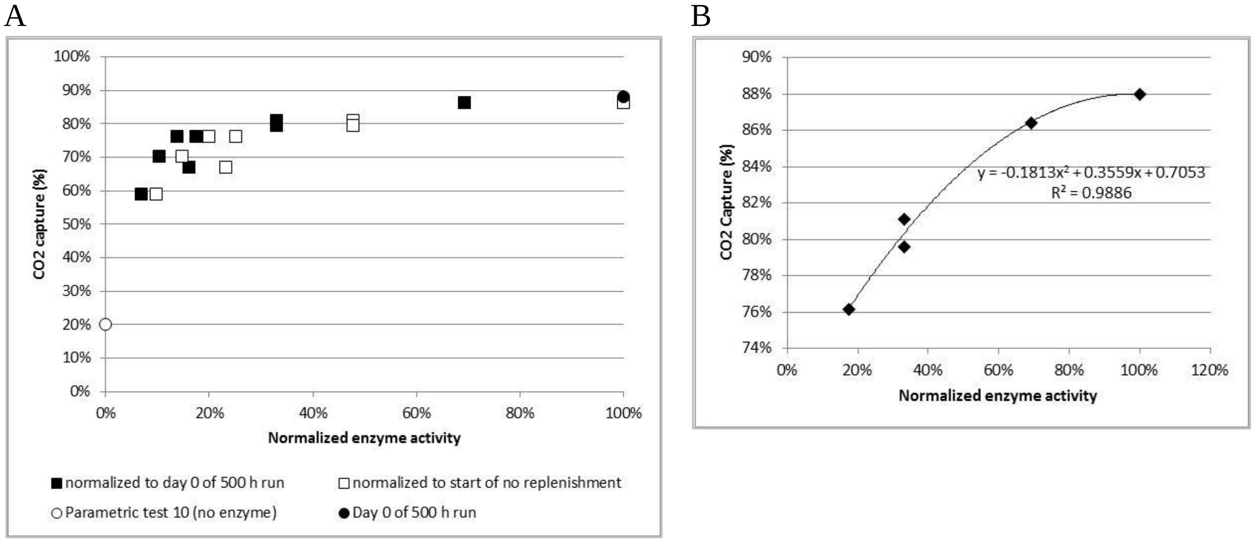


Figure 49. CO_2 capture versus enzyme activity during period of no replenishment (A) Data points are normalized to either day 0 of the 500 h run (filled symbols) or to the start of no replenishment (open symbols). (B) A subset of the data in part A is plotted with a narrower range on the CO_2 capture efficiency axis to highlight the nonlinear relationship between the plotted variables.

Another perspective into active enzyme loss rate during the 500 h run is obtained by comparing samples taken at three timepoints during a run day: after replenishment and mixing, during steady state operation, and at day's end. Comparison of enzyme activity for the three samples suggests that within some run days, a 20-40% activity loss was observed, while no losses were observed on other days (Figure 50) Note that steady state and end of day samples are normalized to the activity of the sample taken after replenishment. Reasons for the different losses among run days is unknown, but the general trend supports both the need for a high active enzyme replenishment rate (Figure 42) and the nonlinear correlation between enzyme activity and CO_2 capture performance (Figure 43) – since a 40% loss in enzyme activity during a run day did not result in the same loss in capture.

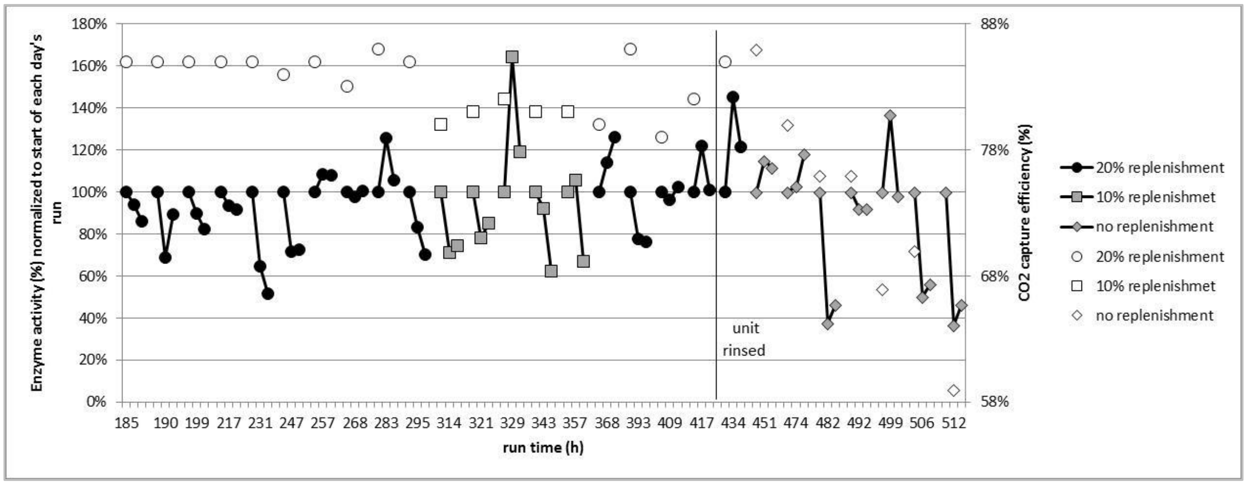


Figure 50. Monitoring of daily variation in enzyme activity during 500 hour testing with enzyme activity and CO_2 capture represented by closed and open symbols, respectively. The timepoint at which the unit was rinsed (as described in Section 6.2.6) is indicated with a vertical line.

A concern during operation of the bench scale unit with a 20% active enzyme replenishment program was that active enzyme might accumulate in the unit, and that eventually the concentration of active enzyme in the unit would match that of the stock solution used to supply the unit (a "washout" scenario). If all added active enzyme accumulated under the adopted replenishment program, such a washout scenario would be achieved at ~ 300 h into the 500 h run (Figure 51.A). However, the measured enzyme activity in samples from the bench scale unit did not approach the level of activity in the stock solution during this time (Figure 51.B).

If active enzyme was not accumulating, we sought to confirm whether intact but inactive enzyme would accumulate, and thereby increase the organic load of the solvent. A comparison of physical intact enzyme (active and inactive – as determined using pixel intensity of bands on SDS-PAGE) with enzyme activity indicates that all intact enzyme molecules were active, and there was no physical accumulation of enzyme (active or inactive) in the working solvent (Figure 52).

Although intact enzyme molecules were not accumulating in the system, the working solvent changed from a clear pale yellow to a turbid dark brown/amber (Figure 53.A) – indicating both soluble and insoluble solids were accumulating in the system. While the finely dispersed insoluble solids were difficult to retain on the bench unit filters (as described in Section 6.3.2), they were removable via off-line lab scale filtration (Figure 53. B). Thus, in support of solids emissions estimations for the preliminary Environmental Health and Safety Assessment, the rate of total insoluble solids generated during bench unit operation were estimated to be 23 g insoluble wet solids per L solvent inventory per avg. 7 h run day. This estimation was derived by combining the maximum wet solids retained on a filter during the 500 h run (~3 g wet solids per L inventory) with the average amount of floating solids (20 g wet solids per L inventory) measured in 16 samples dispersed across the timecourse, beginning at 200 h. The wet solids are believed to comprise water, potassium carbonate and bicarbonate, enzyme protein, antifoam, and some contribution of fermentation derived solids carried over from enzyme manufacturing in the stock solution used to supply the unit. Upon drying, the 3 g wet solids per L inventory retained on a filter reduces to 1.3 g dry solids per L inventory; and the 20 g wet solids per L inventory comprising the floating solids reduces to 4 g dry solids per L inventory.

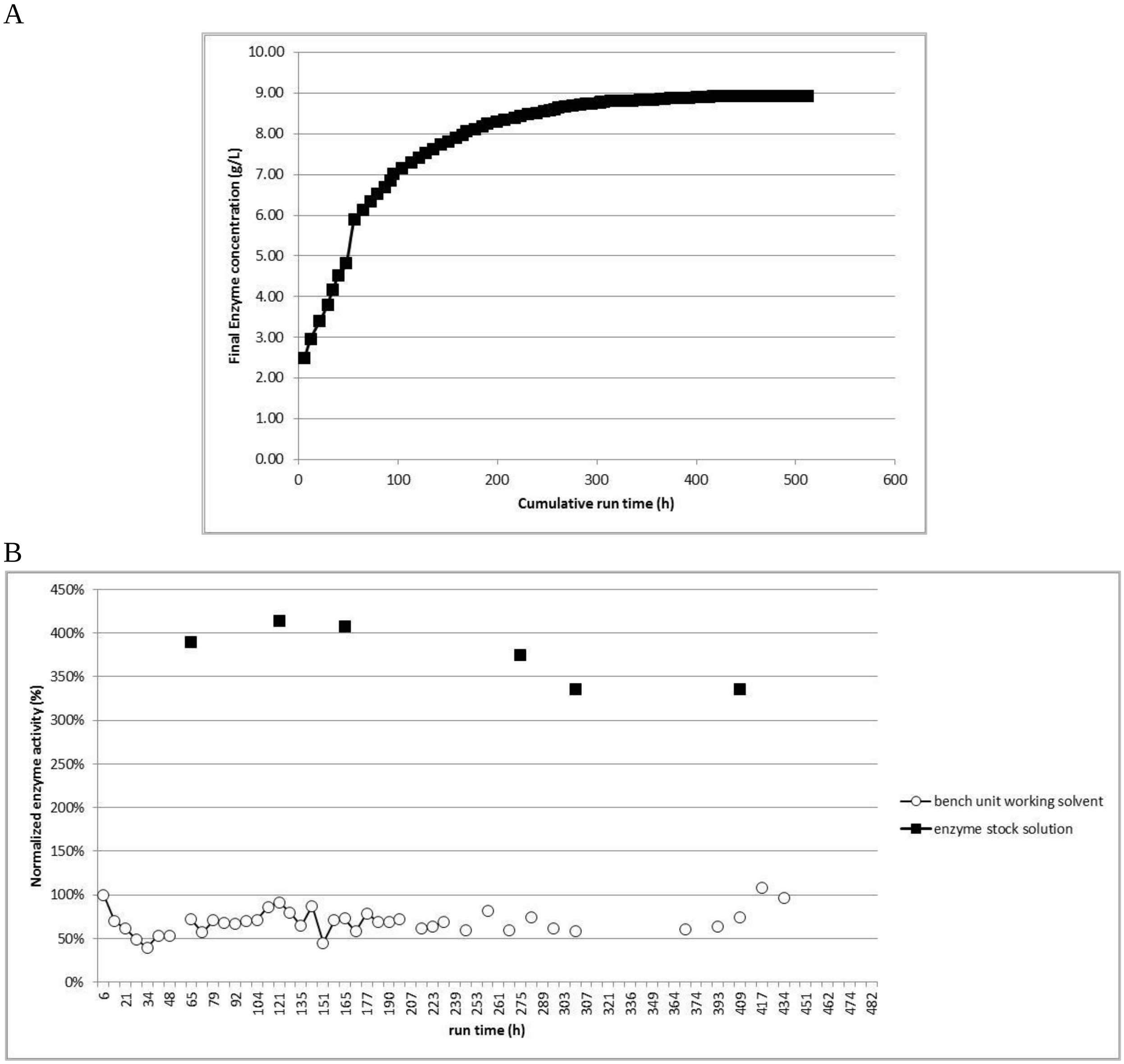


Figure 51. Monitoring for enzyme accumulation in solvent during replenishment (A) Projected active enzyme accumulation in working solvent (if no activity loss occurred) modeled on the replenishment programs during the run. (B) Enzyme activity from the bench-unit working solvent (open symbols) and stock solution used to supply the unit (closed symbols), all normalized to day 0 of the working solvent used for the 500 h run.

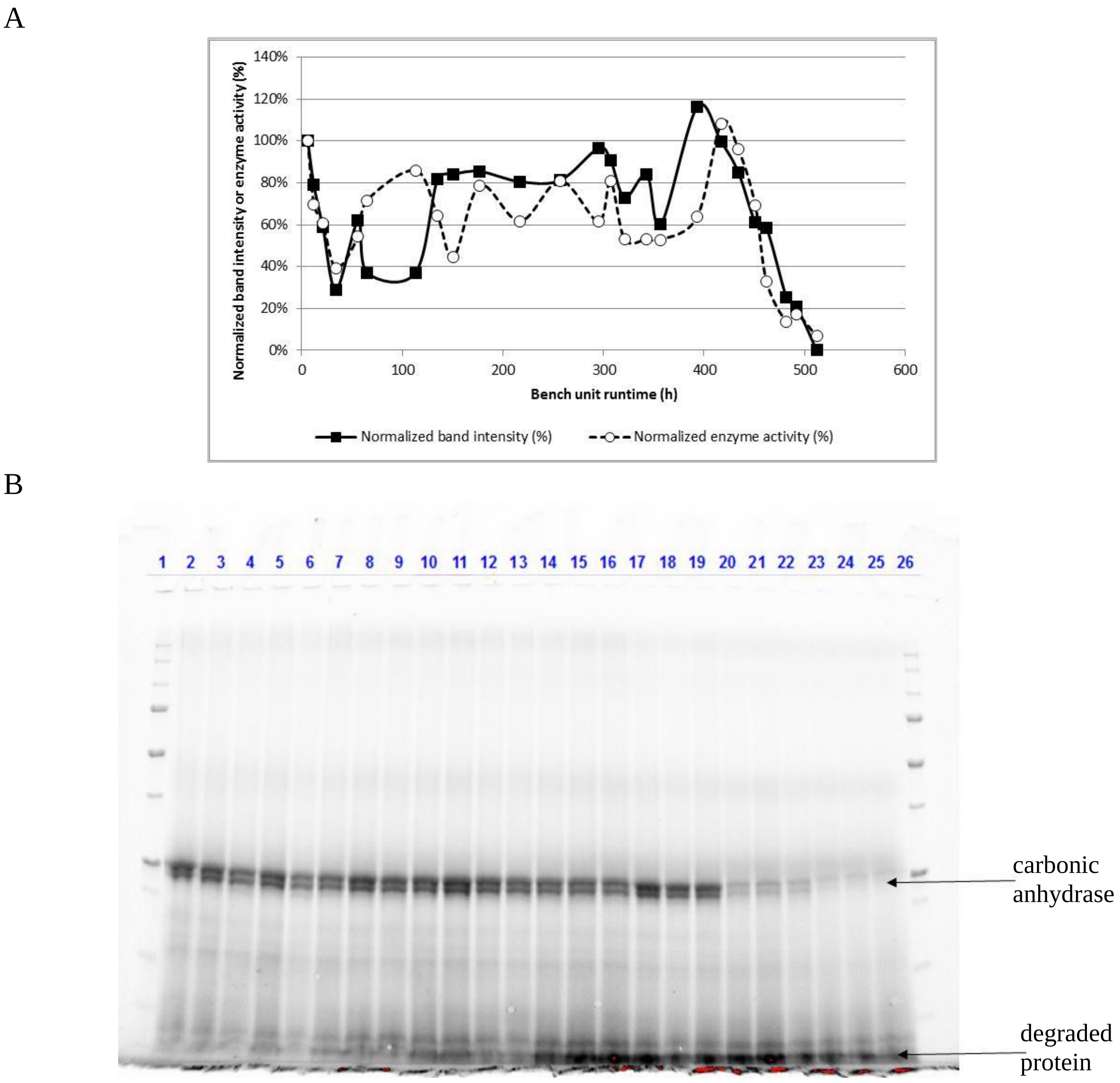


Figure 52. Monitoring enzyme physical changes during 500 hour testing. (A) Total and active carbonic anhydrase are represented by closed and open symbols, respectively. (B) SDS-PAGE results for bench unit samples in order of runtime, such that lanes 2-25 on the gel image align with consecutive closed symbol data points in part A. Intact (active or inactive) carbonic anhydrase appears in the middle of the image, and degraded protein at the bottom.

Figure 53. Solvent visual appearance during 500 hour testing (A) Full 500 h timecourse (B) from left: Start of run rich; Start of run lean; End of run lean after being filtered off-line at lab scale; End of run rich; End of run lean.

8.4 Laboratory Scale Enzyme Thermal Stability Study

The 3.5% per h exponential enzyme activity loss rate measured during the period of no replenishment may be a specific result of the reboiler residence time and temperature condition of the bench-unit build, rather than a generic loss rate for dissolved enzyme in K_2CO_3 solvent in a recirculating absorber/desorber CO_2 capture process. Understanding the effect of different process temperatures or configurations on a particular enzyme candidate is important, as this contributes to the enzyme replenishment basis required to maintain a target CO_2 capture efficiency, and thus impacts process operational costs and considerations, relevant for the project technical and economic assessment (Section 10). To test effects of temperature cycling, with different setpoints and residence times at high temperature, a series of laboratory scale studies were performed using a temperature cycling loop device (Figure 54) in which the solvent containing enzyme cycles from a low temperature coil (mimicking the absorber) to a high temperature coil (mimicking the desorber). In some studies the solvent resided at high temperature for a constant percent (25%) of the total cycle time, and the high temperature setpoint was varied across the experiments. In other studies, the high temperature was held constant (70 and 80°C), and the percent of total cycle time at high temperature was varied. In all temperature cycle tests, 40°C served as the low temperature in the cycle. In yet other studies, the effect of constant temperature incubation was assessed with the exact same device, and in these cases the low and high temperature settings matched. Stainless steel tubes (2 mm ID), of targeted length according to desired residence time, were coiled and immersed in water baths at target temperatures. Lean working solvent (20 wt% K_2CO_3, 37.5% conversion, 3 g/L active carbonic anhydrase, ~27.5 ml) was pumped (0.6 ml/min) between the coils with a peristaltic pump held at room temperature. The calculated volume of tubing (which was not externally heated and therefore was exposed to room temperature) connecting the two coils was ~ 2.7 ml. A 5 ml reservoir (22.5 ml glass vial with screw top and Teflon lined septum, held at 40°C) was used as a planned air gap, to help maintain a steady flow rate, and avoid the introduction of air bubbles when withdrawing samples from the device. Samples (~ 300 – 500 µl) were withdrawn at select timepoints during continuous circulation, and enzyme activity assessed. The percent of active enzyme remaining during the timecourse of continuous temperature cycling was plotted using Microsoft Excel and fitted with an exponential decay curve forced to intersect the y-axis at 100% enzyme activity at the initial timepoint of the cycle (Day 0).

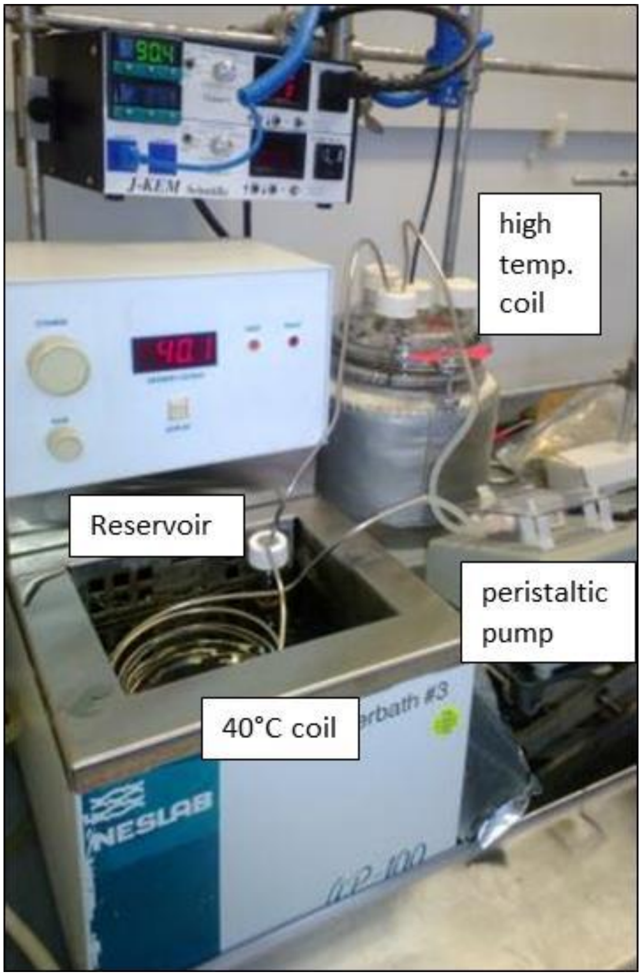


Figure 54. Laboratory-scale temperature cycling loop device.

During a temperature cycle, where the solvent resides at high temperature for 25% of the total cycle time, the active enzyme exponential decay rate (percent loss of active enzyme per day) increased exponentially by ~10% with each degree increase in the high temperature set point, with 40°C as the low temperature set point (Figure 55 and Table 21). For example, a 27% active enzyme loss per day when cycling between 40-80°C, with 25% of total cycle time at the high temperature (80°C) condition, would increase by 2.7 points (10% of 27%) to ~29.7% per day when cycling between 40-81°C, according to the exponential fit of the data. These results can be used to model the expected change in active enzyme replenishment rate as the high temperature in the cycle is changed, and thus aid in balancing costs associated with enzyme replenishment with those required to achieve a target high temperature in the system. The exponential relationship between active enzyme loss per day and high temperature in the system indicated that while an ~2-fold faster decay rate was measured when increasing from 70 to 80°C, an ~8-fold faster decay rate was measured when increasing from 70 to 90°C (Table 21). Further investigation during scale-up studies are needed to confirm these conclusions.

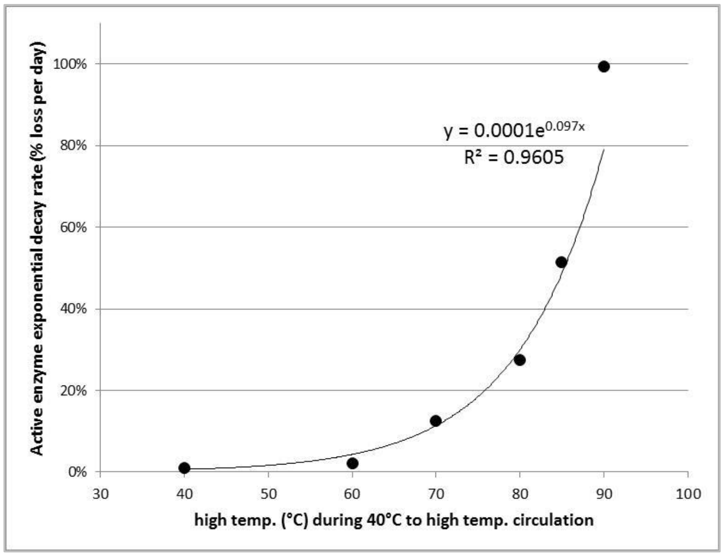


Figure 55. Carbonic anhydrase decay rate as a function of high temperature set point in a lab-scale temperature cycling device with 25% of total cycle time at high temperature.

Table 21. Carbonic Anhydrase Decay Rate as a Function of High Temperature Set Point in a Lab-scale Temperature Cycling Device (25% of cycle time at high temperature)

High temp. setpoint (°C) during 40°C to high temp. circulation	Active enzyme exponential decay rate (% loss per day)
40	1
60	2
70	13
80	27
85	52
90	99

In addition to determining the rate of enzyme activity loss as a function of the high temperature set point during cycling, with the residence time at high temperature set constant, the residence time at 70 and 80°C was varied to determine the effect of residence time at these temperatures on the active enzyme decay rate. The active enzyme exponential decay rate increases with an approximate linear relationship to the percent of total cycle time at high temperature, until reaching a plateau at >60% of the total cycle time at high temperature (Figure 56, Table 22). Each additional percent of total cycle time at 70 or 80°C adds 0.58 or 1.43 points, respectively, to the active enzyme decay rate per day. For example, residing at 80°C for 25% of the cycle results in a 27% active enzyme loss per day; therefore, a 26% cycle time residence would result in an ~28.4% loss per day according to a linear fit of the linearly correlated subset of the data as shown in Figure 56. These results can be used to model the expected change in active enzyme replenishment rate as the residence time per cycle at high temperature is changed. For instance, an ~15-fold reduction in active enzyme loss per day may be achieved by designing a process capable of generating lean solvent at 80°C, with high temperature exposure comprising 5% rather than 60% of the total cycle time. It is expected that limiting the exposure time at high temperature would be beneficial for all types of CAs, and would result in significant performance longevity extension for CAs and CA formulations that exhibit good tolerance of thermal stress (Section 3).

Although further investigation during scale up studies are necessary to confirm these findings, the active enzyme exponential decay rate during the period of no replenishment on the bench-unit measured 84% per 24 h (3.5% per h, see Section 8.3). A data point representing this decay rate as a function of the calculated percent total cycle time in the tube-in-shell reboiler of the bench-unit (with ~77°C bulk liquid, and 90-95°C heating tubes) is plotted in Figure 56, and fits the model generated from the laboratory-scale device.

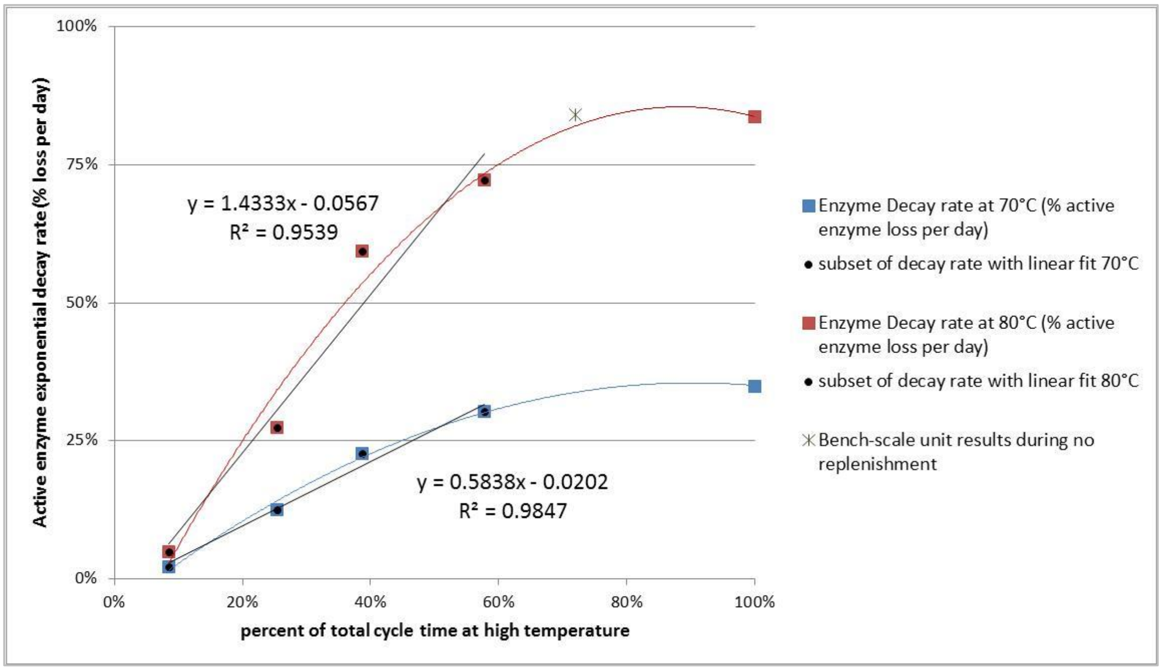


Figure 56. Carbonic anhydrase decay rate as a function of total cycle time at 70 or 80°C in lab-scale device. A subset of the data (as indicated with black filled circles within the data symbols) is used to generate a linear correlation between the plotted variables. Data point from the period of no replenishment on the bench-unit is shown for comparison.

Table 22. Carbonic Anhydrase Decay Rate as a Function of Total Cycle Time at 70 or 80°C in Lab-scale Device or Bench-scale Unit

Percent total cycle time at 70 or 80°C	Enzyme decay rate[a] at 70°C in Novozymes lab-scale device	Enzyme decay rate at 80°C in Novozymes lab-scale device	Enzyme decay rate from UK-CAER bench-scale unit during run period with no enzyme replenishment[b]
8%	2%	5%	
25%	13%	27%	
39%	23%	59%	
58%	30%	72%	
72%			84%
100%	35%	84%	

[a] Enzyme decay rate corresponds to percent active enzyme loss per day (24 h).

[b] Data from the bench-unit during the run period with no enzyme replenishment with the reboiler operating with ~77°C bulk liquid, and 90-95°C heating tubes.

8.5 Summary and Recommendations for Future Work

A dissolved enzyme-promoted K_2CO_3 solvent process was capable of achieving >90% capture in the bench-unit, with capture efficiency dependent on enzyme dose and bench-unit run conditions, the former providing kinetic benefit, and the latter dictating the equilibrium condition that sets the capture efficiency ceiling. Thermal stress experienced by the enzyme during cycling through the high temperature tube-in-shell reboiler (~77°C bulk liquid, and 90-95°C heating tubes) in the bench-unit was a key contributor to the rate of enzyme activity loss. The loss of active enzyme could be corrected by adding a fresh enzyme dose (comprising 20% of the total enzyme in the system) at the start of each run day, resulting in a consistent capture efficiency and enzyme activity in the solvent. This high replenishment rate can be reduced by altering either the high temperature set point of the reboiler, or by reducing solvent residence time per cycle at high temperature (i.e. increasing the efficiency of the stripper). Despite the high active enzyme loss rate, and consequent high replenishment rate, no physical accumulation of active or inactive in-tact enzyme molecules occurred in the liquid. Instead, particles imparting turbidity formed and accumulated in the liquid during bench-scale testing. Analysis of the particles indicated they comprise degraded and aggregated enzyme protein, antifoam, and some contribution of process solids carried over from enzyme manufacturing. In addition to the insoluble particles, dissolved low molecular weight protein – likely resulting from CA thermal degradation – was also detected to gradually accumulate in the solvent over time (Figure 52, B). Thus rather than accumulating as an in-tact molecule, the physical enzyme appears to degrade and to also form insoluble aggregates. A portion of the insoluble particles in the unit were removed via filtration (Section 6.3.2), but others remained in the liquid, and may have caused unstable unit operation (Section 6.2.6). It is expected that improved filtration or a solid-liquid separation, such as centrifugation, could be used to mitigate the impact of undesired solids formation on system performance.

Future work with a dissolved enzyme process should focus on enzyme candidates that can accumulate at the gas-liquid mass transfer interface, which is expected to result in an enzyme-dose reduction, improving process economics. Candidates with enhanced thermal stability will also reduce active enzyme loss, with consequent reduction in the active enzyme replenishment required, and related accumulation of enzyme-derived insoluble solids resulting from thermal degradation/aggregation of inactive enzyme molecules. In addition to identifying and engineering more stable CA candidates using biotechnical techniques, enhanced stability could also be achieved by chemical modification of the enzyme and/or combining the enzyme with a stable physical matrix, coating, or entrapment technology that could protect and prevent the enzyme from unfolding and degrading when exposed to harsh conditions. Reactor configurations that decrease enzyme exposure to the high temperature stripper, via reduced temperature or residence times per cycle, would achieve the same ends. Careful attention should also be paid to mechanisms of removing the insoluble solids that can otherwise accumulate in the system over time, and potentially disrupt unit operation and CO_2 capture efficiency.

9 ENVIRONMENTAL, HEALTH AND SAFETY ASSESSMENT

Due to the nature of many solvents involved in existing carbon capture processes and their by-products, there is a focus on the assessment of the environmental friendliness and safety of the materials and processes of potential technologies. Within Task 7.1 (EH&S Assessment) all potential ancillary or incidental air, water and solid emissions from the process were identified and magnitudes of emissions were estimated to determine potential health and environmental effects and to determine compliance with the following U.S. Federal EH&S laws:

- Comprehensive Environmental Response and Liability Act of 1980 (CERCLA)
- Toxic Substances Control Act (TSCA)
- Clean Water Act (CWA)
- Clean Air Act (CAA)
- Superfund Amendments and Reauthorization Act (SARA) Title III
- Occupational Safety and Health Act (OSHA)

For any potential hazards, an engineering analysis was undertaken to identify ways in which they can be eliminated or minimized. Handling, storage, treatment and disposal of PCC plant feedstock and waste were also considered where applicable.

9.1 Proposed PCC Process Overview

The bulk removal of CO_2 from high volume gases by the use of chemical absorbents is a well-established technique used for the "sweetening" of fuel gas (e.g. natural gas) throughout the petrochemical industry. This conventional amine based process has been adapted with the application of 23.5 wt% K_2CO_3 solvent, CA enzyme and vacuum stripping technologies. Figure 57 provides a simplified process flow diagram (PFD) to describe the flue gas and solvent paths.

The CO_2 is absorbed from the flue gases into an aqueous 23.5 wt% K_2CO_3-based chemical solvent containing dissolved CA enzyme within the CO_2 absorber column removing 90% of the incoming CO_2 with the remaining off-gas discharged to atmosphere through a stack. The soluble CA enzyme accelerates the inter-conversion between dissolved CO_2 and bicarbonate ions and K_2CO_3 in the solvent provides sufficient alkalinity and loading capacity (alternatively called "buffering" capacity) to absorb CO_2 in the form of bicarbonate. The CO_2-laden solvent collected at the bottom of the absorber tower, termed 'rich' solvent, is passed to a regeneration section where the application of heat reverses the inter-conversion between dissolved CO_2 and bicarbonate ions and releases the CO_2 as gas. The gaseous CO_2 is removed from the vacuum stripper and passed to a compression and dehydration system prior to being dispatched for storage or utilized for purposes, such as enhanced oil recovery. The now relatively CO_2-free solvent, termed 'lean' solvent, is returned to the absorber column. Fresh CA enzyme-containing solvent is added to the system as needed via the solvent supply/storage system, and can be metered using conventional liquid handling systems.

An additional feature of the system is the inclusion of a solvent and CA enzyme reclaimer unit which serves to maintain system performance by continuously withdrawing a slipstream of lean solvent and allowing separation of deactivated CA enzyme, which can agglomerate to form suspended solids in the solvent. Replenishment with fresh dissolved CA enzyme makes up for the amount of inactivated CA enzyme withdrawn and the combination of spent CA enzyme removal; together with fresh CA enzyme replenishment keeps the amount of active CA enzyme in the system at the correct level to maintain stable performance. Also, if needed, these systems can be used to increase or decrease the level of active CA enzyme in the system, for example to accommodate fluctuations in flue gas feed or composition of the gas stream. These features use conventional liquid dosing and solid-liquid separation technologies to achieve straightforward, flexible process control.

9.2 Potentially Emitted Species

A review of potential species that could be emitted from the PCC process, the sources of the emissions and potential mitigation was carried out. Areas of the plant where trace amounts of material could be released were ignored for the purposes of the study. Figure 58 gives an overview of the PCC process with potential species emissions, their sources and possible mitigation measures.

Following the identification of potentially emitted species, a literature review was undertaken to identify the EH&S effects of the species. As part of the review, material safety data sheets (MSDS) were sourced and the detailed information was consolidated in a tabular form in the EH&S Topical Report, identifying the potentially emitted species, the sources of emissions, physical states of emissions, the EH&S effects of the species emitted, pertinent properties of the species and the National Fire Protection Association (NFPA) 704 Standard System for the Identification of the Hazards of Materials for Emergency Response categorization.

Risk assessments were carried out for each potential emission species and assigned a risk level using the designations shown in Table 23. Identified risks were considered to be low probability with low consequence; none were high probability with high risk. Mitigation measures were outlined in the report.

Table 23. Risk Assessment Designations

Probabilities		Consequences	
VL – Very Low	Probably will never happen	VM – Very Minor	Temporary Discomfort
L – Low	Might happen but would be an unusual occurrence	Min – Minor	Minor Injury
M – Medium	Expected to happen sometimes	Maj – Major	Major Injury
H – High	Expected to happen frequently	F - Fatality	Fatality

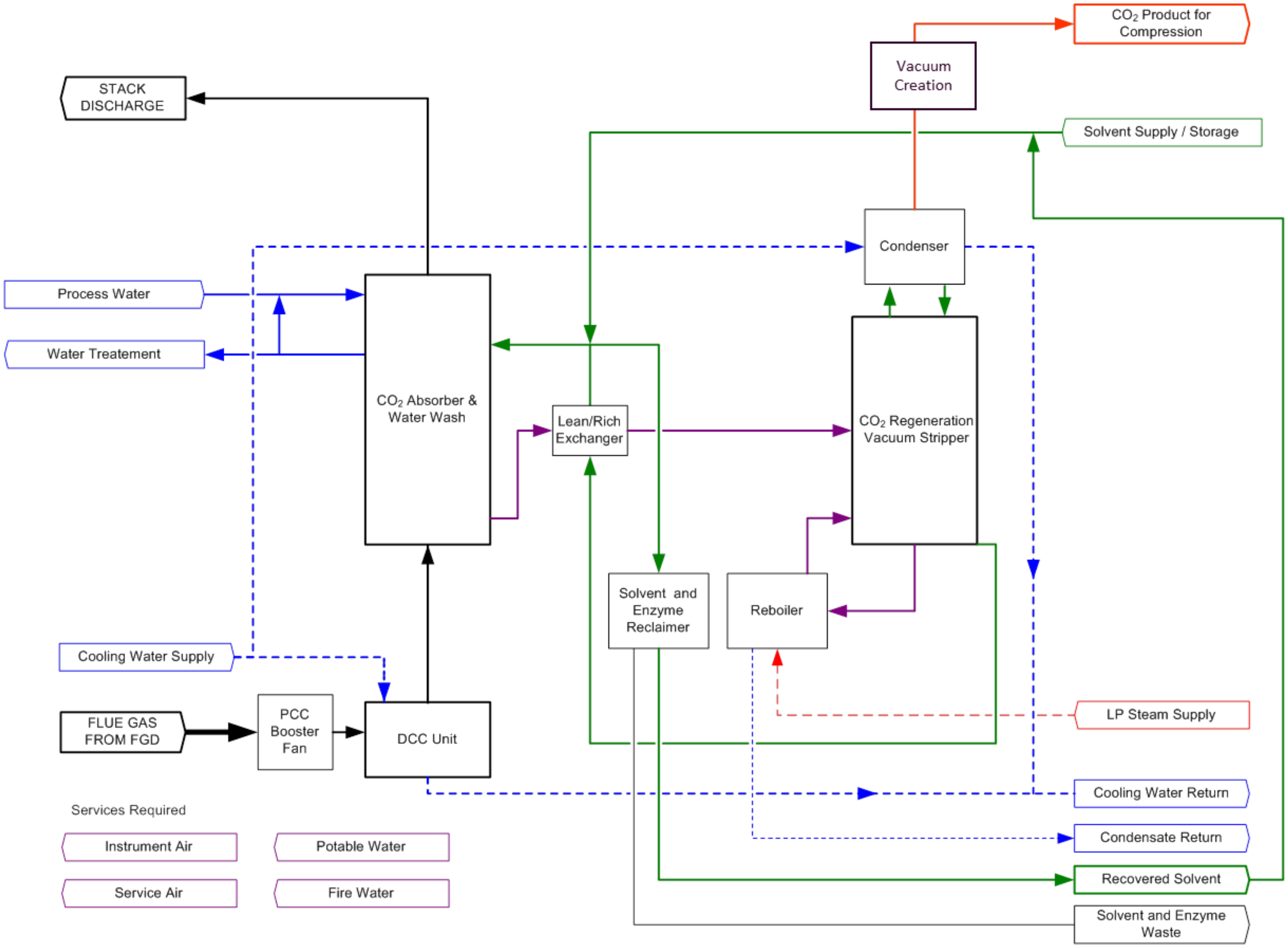
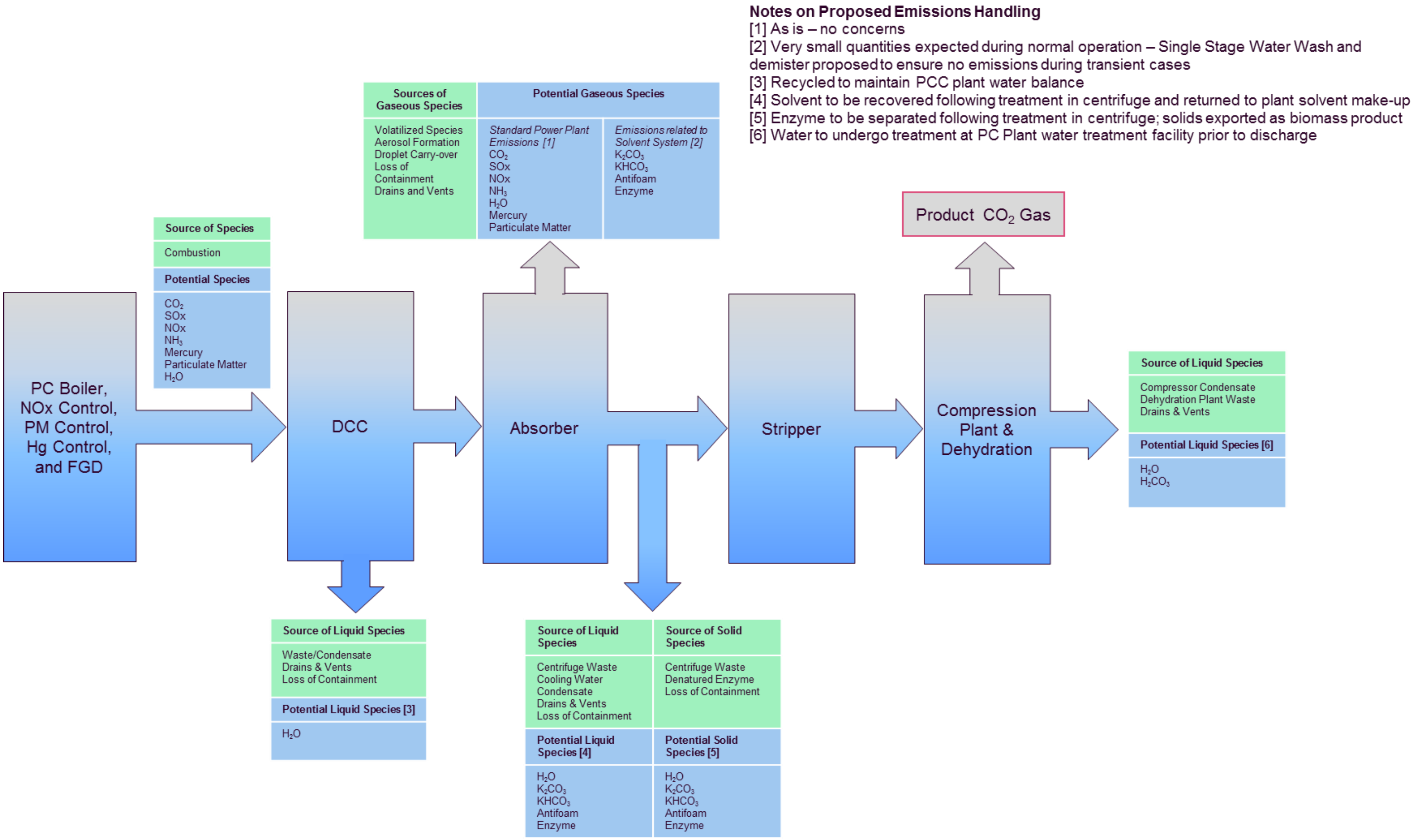


Figure 57. Simplified PFD of full plant PCC system.



Notes on Proposed Emissions Handling
[1] As is – no concerns
[2] Very small quantities expected during normal operation – Single Stage Water Wash and demister proposed to ensure no emissions during transient cases
[3] Recycled to maintain PCC plant water balance
[4] Solvent to be recovered following treatment in centrifuge and returned to plant solvent make-up
[5] Enzyme to be separated following treatment in centrifuge; solids exported as biomass product
[6] Water to undergo treatment at PC Plant water treatment facility prior to discharge

Figure 58. PCC capture plant overview with potential emissions, sources and mitigation.

9.3 Gaseous Emissions

The emissions review shown in Figure 58 determined all species that could be expected to be either emitted as a gas or entrained within the gas stream. Expected emissions during normal steady-state operation were estimated utilizing models of the PCC plant developed in AspenTech's AspenPlus® software, bench scale test results from the University of Kentucky, and industrial experience of emission results from a slipstream PCC plant utilizing amine-based solvents. Emissions during process upset conditions were not included in the scope of the study, although mitigation methods to minimize emissions in transient cases were considered.

The potential species leaving the stack as gases are typical PC plant emissions and as such are well understood. Nitrogen, argon, oxygen and moisture have been ignored here as they are abundant in air and pose no EH&S risks at the plant operating conditions. The remaining expected gaseous species emissions are all similar to the levels that would be emitted from an equivalent PC power plant, other than CO_2, which is removed in the PCC plant. The gases are emitted from the absorber off-gas stack at ambient pressure and a temperature of 40°C. The expected magnitudes of the gaseous species emissions leaving the absorber off-gas stack after the PCC process are shown in Table 24, the values are based on the anticipated output from a 685 MWe power plant with an 85% capacity factor that delivers a net output of 550 MWe and 90% CO_2 capture.

Table 24. Anticipated PCC Plant Gaseous Emissions

Emission	Amount		
	kg/GJ (lb/10^6 Btu)	Tonne/year (Ton/year) 85% CF	kg/MWh (lb/MWh)
SO_2	0.037 (0.085)	1,795 (1,979)	0.353 (0.778)
NO_x	0.03 (0.07)	1,467 (1,617)	0.288 (0.636)
Particulates	0.006 (0.013)	273 (300)	0.054 (0.118)
Hg	4.95 x 10^{-7} (1.15 x 10^{-6})	0.024 (0.027)	4.76 x 10^{-6} (1.05 x 10^{-5})
CO_2	8.5 (19.7)	414,411 (456,810)	81 (180)
CO_2[a]			101 (223)

[a] CO_2 emissions based on net power instead of gross power.

Other potential routes for emissions leaving the absorber off-gas stack are liquid droplets entrained in the off-gas stream or formation and release of aerosols from the SCR, FGD or from within the PCC plant. The potential for aerosol formation and control cannot be estimated at this stage and it is not known whether a simple single-stage water wash and demister would eliminate the emissions during transient cases in their entirety. However, given the benign nature of species utilized in the capture plant and the likely small quantities released during transient operation, the formation of aerosols is not likely to cause EH&S concerns. During normal operation there are not expected to be any liquid species emitted entrained in the off-gas.

The potential for aerosol formation and implementation of more advanced water wash strategies should be investigated further with experimental evidence and measurement from larger-scale demonstrations, particularly with regard to the presence of enzyme in the solvent. Any future study would have to monitor enzyme-containing aerosol emissions in the off-gas to ensure that they do not exceed the generally accepted exposure limit, and demonstrate that the proposed engineering controls to prevent such emissions are adequate.

9.4 Liquid Emissions

The anticipated liquid emissions were determined and quantified utilizing the same methodology as for gaseous emissions. Four potential sources of liquid emissions from the PCC plant were identified.

- *Water condensed from moisture in the flue gas after passage through the direct contact cooler (DCC).* Due to recycling of the condensed water, no water emissions are expected from the DCC and the PCC plant is expected to have a net positive water balance, reducing the PC boiler water make-up requirements.
- *Bleed water from the water wash loop at the top of the absorber*. The emissions expected here are trace amounts of enzyme, antifoam, K_2CO_3 and potassium bicarbonate ($KHCO_3$) with almost all the remaining waste stream being water. Analysis of the water wash bleed stream needs to be carried out on a larger-scale process demonstration plant to determine the expected levels of emissions.
- *Water from the compressor inter-stage coolers where condensate is removed from the CO_2 product stream before export*. As for the DCC, there is potential for the condensate to be slightly acidic due to the presence of H_2CO_3, however, the model was not able to predict the acidity. As with the DCC condensate, it is proposed to utilize the compressor condensate within the PCC plant for water make-up with excess being sent along with DCC condensate to the PC boiler water treatment plant to undergo demineralization for use as boiler feed water.
- *Liquid emissions from the enzyme and solvent reclaimer*. During normal operation of the PCC plant, the enzyme degrades thermally, loses its catalytic activity and needs to be replenished. Maintaining performance in the system requires replenishment with fresh enzyme and removal of produced solids. To do this, a slipstream of lean solvent is extracted from the system and passed to a centrifuge separator where the deactivated enzyme is removed as a moist solid sludge along with some K_2CO_3 solution.

9.5 Solid Emissions

The anticipated solid emissions were determined and quantified utilizing the same methodology as for gaseous and liquid emissions. There is only one source of solid emissions during normal operation of the PCC plant and that is the waste stream from the solvent and enzyme reclaimer. During normal operation of the PCC plant, the enzyme degrades thermally, loses its catalytic activity and needs to be replenished. The loss of enzyme activity decreases the solvent effectiveness and increases the energy consumption of the capture process, and causes a build-up of solids that have to be removed. To do this, a slipstream of lean solvent is extracted from the system and passed to a centrifuge separator where the deactivated enzyme is removed as a moist solid sludge along with some K_2CO_3 solution.

Using wet solids removal and solvent flow rate data from the bench-scale unit, lab-scale thermal cycling tests, the observed enzyme thermal degradation rates and model-predicted solvent flow rates, the amount of solid removed during centrifuge separation has been estimated and is displayed in Table 25.

Table 25. Anticipated PCC Plant Wet Solid Emissions

Species	Anticipated Emissions at 85% capacity factor, Tonne/year (Ton/year)
Denatured Enzyme	125.7 (138.6)
Enzyme/K_2CO_3/$KHCO_3$/Antifoam/H_20	712.5 (785.4)
Total Wet Solids	838.2 (924.0)

The solid emissions will consist of K_2CO_3 salt, denatured enzyme, enzyme and antifoam although the contribution of each of the individual components could not be easily quantified because the waste was removed during bench-scale testing as a wet solid for which there was insufficient data to provide exact quantities of constituent components during the course of the project. The anticipated emissions are based on a slipstream to be sized for removal of solids at the rate of production and enzyme denaturation after taking typical centrifuge separator solid removal efficiency into account. To eliminate the uncertainty regarding exact quantities and compositions, the application of a centrifuge separator should be tested on a larger-scale demonstration plant with the emissions measured and closely monitored.

The ultimate fate of the solid species is dependent on the final destination of the moist solid sludge waste stream. The preferred route is to create an additional product stream from the waste, much like the gypsum product stream from the FGD waste. It is proposed that the moist solids be removed by road tanker for composting applications or used as fertilizer where the potassium content would provide a benefit and the antifoam would have no negative effect. The product potential of any waste stream would have to be evaluated once confirmed compositions and quantities had been determined from a larger-scale process demonstration plant employing the proposed separation technology. If the formation of a product stream is not viable then it is proposed that the solid sludge be removed from the plant by a specialist contractor for disposal as landfill. This waste stream would be considered as non-hazardous.

9.6 Conclusions

A preliminary environmental, health and safety (EH&S) risk assessment for an enzyme-activated potassium carbonate (K_2CO_3) solution post-combustion CO_2 capture (PCC) plant delivering 90% capture, integrated with a subcritical pulverized coal (PC) power plant with a net output of 550 MWe, was prepared and submitted as a Topical Report containing additional details beyond what is presented in this summary.

The expected emissions during normal steady-state operation were estimated utilizing models of the PCC plant developed in AspenTech's AspenPlus® software, bench scale test results from the University of Kentucky, and industrial experience of emission results from a slipstream PCC plant utilizing amine based solvents. A review of all potential emission species and their sources was undertaken that identified two credible emission sources, the absorber off-gas that is vented to the atmosphere via a stack and the waste removed from the PCC plant in the centrifuge used to reclaim enzyme and solvent. The conditions and compositions of the emissions were calculated and the potential EH&S effects were considered as well as legislative compliance requirements. Potential mitigation methods for emissions during normal operation were proposed and solutions to mitigate uncontrolled releases of species were considered.

The potential gaseous, liquid and solid emissions were quantified and assessed for PCC plant normal operation and were found to pose no significant EH&S concerns and were compliant with the Federal EH&S legislation reviewed. However, the limitations of scaling up a process from bench scale data to representative full scale plant are understood and several areas were identified for further monitoring and measurement on a larger scale demonstration, utilizing the proposed mitigation and separation methods to confirm expected emissions and reduce uncertainty.

10 TECHNICAL AND ECONOMIC ASSESSMENT

Both a preliminary and full Technical and Economic Assessment (TEA) of the proposed CO_2 capture system were prepared and submitted as Topical Reports. Key elements of the two reports are summarized here.

The preliminary TEA focused on assessment of a novel enzyme-activated potassium carbonate PCC process using ultrasonically-enhanced regeneration. As described in previous sections of this report, although the preliminary TEA was favorable, the prototype ultrasonic regenerator evaluated during Budget Period 2 testing did not deliver the necessary level of CO_2 release. As a result, the remaining bench-scale work focused on the vacuum regeneration approach. A summary of the preliminary TEA findings is included in this Final Report, and further details of that assessment can be found in the corresponding Topical Report [69].

The full TEA focused on evaluation of five cases consisting of a subcritical PC fired power plant with different PCC plant configurations utilizing enzyme-activated potassium carbonate solvent together with vacuum regeneration at different pressures and with different sources of steam. The design of each power plant was based on a PC steam generator firing Illinois No. 6 coal and a steam turbine. The entire coal-fired power plant, including the integrated PCC plant, was modelled and optimized for 550 MWe net output to allow for a meaningful comparison among the five cases and the baseline cases of NETL Case 9 (subcritical PC boiler without CO2 capture) and NETL Case 10 (subcritical PC boiler with amine based CO_2 capture). The full TEA Topical Report [72] is appended to this Final Report as Appendix I.

10.1 Preliminary Technical and Economic Assessment (Preliminary TEA)

A preliminary technical and eeconomic evaluation of a novel enzyme-activated potassium carbonate PCC process using ultrasonically-enhanced regeneration integrated with a subcritical pulverized coal (PC) power plant was carried out during Budget Period 1 of the project. The evaluation utilized DOE/NETL Case 10 cost and performance baseline study results for a pulverized coal subcritical power plant integrated with Econamine FG Plus^{SM} post-combustion carbon capture process [106]. Process simulation and modeling for absorption was performed using AspenTech's AspenPlus$^{®}$ (with Radfrac module) software together with project partner technical know-how of the operation of the individual unit operations in the PCC process. The resulting performance parameters of the optimized PCC plant were used to calculate the power requirements of the process and size the equipment for cost estimation. AspenTech's Capital Cost Evaluator$^{®}$ (CCE$^{®}$) Parametric Software and recent vendor quotations were utilized to perform the cost estimation of the PCC process.

The preliminary techno-economic assessment compared four cases utilizing the novel enzyme-activated solvent with four different regeneration approaches versus the DOE/NETL reference Case 10 [106]:

- Case 1: Vacuum Stripping using Low Pressure (LP) steam
- Case 2: Vacuum Stripping using Very Low Pressure steam, at 8 psia
- Case 3: Ultrasonic Regeneration using LP steam
- Case 4: Ultrasonic Regeneration using VLP steam, at 8 psia

Unlike the ultrasonic regeneration cases, where the lean and rich solvent boundaries were fixed, process modeling of the vacuum stripping cases was performed in Aspen Plus® for the entire process (including the regeneration section). Several simulations were performed to reproduce the process conditions in the system boundaries. The recirculation pumps in all cases were sized so that the residence time of the solvent in the hot section of the PCC process is as short as possible to minimize thermal degradation of the enzyme.

10.1.1 Kinetic Assumptions for Modeling

In order to address the system mass transfer for the proposed enzyme-promoted solvent adequately, it was necessary to provide an absorber column mass transfer coefficient consistent with the proposed enzyme-promoted system. Since mass transfer coefficients were not available for the enzyme-promoted carbonate solvent, it was necessary to determine them for the purpose of modeling the process from the basis of the fundamental reactions and the experimental work conducted as part of the project.

The system mass transfer coefficients were established by reducing the energy of activation of the water hydrolysis reaction, Reaction 5, to achieve the target overall mass transfer coefficient. The target mass transfer coefficient was set at 50% of the value for MEA. This value was established using the overall mass transfer coefficient obtained from WWC experiments at the same temperature and gas flow rates.

10.1.2 Ultrasonic Energy Demand Assumptions

PNNL batch laboratory testing provided measurements of the release of CO_2 from a loaded 20 wt% K_2CO_3 solution using ultrasonic energy. The type of ultrasonic horn used in the batch testing was for laboratory demonstration purposes only and not representative of a commercial-scale energy efficient system. Further, the batch system was not optimized for stripping the evolved CO_2 as it formed, resulting in a significant amount of gas bubble re-absorption. Nevertheless, using both the ultrasonic power input and CO_2 evolution from the batch tests, an electricity demand of 10.3 kJ/mol of CO_2 was calculated. Aspen Plus® simulations for K_2CO_3 solvent with vacuum stripping, within the operating condition constraints, predicted solvent recirculation rates of approximately 60 MM lb/h, and a normalized CO_2 removal rate of 0.021 lb CO_2/lb recirculated solvent. Based on this metric, the "scaled-up" batch laboratory energy demand is 4.9 J/g of solvent, and a total electric parasitic power load of 37 MW_e for application of the ultrasonic regeneration system to Case 10 of the DOE/NETL Study [106].

In order to project a more accurate estimate of commercial ultrasonic energy demand, several literature sources were reviewed. One of the most developed applications for liquid treatment using ultrasonic energy is water sterilization. A comprehensive reference of ship ballast water gives ranges of both energy and capital costs for large-scale ultrasonic waste treatment systems. The normalized energies for that application ranged from 0.24 to 0.79 J/g of water [100]. Using a conservative assembly of commercial sonication devices, the power estimate for the proposed degassing system is 1.5 J/g of solvent, which is twice that of the maximum value for ship ballast water treatment and a third of that demonstrated in the batch ultrasonic system. This normalized energy parameter is recommended for use in large-scale electricity projections for ultrasonic regeneration, and equates to just over 11 MW_e of parasitic power for the ultrasonic system applied to Case 10 of the DOE/NETL Study [106].

Process modeling for the ultrasonic regeneration case was carried out by assuming that a sufficiently lean solvent can be obtained from the ultrasonic regeneration section, when provided with the rich solvent from the absorber section. The process conditions and stream properties for the rich and lean solvent entering and exiting the ultrasonic regeneration section were assumed to be identical to the vacuum stripping case.

10.1.3 Preliminary Assessment Results

The results compared the energy demand for post-combustion CO_2 capture and the net plant efficiency based on the higher heating value (HHV) of the power plant integrated with the PCC plant. A levelized cost of electricity (LCOE) assessment was performed showing the costs of the options presented in the study. Key factors contributing to the reduction of LCOE were identified as enzyme utilization and the capability of the ultrasonic regeneration process.

Table 26 shows the power consumption (and generation) summary for the various cases considered in comparison with Case 10 of the 2007 DOE/NETL Study [106]. Note that unused steam in stream 17 of Exhibit 4-15 of the DOE/NETL Study [106] was used to calculate the additional gross power that could be generated from the steam turbine using the electric power equivalent provided in the Funding Opportunity Announcement [107]. An alternative to using steam from the intermediate-to-low pressure (IP/LP) steam turbine crossover, as in the NETL MEA-based reference Case 10, would be the use of low-pressure (and low quality) steam at 8 psia and 85°C. Additional steam turbine performance calculations were performed for Cases 2 and 4, to evaluate the power consumption of the PCC process based on extracting VLP steam. VLP steam has a power generating efficiency of 11% compared with the typical 24% in the case of the IP/LP crossover steam.

In all the cases, additional compression requirements were considered to achieve the outlet composition and conditions of stream 19 in Exhibit 4-15, Case 10 of the DOE/NETL Study [106]. Note that Aspen Plus® accounts for all the elements of energy required for vacuum stripping (Cases 1 and 2). However, in the case of ultrasonic regeneration, due to the thermal energy being supplemented by electrical energy, the regeneration energy was calculated as the sum of the minimum energy required to strip the solvent (based on the heat of CO_2 desorption) plus the heat lost due to the evaporation of water. This value represents the theoretical minimum that is required for solvent regeneration. The minimum energy required for reversal of the CO_2 absorption reaction is 78.914 MW_e, and 59.555 MW_e for the evaporation of water (Case 3). In Case 4, a conservative value of 15MW_e was assumed for ultrasonics, and 123.469MW_{th} for the thermal contribution. The heat of regeneration for the PCC plant was calculated in terms of kilograms of CO_2 scrubbed per kilowatt-hour of electrical energy that could have been produced.

The LCOE was calculated for all cases using estimated capital and O&M costs (as described in in the Topical Report [69]. Table 27 provides the LCOE values for all the cases investigated. Note that these were the values from a preliminary evaluation that was used as a starting point for optimization of the technology. At this preliminary point in the evaluation, the optimized case for ultrasonic regeneration provided the lowest LCOE of all the cases considered. Even though it represented a 68.51% increase in LCOE compared with the PC power plant without PCC, it was anticipated that this value could be reduced through better understanding of the technology.

Table 26. Preliminary TEA Power Summary

	NETL_2007 Case 10	Case 1	Case 2	Case 3	Case 4
GROSS (STEAM TURBINE) POWER, kW_e	**679,923**	**702,321**	**826,695**	**861,695**	**843,695**
CO_2 Capture System Auxiliaries	23,500	27,798	27,798	27,798	27,798
Vapor Compression	N/A	30,459	30,459	791	791
Ultrasonic Energy Demand	N/A	N/A	N/A	138,469	15,000
TOTAL AUXILIARIES, kW_e	130,310	165,067	165,067	273,868	150,399
NET POWER, kW_e	**549,613**	**537,254**	**661,628**	**587,827**	**693,296**
Net Plant Efficiency (HHV)	24.90%	24.34%	29.97%	26.63%	31.41%
Net Plant Heat Rate (Btu/kWh)	13,724	14,040	11,401	12,832	10,880
CO_2 Regeneration Energy (kg of CO_2/kWh_e)	3.445	3.299	9.566	4.497	18.531
% Improvement over Case 10 [2]	-	- 4.25	177.68	30.52	437.91

Table 27. Preliminary TEA LCOE Calculations

Summary of Levelized Costs (2007 $/$MWh_e$)	NETL Case 9	NETL Case 10	Case 1	Case 2	Case 3	Case 4
Fuel Cost	20.43	30.06	30.75	24.97	28.11	23.83
Capital Cost	34.44	68.71	70.51	67.72	67.37	65.80
Variable Operating Cost	5.88	10.92	13.94	11.32	12.51	10.61
Fixed Operating Cost	3.89	5.86	5.99	4.867	5.47	4.64
Transportation, Sequesration & Monitoring (TSM)	-	4.04	4.04	4.04	4.04	4.04
Total LCOE	64.64	119.59	125.23	112.92	117.50	108.92
Increase versus No Capture	-	85.04%	93.78%	74.72%	81.79%	68.51%

A comparison of Case 2 (Vacuum Regeneration) to Case 4 (Ultrasonic Regeneration) including consideration of the steam quality used is summarized in Table 28. The 0.0665 kWh/lb of steam power equivalent option represents the optimized turbine steam extraction location, taking advantage of the very low solvent regeneration temperatures enabled by the K_2CO_3-based capture system, hence reducing the overall energy penalty.

Table 28. Efficiency and LCOE for Preliminary Cases 2 (Vacuum) and 4 (Ultrasonic)

Power Equivalent (kWh/lb steam)	Case	Net Efficiency (%)	LCOE (2007$/MWh$_e$)
	DOE/NETL Case 10	24.9	119.6
0.0911	Case 2, Vacuum Regeneration	24.3	125.2
	Case 4, Ultrasonic Regeneration	26.6	117.5
0.0665	Case 2, Vacuum Regeneration	30.0	112.9
	Case 4, Ultrasonic Regeneration	31.4	108.9

The preliminary techno-economic evaluations of the ultrasonic and vacuum regeneration processes integrated with a subcritical PC power plant predicted net efficiency improvement of up to 25% versus NETL Case 10. Subsequent to this analysis, based on the limitations in actual ultrasonics performance discussed in Section 4, the work with ultrasonic regeneration was discontinued, and remaining project efforts were focused on closer evaluation of the vacuum regeneration approach. This approach was supported by the preliminary TEA prediction that vacuum regeneration using VLP steam could require 43% less parasitic power from a PC power plant compared with NETL Case 10 (Table 7).

A summary of the full techno-economic assessment of the vacuum regeneration cases considered is presented in Section 10.2, where it should be noted that assumptions used during the preparation of the preliminary TEA were updated as further knowledge of the system and system performance were gained. Therefore, a direct comparison between the preliminary and full TEA findings may not be possible, and the findings presented in the full TEA are deemed to be the more reliable.

10.2 Full Technical and Economic Assessment (Full TEA)

A full technical and economic evaluation of a novel enzyme-activated potassium carbonate PCC process using vacuum regeneration integrated with a subcritical pulverized coal (PC) power plant was carried out during Budget Period 3 of the project. Aspects of the process include the application of a dissolved CA enzyme catalyst to promote CO_2 absorption in a low enthalpy K_2CO_3 based solvent and the incorporation of a vacuum stripping process to release CO_2 at a moderate temperature. The preliminary TEA indicated potential for energy savings using a vacuum regeneration process, and, with respect to a process where the dissolved enzyme travels throughout the system together with the solvent, an important benefit of being able to use low temperature regeneration would be to extend enzyme longevity. The purpose of the full techno-economic assessment was to more comprehensively determine the potential energy benefit of a low temperature regeneration process, including closer consideration of capital costs and practical feasibility of the necessary vacuum generation, as well as more rigorous assessment of the prototype enzyme longevity and replenishment requirements. The full TEA was submitted as a Topical Report [71]. A simplified process flow diagram of the PCC plant is shown in Figure 57. A simplified composite schematic showing the integration of the PCC plant with the PC power plant is shown in Figure 59 to illustrate key features of the five cases evaluated in comparison to NETL cases 9 and 10. A summary of the full TEA findings is presented in this section.

10.2.1 Case Descriptions

Using information gathered from the bench scale unit, validated kinetic data, PCC plant predictive models and industrial experience of PCC plant design and cost estimation. The process and cost performance of several cases were analyzed and compared to NETL baseline Case 9 and Case 10 to judge relative performance. Four cases utilizing the enzyme-activated solvent and one case with solvent containing no enzyme were compared, using vacuum regeneration at different pressures with different sources of steam, against the NETL Case 10 [72] as described in Table 29.

Table 29. Full Techno-economic Analysis Case Descriptions

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

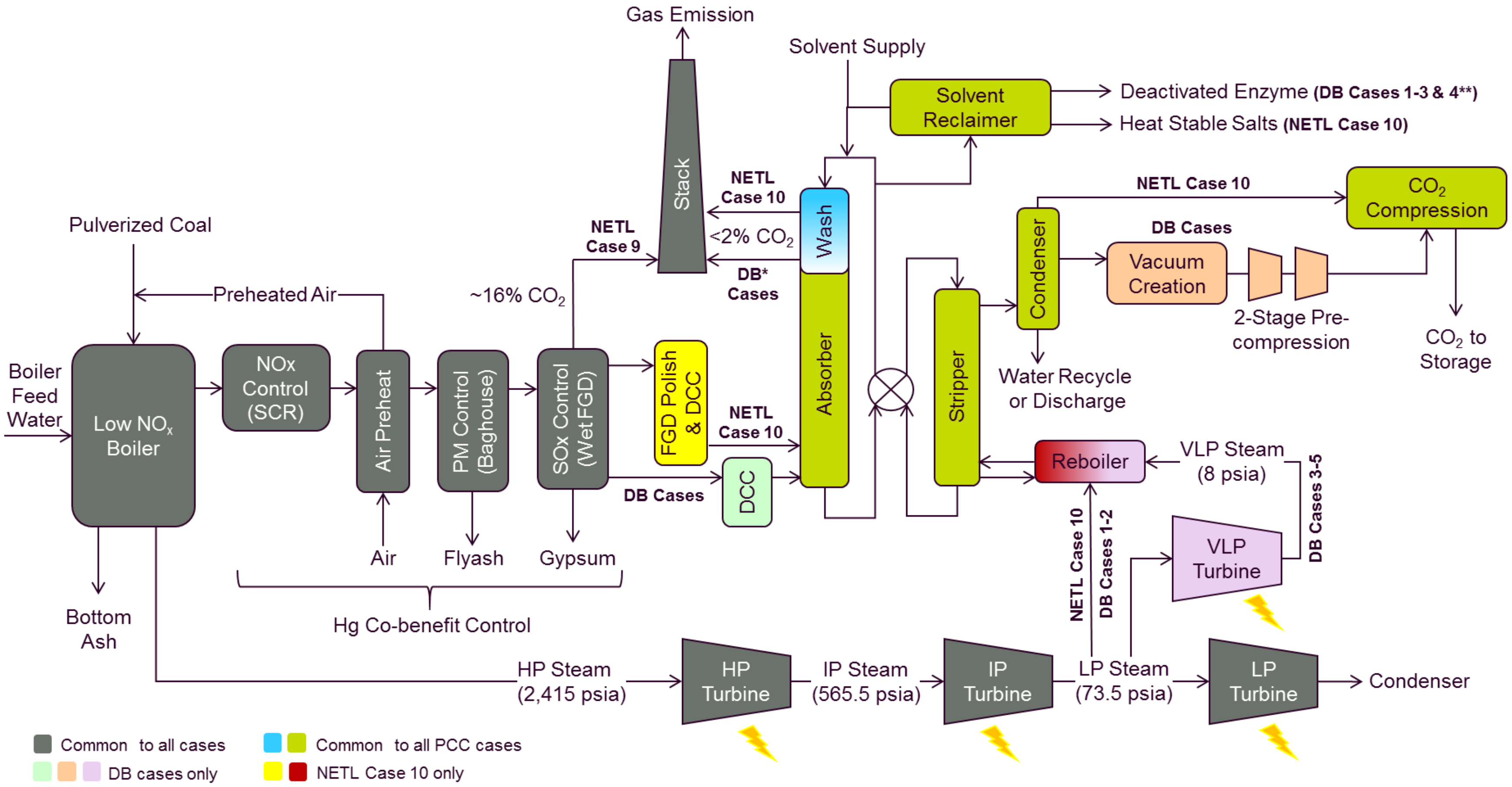


Figure 59. PC Power plant schematic with PCC cases considered. Notes: * DB cases use environmentally benign solvent with expectation for lower solvent carryover versus NETL Case 10; ** Although enzyme does not enter the stripper in case DB4, replenishment estimations were based on case DB3 to account for process adaptation to exclude enzyme from the stripper.

10.2.2 Plant Description

Five subcritical PC fired power plants with different PCC plant configurations were evaluated. The design of each PC plant is based on a PC steam generator firing Illinois No. 6 coal and a steam turbine. The entire coal-fired power plant, including the integrated PCC plant, has been modelled and optimized for 550 MWe net output to allow for a meaningful comparison among the five cases and the baseline cases of NETL Case 9 (subcritical PC boiler without CO_2 capture) and NETL Case 10 (subcritical PC boiler with amine based CO_2 capture) [72].

Each design is based on market-ready technology that is assumed to be commercially available for the plant startup date. To maintain consistency with the NETL baseline Cases in [72] the following single-reheat steam conditions were used in all cases:

16.5MPa/566°C/566°C (2,400 psig/1,050°F/1,050°F)

The steam conditions were selected based on a survey of boiler and steam turbine original equipment manufacturers (OEM), who were asked for the most advanced steam conditions that they would guarantee for a commercial project in the US with a subcritical PC unit rated at nominal 550 MWe net capacity and firing Illinois No. 6 coal as reported in [72]. Detailed plant descriptions are provided in the full TEA Topical Report [71].

10.2.3 Performance and Cost Results

The full tabulated performance and cost summary of results from NETL Cases 9 and 10, and Cases DB1-5 is shown in Table 30. The cost of energy (COE) contribution for each case, comprising CO_2 transportation, storage and maintenance (TS&M) costs, fixed costs (e.g. labor), fuel costs (coal), capital costs (equipment), variable costs (e.g. solvent and biocatalyst), is presented in Figure 60.

Table 30. Full TEA Performance and Cost Results

Case	**Case 9[1]**	**Case 10[1]**	**Case DB1**	**Case DB2**	**Case DB3**	**Case DB4**	**Case DB5**
Performance							
CO_2 Capture	0%	90%	90%	90%	90%	90%	18%
Gross Power Output (kWe)	582,600	672,700	682,814	724,569	668,721	666,275	N/A
Auxiliary Power Requirement (kWe)	32,580	122,740	132,814	174,569	118,721	116,275	
Net Power Output (kWe)	550,020	549,960	550,000	550,000	550,000	550,000	
Coal Flowrate (lb/hr)	437,378	614,994	533,723	560,964	478,278	476,528	
HHV Thermal Input (kWth)	1,495,379	2,102,643	1,823,296	1,916,357	1,633,886	1,627,909	
Net Plant HHV Efficiency (%)	36.8%	26.2%	30.2%	28.7%	33.7%	33.8%	
Net Plant HHV Heat Rate (Btu/kWh)	9,277	13,046	11,312	11,889	10,136	10,099	
Raw Water Withdrawl (gpm/MW_{net})	10.7	20.4	16.9	19.2	15.2	13.4	N/A
Process Water Discharge (gpm/MW_{net})	2.2	4.7	4.4	5	4	3.5	
Raw Water Consumption (gpm/MW_{net})	8.5	15.7	12.5	14.2	11.2	9.9	
CO_2 Emissions (lb/MMBtu)	204	20	19.7	19.9	19.9	19.9	N/A
CO_2 Emissions (lb/MWh_{gross})	1,783	217	180	179	179	165	
CO_2 Emissions (lb/MWh_{net})	1,888	266	223	236	236	200	
SO_2 Emissions (lb/MMBtu)	0.0858	0.0017	0.085	0.067	0.067	0.067	
SO_2 Emissions (lb/MWh_{gross})	0.7515	0.0176	0.778	0.604	0.558	0.558	
NO_x Emissions (lb/MMBtu)	0.070	0.070	0.070	0.070	0.070	0.070	
NO_x Emissions (lb/MWh_{gross})	0.613	0.747	0.636	0.634	0.586	0.586	
PM Emissions (lb/MMBtu)	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	
PM Emissions (lb/MWh_{gross})	0.114	0.139	0.118	0.118	0.109	0.109	
Hg Emissions (lb/TBtu)	1.143	1.143	1.15	1.16	1.16	1.16	
Hg Emissions (lb/MWh_{gross})	1.00E-05	1.22E-05	1.05E-05	1.05E-05	9.67E-06	9.67E-06	
Cost							
Total Plant Cost (2007$/kW)	1,622	2,942	2,964	3,141	3,006	3,006	N/A
Total Overnight Cost (2007$/kW)	1,996	3,610	3,658	3,863	3,699	3,699	
- Bare Erected Cost	*1,317*	*2,255*	*2,258*	*2,387*	*2,268*	*2,268*	
- Home Office Expenses	*124*	*213*	*213*	*225*	*214*	*214*	
- Project Contingency	*182*	*369*	*373*	*397*	*385*	*385*	
- Process Contingency	*0*	*105*	*120*	*132*	*139*	*140*	
- Owner's Costs	*374*	*667*	*694*	*722*	*693*	*693*	
Total Overnight Cost (2007$ x 1000)	1,098,124	1,985,432	2,011,701	2,124,549	2,034,724	2,034,574	
Total As Spent Capital (2007$/kW)	2,264	4,115	4,170	4,404	4,217	4,217	
COE (mills/kWh, 2007$)	59.4	109.6	119.6	119.0	116.3	116.2	
- CO_2 TS&M Costs	*0*	*5.8*	*5.9*	*5.9*	*5.9*	*5.9*	
- Fuel Costs	*15.2*	*21.3*	*18.5*	*19.4*	*16.6*	*16.5*	
- Variable Costs	*5.1*	*9.2*	*21.2*	*15.7*	*19.0*	*18.9*	
- Fixed Costs	*7.8*	*13.1*	*13.1*	*13.6*	*13.2*	*13.2*	
- Capital Costs	*31.2*	*60.2*	*60.9*	*64.3*	*61.6*	*61.6*	
LCOE (mills/kWh, 2007$)	75.3	139.0	151.7	150.9	147.5	147.3	
Cost of CO_2 Captured ($2007/tonne)	N/A	48.1	68.0	63.5	70.7	70.8	
Cost of CO_2 Avoided ($2007/ton)	N/A	68.2	80.0	79.8	74.6	74.4	

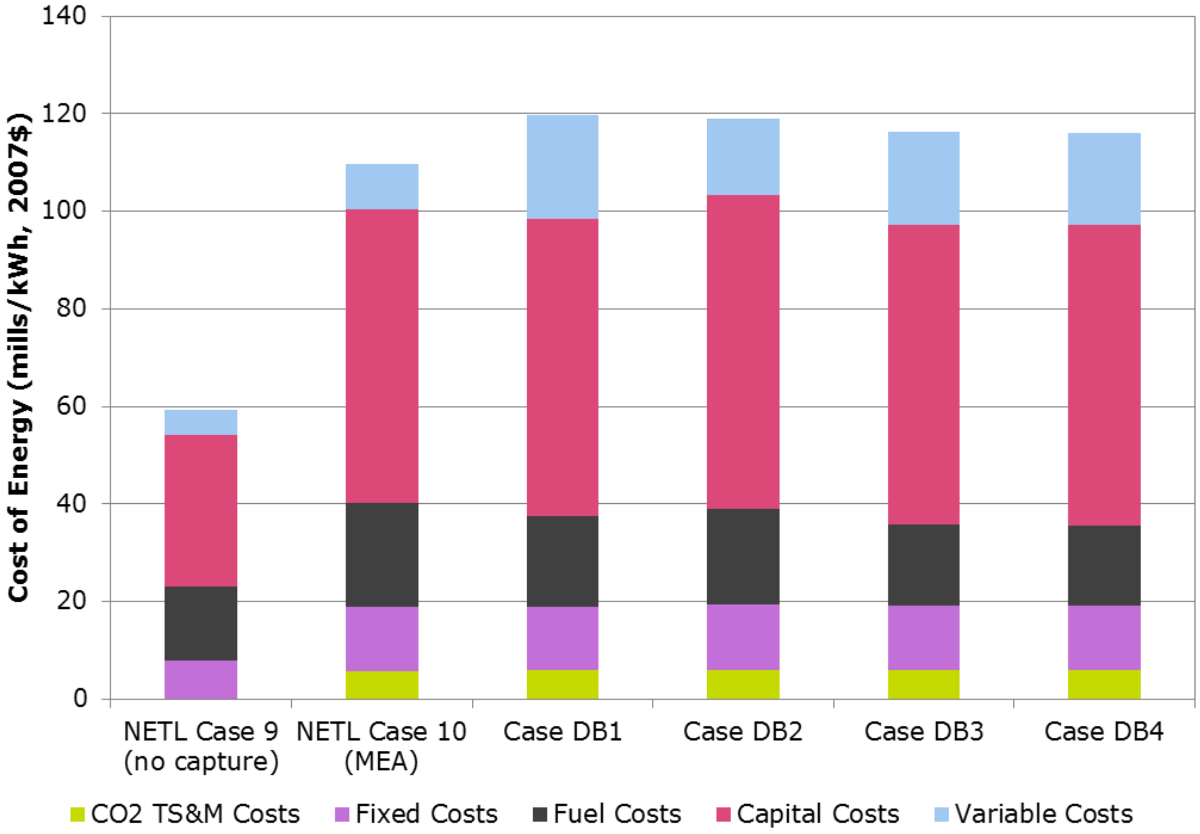


Figure 60. COE summary for full TEA main cases.

Case DB1, the best case in terms of minimized technical risk, was found to have a poorer COE performance than the NETL MEA PCC base Case 10. However, a potential benefit of the enzyme-activated K_2CO_3 solvent over MEA is the fact that the solvent and solvent degradation products are benign and therefore pose no significant environmental, health or safety concerns and are compliant with U.S. Federal legislation concerning environmental, health and safety [69].

Case DB5 was modelled with no enzyme present, and used default kinetic parameters for K_2CO_3. The model predicted results show that the presence of enzyme, simulated using modified and validated kinetic parameters, has a significant effect on the performance of the solvent resulting in 90% CO_2 capture observed in case DB3 rather than the maximum 18% CO_2 capture observed in DB5.

Case DB4 gave the best performance with a COE of 116.2 mills/kWh (2007$), a 6.0% increase on the equivalent MEA PCC case 10 from the NETL report [72]. Case DB3 shows a similar result with a COE of 116.3 mills/kWh (2007$). Without enzyme present, case DB5, the levels of CO_2 capture only reached 18%, far below the 90% capture target, and clearly illustrating why un-promoted K_2CO_3 solvent has not been considered viable for ambient pressure flue gas scrubbing applications. Case DB2 shows that the application of a deeper vacuum in the stripper has a small benefit with a slight reduction in COE when compared to case DB1.

Despite cases DB2, DB3 and DB4 showing the best COE result based on the bench scale test data and process model predictions, case DB1 is considered to be the most practical solution. The basis for case DB1 is considered to have the lowest inherent technical risk with the highest confidence in physical system performance, utilizing commercially available equipment and related process technologies. Cases DB2, DB3 and DB4 each consider equipment requirements or operation at or beyond the limit of current available technology, and therefore provide a greater degree of uncertainty.

Case DB1 shows a COE of 119.6 mills/kWh (2007$) which represents a 9.1% increase on the equivalent MEA case considered, NETL Case 10 [72].

Cases DB3 and DB4 show a relatively lower auxiliary power requirement compared to the other cases. This is due to the additional power output generated from the VLP turbine when producing VLP steam from the LP steam extracted from the power turbine. The additional power output means that a smaller PC plant, PCC plant and turbine are required to produce the net 550MWe output. However, this benefit is slightly offset by the corresponding additional capital costs of installing the VLP turbine, but overall still delivers the best economic performance in terms of COE.

10.2.4 Potential Performance and Cost Improvements

The performance summary shows that variable costs are the key differentiator in COE performance between the enzyme-activated cases and NETL Case 10. In Case DB1 the variable costs contribution to COE is more than double that of NETL Case 10. Exposure of the prototype enzyme under consideration for this assessment to thermal stress, even at moderate temperatures such as 70°C, results in degradation of the enzyme and a loss in performance that requires removal and replacement of degraded enzyme. The high enzyme make-up rate required to maintain system performance results in a significant operating cost that is reflected in the increased variable costs and ultimately the COE.

Using Novozymes' expertise it has been determined that the longevity of the enzyme could be improved from the current prototype in two stages of commercial development. The first stage could involve a combination of further enzyme-solvent dose optimization and selection among known CA variants with favorable longevity characteristics at the required process conditions compared to the prototype enzyme used in the present study. The second stage could involve a variety of different approaches, such as protein engineering, chemical modification and enzyme-immobilization, used alone or in combination to achieve further enzyme longevity improvements, resulting in reduced replenishment rates and corresponding cost reductions. As supported by findings published in the literature [28], the probability of success for both stage 1 and stage 2 enzyme developments are deemed by Novozymes to be high. Results of the application of these potential enzyme developments to Cases DB1, DB2 and DB3 in the form of a sensitivity study are shown in Figure 61 and Table 31.

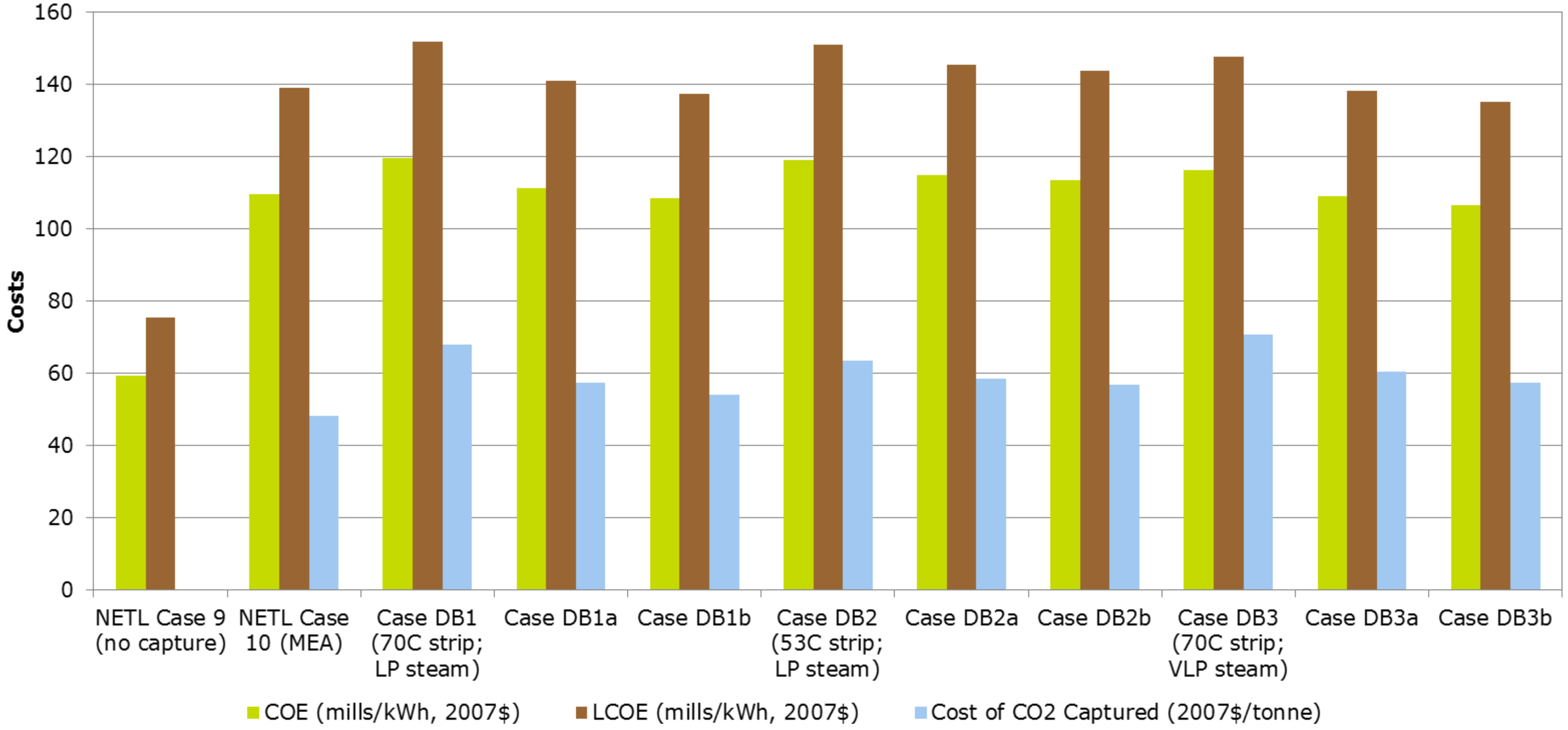
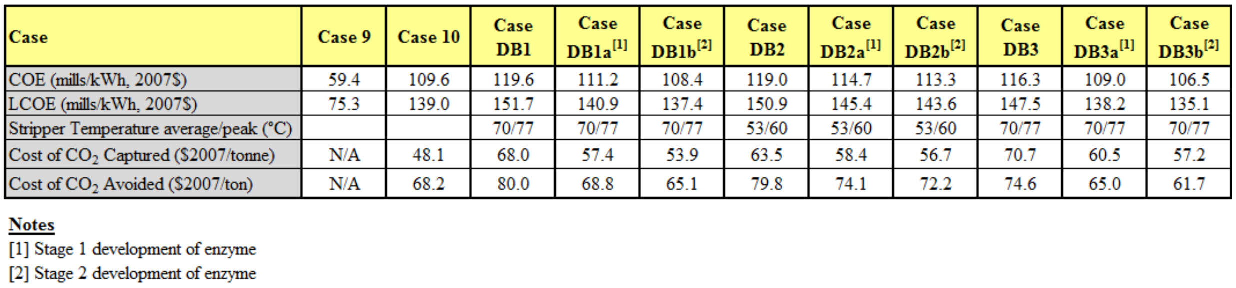


Figure 61. COE, LCOE and Cost of CO_2 Captured summary for sensitivity study on Cases DB1, DB2, and DB3.

Table 31. Impact of Enzyme Developments on Cost of Energy for the TEA Cases



Case	Case 9	Case 10	Case DB1	Case DB1a[1]	Case DB1b[2]	Case DB2	Case DB2a[1]	Case DB2b[2]	Case DB3	Case DB3a[1]	Case DB3b[2]
COE (mills/kWh, 2007\$)	59.4	109.6	119.6	111.2	108.4	119.0	114.7	113.3	116.3	109.0	106.5
LCOE (mills/kWh, 2007\$)	75.3	139.0	151.7	140.9	137.4	150.9	145.4	143.6	147.5	138.2	135.1
Stripper Temperature average/peak (°C)			70/77	70/77	70/77	53/60	53/60	53/60	70/77	70/77	70/77
Cost of CO_2 Captured (\$2007/tonne)	N/A	48.1	68.0	57.4	53.9	63.5	58.4	56.7	70.7	60.5	57.2
Cost of CO_2 Avoided (\$2007/ton)	N/A	68.2	80.0	68.8	65.1	79.8	74.1	72.2	74.6	65.0	61.7

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

The result, when stage 1 development of enzyme is applied to case DB1, is a reduction in COE from 119.6 mills/kWh (2007$) to 111.2 mills/kWh (2007$) representing a 1.5% (rather than 9.1%) increase when compared to NETL Case 10. The results of applying the stage 2 enzyme development are a further reduction in COE to 108.4 mills/kWh (2007$), a performance that represents an improvement of 1.1% when compared to NETL Case 10. Application of the stage 2 enzyme development to case DB3 results in a COE of 106.5 mills/kWh (2007$), which represents an improvement of 2.8% on NETL Case 10. Application of enzyme development stages to Case DB2 had a lower impact on COE because part of the projected enzyme longevity improvements for the other cases, operating at a modelled average and peak stripper temperature of 70°C and 77°C, respectively, were already accounted for in the lower enzyme replenishment required for operation at the 53°C/60°C stripper temperatures in Case DB2. Although not specified for NETL Case 10, it is understood that a conventional amine plant with an atmospheric pressure stripper would have a stripper temperature in the range of about 100-130°C. For all cases it should be noted that further enzyme-related improvements do not have as great an effect on the COE since other factors such as CAPEX become more dominant than OPEX.

Cases DB3 and DB4 were found to have an almost identical performance in all aspects despite having differing reaction kinetics specified in the stripper. The stripper simulation for case DB3 utilizes enzyme-catalyzed reaction kinetics based on the validated bench scale models; whereas case DB4 uses Aspen Plus® default reaction kinetics; meaning, case DB4 simulates the stripper performance absent of any kinetic contribution by enzyme. The slightly better performance of case DB4 compared to DB3 observed is likely to be due to small differences in the convergence of the respective process models. Since the results of the two cases can be considered identical within process modeling tolerances, they show that the enzyme has limited effect on the regeneration stage under the process conditions considered. Potentially the regeneration stage could be equilibrium-limited with respect to CO_2 gas release from the liquid and therefore may not benefit from the effect of enzyme increasing the rate of bicarbonate conversion to dissolved CO_2. However, these results are based only on process models and should be tested on plant, both at bench scale and larger, to determine the process performance of the regeneration stage with no kinetic contribution from the enzyme. If the limited model predicted effect of the enzyme on the regeneration stage is observed in plant tests then further economic improvement could potentially be made by redesigning the process to localize the enzyme to the absorption stage. As the absorption stage operates at a lower temperature than the stripper, there would be a significant improvement in the enzyme longevity and an increased flexibility in the stripper stage to use the optimal combination of heat and pressure conditions without concern for enzyme degradation. For example, with enzyme localized to the absorption stage, low temperature vacuum stripping would not necessarily be required. Elimination of vacuum operation would reduce capital costs, reduce auxiliary power consumption and hence require a smaller PC boiler and associated equipment to achieve 550MWe net output. These cost reductions would be offset to some extent by the cost of restraining the enzyme in the absorber by some means, such as immobilization, and the impact on process performance would have to be assessed. Given the results observed in case DB4 it is certainly possible that such a solution could result in a COE a few percent lower than that of NETL Case 10, however the performance of the configuration where enzyme is localized to the absorption stage and the effect of vacuum regeneration and non-vacuum regeneration on such a case would have to be assessed through practical demonstration.

All of the results presented in this report are based on bench scale data and process models. The limitations of predicting full scale plant performance from such data has been noted. It is recommended that further work on a larger scale test unit be carried out to reduce the level of uncertainty by validating performance on a larger scale particularly with regards to vacuum performance, enzyme longevity and enzyme kinetics. A number of potential process improvements have been determined from the results presented in this report and these should be investigated further to determine the best possible operating parameters for the enzyme-activated process. A notable and practical aspect of the bench scale to full scale feasibility assessment was establishment of a dissolved enzyme replenishment approach, including spent enzyme removal via a continuous slipstream, offering a straightforward means for maintaining system performance. This approach, supported by both lab and bench scale data, provided the basis for determining the projected enzyme make-up rates.

10.2.5 Future Developments

Based on findings collected throughout the project and considering the results of the full techno-economic analysis and adjacent technology developments within the CO_2 capture field, further aspects and improvements for investigation related to use of enzyme-enhanced solvents include:

- Process and cost performance with enzyme localized in the absorber stage and utilizing vacuum regeneration with low enthalpy K_2CO_3 based solvent.

- Process and cost performance with enzyme localized in the absorber stage and utilizing non-vacuum regeneration, to avoid the additional capital costs and auxiliary power consumption associated with the construction and operation of vacuum systems.

- Utilization of heat sources from outside the PC plant steam cycle to provide heating in the reboiler, such as process waste heat or low grade steam, and determine cost and process performance.

- Utilization of direct steam injection in the stripper.

- Utilization of second-stage air stripper to deliver leaner solvent to the absorber.

- Utilization of advanced contactors for absorption and desorption.

- Utilization of less costly materials of construction that could be compatible with K_2CO_3, or other bicarbonate based solvents.

- Utilization of alternative solvents, mixed solvents, or additives that could provide higher CO_2 loading capacity, minimize heat of water vaporization, and reduced recirculation rates to reduce equipment sizing and minimize pumping energy and reboiler duty.

- Development of enzymes with improved longevity, especially improved longevity at elevated temperature conditions. Such longevity improvements could also be possible by developing modified enzymes. The modification of enzymes could be achieved by utilizing enzymes in combination with physical matrices, such as particles, or through chemical modifications.

- Development of enzymes or modified enzymes with reduced dosage requirement to minimize initial fill and replenishment costs. Reduced dosage could, for example, be achieved by increasing the enzyme activity per unit amount or by localizing the enzyme to the gas-liquid interface.

Further investigation of the cases presented herein or potential improvements to these should be validated on a larger scale PCC test plant utilizing enzyme-activated K_2CO_3 solvent to reduce uncertainties and confirm the predicted process and cost performance for implementation at full scale.

11 CONCLUSIONS AND RECOMMENDATIONS

A bench-scale study and a corresponding full technical and economic assessment of an aqueous K_2CO_3 solvent-based post-combustion carbon dioxide capture (PCC) system catalyzed by carbonic anhydrase and utilizing low temperature vacuum regeneration was completed. A comprehensive summary of test methods, testing results, and the corresponding technical and economic feasibility is provided in the present report. Overall conclusions and recommendations are presented below in the context of the overall DOE program objectives for the solvent-based, post-combustion category – achieve 90% CO_2 removal from PC power plants and demonstrate progress toward the DOE target of < 35% increase in LCOE versus a no-capture plant. Conclusions specific to this project's objectives are presented as well.

11.1 90% CO_2 Removal

With respect to 90% CO_2 removal, the bench-scale testing and full feasibility analysis carried out under the present project, together with flue gas contaminant tolerance studies carried out in prior and parallel investigations, demonstrated the technical capability of benign, readily available aqueous K_2CO_3 solvent catalyzed by dissolved carbonic anhydrase to capture 90% CO_2 from a PC flue gas stream. Thus, results from this project are consistent with and further validate the K_2CO_3-CA combination as a useful solvent system for post-combustion gas treatment. Laboratory WWC tests showed absorption rates for CO_2 in K_2CO_3-CA were equally good across the range of 30-50°C, meaning that, unlike MEA, the K_2CO_3-CA combination can be used with considerable flexibility in absorber temperature, and the low heat of absorption of CO_2 into K_2CO_3-CA means that special absorber temperature management, such as intercooling, is not needed. Bench-scale tests proved the technical capability of K_2CO_3-CA to deliver 90% capture with a 30°C or 40°C absorber temperature. The benign nature of the K_2CO_3 solvent, its negligible vapor pressure, low price, and ready availability are compelling reasons to routinely consider K_2CO_3-CA along with other solvent options for further PCC process developments.

One drawback of K_2CO_3 solvent is the limitation on absorption capacity for CO_2, which arises from bicarbonate solubility limitations, setting a rich loading limit. Therefore, mixtures of K_2CO_3-CA with compatible components that could increase the overall solvent loading capacity and limit non-beneficial water vaporization in the stripper should be further investigated. The present work further clarified that aqueous K_2CO_3 without added catalyst is not a viable option for CO_2 absorption under the near ambient pressure conditions at which PC flue gas typically exits the pollution control train, because the maximum CO_2 capture observed in bench-scale tests and in the full feasibility simulations for K_2CO_3 solvent without enzyme was < 20%. Importantly, carbonic anhydrase biocatalyst makes it possible to seriously consider aqueous K_2CO_3-based liquids as CO_2 scrubbing solvents for ambient inlet pressure applications.

11.2 Energy Costs

High pressure, high temperature gas scrubbing processes using aq. K_2CO_3 for CO_2 absorption ("Hot Pot") have been known for many years (Section 3), yet not applied for flue gas scrubbing due to the low inlet gas pressure of this application. Therefore, it was already well-known that pressure swing (high-to-low) and increased temperature can be applied in the stripper to release CO_2 from aq. K_2CO_3 and regenerate lean solvent. A key question addressed in the present work was to determine whether pressure swing at low temperature, established by applying vacuum to the stripper, could result in an energy demand for the system that was lower compared to the

NETL Case 10 reference, based on MEA. Furthermore, it was important to determine whether the overall cost of energy for a K_2CO_3-CA based CO_2 capture system using vacuum regeneration would be lower compared to NETL Case 10.

Consideration of process development cases in which enzyme replenishment costs were not a dominant factor showed that the overall cost penalty of carrying out the K_2CO_3-CA-Vacuum process in a simulated 550 MWe net PC power plant could be similar to the COE for the NETL Case 10 aqueous 30 wt% MEA reference case. In essence, the benefit of using low quality steam for solvent regeneration was balanced by the added capital and operational costs of vacuum creation and consequential added compression. If the developmental features of a more thermostable enzyme and inclusion of a VLP turbine are not considered, Case DB1 is considered to represent the most realistic projected outcome for scaling-up the vacuum-based system using equipment and processes that are already proven in smaller-scale operations and could be commercially available for 550 MWe net power plant scale. In this case, the model-predicted COE and LCOE performance for DB1 was 9% higher than NETL Case 10, representing a cost of energy increase for the enzyme-activated case with minimized technical risk and highest confidence in physical system performance. The primary reason for the higher COE/LCOE is the very high prototype enzyme replenishment cost due to insufficient thermo-stability.

Case DB1b (considering a thermostable CA), representing two stages of enzyme development and having significantly lower enzyme replenishment costs compared to Case DB1 (based on the prototype CA), is also deemed to be realistic in the near term because the probability of success in the two enzyme development stages is high. The result of applying the two stage enzyme development to the enzyme-assisted main Case DB1 brings the COE for Case DB1b to 108.4 mills/kWh (2007$), representing a 1.1% improved COE compared to NETL Case 10. The COE result for developmental Case DB1b is therefore considered to be roughly equivalent to NETL Case 10.

Application of two stage enzyme development to case DB3, to take advantage of additional electrical power generation from an installed VLP turbine, results in a COE of 106.5 mills/kWh (2007$), representing a 2.8% improvement compared to NETL Case 10. This result points towards possible benefits of installing a VLP turbine, however the level of projected improvement is modest and a higher level of confidence in the technical integration of the VLP turbine approach would be needed to conclude that the predicted COE improvement could actually be realized.

For all enzyme-assisted cases, the Cost of CO_2 Captured is higher than the 48.1 $/tonne (2007$) modelled for NETL Case 10, an indicator of the dominating effect of capital costs in the vacuum regeneration approach. The best case in this respect was enzyme development Case DB1b, which gives a Cost of CO_2 Captured of 53.9 $/tonne, 12% higher than NETL Case 10. The Cost of CO_2 Avoided for Case DB1b, at 65.1 $/tonne, is 4.5% lower than the 68.2 $/tonne CO_2 avoided cost for NETL Case 10, pointing to the reduced power plant fuel consumption (and consequent lower CO_2 generation) needed to achieve a 550 MWe net power output.

A further finding was that the additional vacuum and compression capability, and corresponding capital costs, required to achieve very low regeneration temperatures (Cases DB2, DB1a and DB1b) completely negated the reboiler energy benefit of low temperature regeneration.

Therefore, taking advantage of low enthalpy regeneration features of low enthalpy solvents will require a different approach than vacuum regeneration alone. Also, for all enzyme-assisted cases it was observed that further enzyme-related improvements beyond two stages of development do not have as great an effect on the COE because other factors such as CAPEX become more dominant than OPEX.

Regarding enzyme performance, it is concluded that the prototype CA used for the bench-scale studies does not have adequate longevity to perform in full scale as a dissolved biocatalyst in the recirculating solvent configuration of cases DB1 through DB3.

Regarding vacuum performance, it is concluded that operation of the vacuum condition at full scale could involve significant development effort, as systems for flue gas flow rates at 550 MWe scale are not commercially available today, although certain vendors represent they have the capability to supply such systems.

11.3 Specific Project Conclusions and Recommendations

11.3.1 Enzyme Supply and Enzyme-Solvent Properties

At the start of the project, carbonic anhydrase (of which there are numerous types, Section 1.4) was essentially only available in research quantities. A commitment by Novozymes under the present project was to make sufficient prototype CA available to the project, at no cost, to carry out the bench-scale testing and related tasks. As a consequence of this approach, as well as parallel efforts, availability and suitability of carbonic anhydrases for scale-up testing has now been confirmed, meaning that, from Novozymes' perspective it would be feasible to supply carbonic anhydrase for slip-stream or full scale CO_2 capture testing, and availability of enzyme should not be considered an obstacle.

Long term storage stability of Novozymes prototype CA liquid concentrate at frozen (-25°C), cold (5°C) and room temperature (~22°C) conditions showed no loss in activity over 1.5 years, meaning that enzyme storage at a power plant site may require moderately conditioned storage. Even though specific efforts to stabilize the enzyme formulation for un-conditioned storage were not carried out within the project, the inherent CA storage stability results presented here indicate that storage stability at an industrial site should not present any major issues.

Enzyme-solvent characteristics pertaining to the operation of the bench-scale unit and full feasibility assessment were determined:

- Dissolved prototype CA is compatible with K_2CO_3 solvent across a range of concentration and pH conditions, and demonstrates especially high activity at temperatures near the absorber temperature (40°C).
- The CO_2 mass transfer coefficient measured in 20 wt% K_2CO_3 was 0.52-0.62 $mmol/m^2.s.kPa$ with a prototype CA concentration $\geq$ 2g/L and temperature of 30-50°C. The Kg for 20 wt% K_2CO_3 alone was 0.11 $mmol/m^2.s.kPa$.
- A similar dose-response effect was observed in the bench-scale unit as was observed in the WWC, leading to selection of 2.5 g/L CA as the active enzyme concentration level for the 500 h test.

- Modelled kinetic rate parameters for the reaction $CO_{2(aq)} + HO^{-} \leftrightarrow HCO_3^{-}$ were determined to be 4.32 x 10^{13} M^{-1} s^{-1} and 3.57 x 10^{18} M^{-1} s^{-1} for the forward and reverse reactions, respectively. The addition of enzyme reduces the activation energy of the forward reaction from 13 to 7.9 kcal/mol, and reduces the activation energy of the reverse reaction from 31 to 26 kcal/mol. The modeled rate parameters consider the reaction of CO_2 with hydroxide ion, although the true substrates for the enzyme are CO_2 and H_2O. However, substantial effort was invested in modifying the above kinetics for modeling, and insufficient time remained to adapt the rate expression for the true enzyme substrates. Future work should continue to refine the model towards this end.
- Working capacity of the 23.5 wt% K_2CO_3 solvent selected for the study was 0.2 mol CO_2/mol K_2CO_3 (0.013 kg CO_2/kg solvent).
- Temperature dependent enzyme inactivation rates were measured to be 1% and 84% active enzyme loss per 24 h at 40°C and 80°C, respectively. Apparent, enzyme longevity was extended with shorter exposure to high temperatures per absorption/desorption cycle. This demonstrated that rate of inactivation was a cumulative effect of temperature-time exposure and that enzyme performance could be extended in processes with shorter periods of high temperature exposure.
- A high level of foaming in the aq. K_2CO_3 system occurred upon addition of prototype enzyme concentrate. This behavior caused excessive pressure drop in the stripper under vacuum conditions. The foaming could be mitigated by addition of antifoam. For optimal system performance it would be preferable to use CAs and CA formulations with low foaming propensity.

11.3.2 Process Component Integration and Completion of 500 Hour Bench-scale Test

The integrated bench-scale system was successfully designed and built to operate with 30 SLPM inlet gas flow to the absorber. Two regeneration options – ultrasonic regeneration and vacuum regeneration – were considered.

Prior to integrated assembly, the ultrasonic regeneration option was tested separately at PNNL as a stand-alone unit. A variety of different configurations were tested, including batch-mode and flow-through, with application of ultrasonic energy to the liquid via a horn or a clamp-on transducer. In a flow-through configuration, a total CO_2 release of 0.089 mol/L was measured, falling within the 0.169 mol/L equilibrium projection due solely to the temperature increase imparted with ultrasonic energy. This means, although application of ultrasonics resulted in significant visible bubble formation and was able to provide CO_2 release commensurate with thermal regeneration effects, which could offer a novel approach to rapidly heating liquids in the system, further exploratory work would be required to determine whether rectified diffusion could deliver additional benefits. In view of this result, vacuum regeneration was selected as the focus for developing the integrated bench-scale system and was used for conducting the parametric and 500 hour testing.

The bench-scale integrated carbon capture test unit, comprising a recirculating absorber-stripper system with vacuum regeneration, was central to the evaluation of the enzyme enhanced potassium carbonate solvent process for post-combustion capture. As such, careful design considerations, and several iterative changes were invested during bench unit construction. The unit was put through a series of shakedown tests that included operational extremes with and without enzyme. With evidence of reproducible operation, unit parametric testing was conducted, followed by a cumulative 500 h test that comprised 75 run days. Overall, the bench-scale system performed as required, tolerating daily start-up/shut-down, and supplying the necessary instrumentation outputs to the data monitoring system. Stabilizing the vacuum condition in the bench-scale unit required continuous control due to the high chance of foaming in the presence of prototype enzyme leading to excessive pressure drop in the stripper, but foaming was controllable using antifoam. Dissolved enzyme replenishment was demonstrated as straightforward approach to maintain system performance. Spent enzyme reclamation based on a “cook and filter” concept was demonstrated, where inactivation of prototype enzyme caused by passing through the 65-95°C temperature conditions in the stripper gradually “cooked” the enzyme to form insoluble solids that could be removed by filtration, allowing residual active enzyme to remain dissolved in the recirculating solvent. The system tolerated the turbidity caused by formation of the fine suspended solids during operation, and solvent could be clarified using proper filtration. During the 500 hour test, an average of 84% CO_2 capture efficiency was maintained for the 450 hour period of routine enzyme replenishment. Stopping enzyme replenishment during the final test period resulted in decreased CO_2 capture efficiency, proving the importance of catalyst for CO_2 absorption in K_2CO_3-based solvents at ambient pressure.

Because CA thermal instability led to solids formation in the solvent, for optimal system performance, CAs or CA preparations with improved thermo-stability should be utilized. Shortening CA exposure to high temperature, such as by shortening the residence time in the stripper, will also lead to improved enzyme longevity and reduced replenishment requirements.

11.3.3 Determination of the Energy Required to Regenerate the Solvent Ultrasonically or Using Vacuum and Very Low Pressure (VLP) Steam Approaches

Under bench-scale conditions, carbonic anhydrase was shown to be essential for enabling 90% CO_2 capture when employing an environmentally benign aqueous 23.5 wt% K_2CO_3-based solvent for scrubbing simulated flue gas at ambient absorber pressures. The average actual bench-scale reboiler energy requirement with K_2CO_3 and no-enzyme was 1600 kJ/mol CO_2 captured and only achieved 19% CO_2 capture, whereas the reboiler energy requirement for K_2CO_3 together with enzyme was 313 kJ/mol and achieved a stable 84% capture under the conditions of the 500 h test.

In the full scale simulation for a 550 MWe PC power plant with PCC operating at 90% CO_2 capture, including full scale process configuration assumptions that differed from the equipment and process flow parameters actually tested on the bench-scale unit, a regeneration energy of 147 kJ/mol (comprising reboiler and vacuum duty) was projected for the DB1 main case (utilizing LP steam). Simulation of the NETL Case 10 reference gave a higher regeneration energy requirement of 156 kJ/mol for 30 wt% MEA. The regeneration energy requirement projected for Case DB3 (utilizing VLP steam) was 150 kJ/mol. The liquid-to-gas (L/G) ratio for the bench-scale tests was 50 (on mass basis) versus 27 for the full scale projection. This difference translates into significant differences in sensible heat duty, and, therefore, is the primary driver for the differences observed between the actual bench-scale and predicted reboiler duties.

Cases modelled for the preliminary feasibility assessment predicted that ultrasonic regeneration paired with VLP steam could require ~50% less parasitic power from a coal-fired power plant compared to NETL Case 10, on the assumption that CO_2 release could be achieved at atmospheric pressure through the ultrasonic phenomenon of rectified diffusion. The demonstrated batch testing ultrasonic energy was 4.9 kJe/kg solvent or 10.3 kJe/mol of CO_2 released. Based on this measurement, a full-scale CO_2 regeneration system was estimated to be possible with an ultrasonic energy requirement of 1.5 kJe/kg solvent, equating to just over 11 MWe of parasitic power for the ultrasonic system in the 550 MWe reference system. However, because the level of CO_2 release required for integration with the bench-scale unit was not achieved in the flow-through ultrasonic testing, this aspect of the project was not further pursued.

11.3.4 Preliminary Assessment of the Environmental Friendliness and Safety of the Materials and Processes Employed

In order to assess the environmental friendliness and safety of the materials and processes employed, a preliminary environmental, health and safety (EH&S) risk assessment for an enzyme-activated potassium carbonate (K_2CO_3) solution post-combustion CO_2 capture (PCC) plant delivering 90% capture, integrated with a subcritical pulverized coal (PC) power plant with a net output of 550 MWe, was prepared. The expected emissions during normal steady-state operation were estimated utilizing models of the PCC plant developed in AspenTech's AspenPlus® software, bench scale test results from the University of Kentucky, and industrial experience of emission results from a slipstream PCC plant utilizing amine based solvents. Two credible emission sources for the PCC process were identified: (1) the absorber off-gas that is vented to the atmosphere via a stack, and (2) the solids-containing waste removed from the PCC plant in the centrifuge used to reclaim enzyme and solvent. These emissions were quantified and assessed for PCC plant normal operation and were found to pose no significant EH&S concerns and were compliant with the Federal EH&S legislation reviewed. With respect to the off-gas emission, future studies are recommended to monitor enzyme-containing aerosol emissions in the off-gas to ensure they do not exceed the generally accepted exposure limit, and to demonstrate that the proposed engineering controls for preventing such emissions are adequate. Analogous to the gypsum product stream from FGD waste, it is proposed that a product stream could be generated from the enzyme reclamation solids-containing waste. The moist solids would be removed from the power plant site by road tanker for composting applications or used as fertilizer where the potassium content would provide a benefit. If a revenue-generating product stream is not viable then the solid sludge would be removed from the plant by a specialist contractor for disposal as non-hazardous waste. Note that due to the uncertainty in waste stream revenue generation, no credit was taken for this in the economic assessment. Furthermore, the limitations of scaling up a process from bench scale data to a representative full scale plant are understood and several areas were identified for further monitoring and measurement on a larger scale demonstration.

11.4 Overall Conclusions and Recommendations

Overall, the economic analysis shows potential for an enzyme developmental case of the K_2CO_3-CA system with vacuum regeneration to match NETL Case 10 in terms of COE/LCOE, however a significant reduction in these costs was not demonstrated, and some concerns about the availability of vacuum generation at 550 MWe power plant scale were noted. In case the availability of vacuum generation at scale were resolved, the K_2CO_3-CA-Vacuum system could be considered as an alternative CO_2 capture option in cases where the MEA-based Case 10 system would be economically viable. For example, the PCC system at Boundary Dam utilizes MEA-based CO_2 capture technology, where the economic feasibility is bolstered by proximity to and revenue from EOR. In such cases, it is recommended to consider the K_2CO_3-CA-Vacuum system because the benign nature of the solvent may be advantageous to meet site-specific environmental and safety regulations, which could have a favorable impact on total project costs and site selection. It is furthermore noted that the K_2CO_3-CA-Vacuum approach could be relevant for smaller scale CO_2 capture, such as from industrial boilers, where the concerns about commercial-ready vacuum generation availability are diminished. Therefore, although economic progress towards < 35% increase in LCOE was not demonstrated, the low hazard enzyme-assisted technology was confirmed to enable CO_2 capture in a benign K_2CO_3-based solvent system that could not previously be considered, and the principle of enzyme replenishment to maintain system operation was demonstrated.

In addition to the conclusions and recommendations presented here, numerous opportunities for further developments, system improvements, and concept demonstrations have been presented in this report, also with reference to prior and on-going evaluation and demonstration activities. Importantly, this report provides numerous benchmarks for enzyme-assisted CO_2 capture that were not previously available, and against which the envisioned technology improvements can be gauged. The knowledge base needed to implement enzyme-based CO_2 capture technologies, where the enzyme could play a process-enabling role in both CO_2 separation and in CO_2 sequestration, is rapidly expanding, supported by participation from industry, academia, and by funding from the DOE and other national and international organizations. It is recommended that projects utilizing carbonic anhydrase biocatalyst technology for CO_2 capture be kept within the scope of present and future funding opportunities to identify processes that could derive maximum benefit from incorporation of biocatalysts in addressing the global CO_2 management challenge and help mature these developments towards commercialization.

12 REFERENCES

[1] U.S. Energy Information Administration, "International Energy Outlook 2013," DOE/EIA-0484(2013), U.S. Department of Energy, Office of Energy Analysis, Washington DC, 2013. [Online]. Available: http://www.eia.gov/forecasts/ieo/pdf/0484(2013).pdf.

[2] Prepared by Working Group III of the Intergovernmental Panel on Climate Change, "IPCC Special Report on Carbon Dioxide Capture and Storage," B. Metz, O. Davidson, H. de Coninck, M. Loos and L. Meyer, Eds., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2005. [Online]. Available: http://digital.library.unt.edu/ark:/67531/metadc12051/m2/1/high_res_d/srccs_wholereport.pdf.

[3] U.S. Environmental Protection Agency, "Summary of the Clean Air Act," EPA, [Online]. Available: http://www2.epa.gov/laws-regulations/summary-clean-air-act. [Accessed 12 May 2015].

[4] U.S. Energy Information Administration, "Annual Energy Outlook 2015," DOE/EIA-0383(2015), April 2015. [Online]. Available: http://www.eia.gov/forecasts/aeo/.

[5] U.S. Environmental Protection Agency, "Carbon Pollution Standards, Fact Sheet: Clean Power Plan Overview," U.S. EPA, [Online]. Available: http://www2.epa.gov/carbon-pollution-standards/fact-sheet-clean-power-plan-overview. [Accessed 12 May 2015].

[6] U.S. Environmental Protection Agency, "U.S. Greenhouse Gas Emissions from Electricity Generation, 1990-2013," Greenhouse Gas Inventory Data Explorer, EPA. [Online]. Available: http://www.epa.gov/climatechange/ghgemissions/inventoryexplorer/#electricitygeneration/allgas/source/all. [Accessed 12 May 2015].

[7] National Energy Technology Laboratory, "DE-FOA-0000403: Bench-Scale and Slipstream Development and Testing of Post-Combustion Carbon Dioxide Capture and Separation Technology for Application to Existing Coal-Fired Power Plants," Federal Grants, 31 January 2011. [Online]. Available: http://www.federalgrants.com/Bench-Scale-and-Slipstream-Development-and-Testing-of-Post-Combustion-Carbon-Dioxide-Capture-and-Separation-Technology-for-Application-to-Existing-Coal-Fired-Power-Plants-27842.html. [Accessed 22 August 2015].

[8] International Energy Agency, "Technology Roadmap: Carbon Capture and Storage," OECD/IEA, Paris, 2013. [Online]. Available: www.iea.org.

[9] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, "Advances in CO2 capture technology - The U.S. Department of Energy's Carbon Sequestration Program," *Int. J. Greenhouse Gas Control*, vol. 2, pp. 9-20, 2008.

[10] S. Anderson and R. Newell, "Prospects for Carbon Capture and Storage Technologies," RFF DP 02-68, Resources for the Future, Washington, DC, January 2003. [Online]. Available: www.rff.org.

[11] MIT, "Carbon Capture & Sequestration Technologies: CCS Project Database," [Online]. Available: https://sequestration.mit.edu/tools/projects/index.html. [Accessed 29 August

2015].

[12] J. Dooley, C. Davidson and R. Dahowski, "An Assessment of the Commercial Availability of Carbon Dioxide Capture and Storage Technologies as of June 2009 (PNNL-18520)," Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830. [Online]. Available: http://www.pnl.gov/main/publications/external/technical_reports/PNNL-18520.pdf. [Accessed 29 August 2015].

[13] National Energy Technology Laboratory, "Carbon Capture Technology Program Plan," January 2013. [Online]. Available: http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/Program-Plan-Carbon-Capture-2013.pdf. [Accessed 12 May 2015].

[14] IEAGHG, "Seminar on CCS in the Process Industries," Greenhouse News, no. 117, p. 3, March 2015. [Online]. Available: http://www.ieaghg.org/docs/General_Docs/Newsletter/March%202015%20High%20Resolution.pdf. [Accessed 12 May 2015].

[15] International Energy Agency, "GHGT-12 Conference Summary," 12th International Conference on Greenhouse Gas Control Technologies, Austin, TX, 5-9 October 2014. [Online]. Available: http://www.ieaghg.org/docs/General_Docs/GHGT-12%20Summary%20Brochure.pdf. [Accessed 12 May 2015].

[16] S. Gollakota and S. McDonald, "Carbon dioxide capture, utilization, and storage: An emerging economic opportunity for fuel ethanol plants in the U.S.," International Fuel Ethanol Workshop & Expo (FEW), St. Louis, MO, 2013. [Online]. Available: http://www.netl.doe.gov/File%20Library/Research/Coal/major%20demonstrations/iccus/Gollakota_Wed12June_Track3_FEW2013.pdf. [Accessed 12 May 2015].

[17] MIT Carbon Sequestration Initiative (CSI), "Sleipner Fact Sheet: Carbon Dioxide Capture and Storage Project," CCS Project Database, MIT, [Online]. Available: https://sequestration.mit.edu/tools/projects/sleipner.html. [Accessed 12 May 2015].

[18] SaskPower, "Boundary Dam Carbon Capture Project," SaskPower CCS, [Online]. Available: http://saskpowerccs.com/ccs-projects/boundary-dam-carbon-capture-project/. [Accessed 12 May 2015].

[19] National Enhanced Oil Recovery Initiative, "Carbon dioxide enhanced oil recovery: A critical domestic energy, economic, and environmental opportunity," February 2012. [Online]. Available: http://www.neori.org/NEORI_Report.pdf.

[20] K. van 't Veld, C. F. Mason and A. Leach, "The economics of CO2 sequestration through enhanced oil recovery," *Energy Procedia*, vol. 37, pp. 6909-6919, 2013.

[21] M. Sander and C. Mariz, "The Fluor Daniel Econamine FG process: Past experience and present day focus," *Energy Convers. Mgmt.*, vol. 33, no. 5-8, pp. 341-348, 1992.

[22] National Energy Technology Laboratory, "Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity, Revision 2a," DOE/NETL-2010/1397, September 2013. [Online]. Available: http://www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/OE/BitBase_FinRep_Rev2a-3_20130919_1.pdf. [Accessed 17 July 2014].

[23] U.S. Department of Energy National Energy Technology Laboratory, "DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update," May 2013.

[Online]. Available: http://netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/handbook/CO2-Capture-Tech-Update-2013.pdf. [Accessed 8 August 2015].

[24] U.S. Department of Energy National Energy Technology Laboratory, "Post-combustion CO2 Control," [Online]. Available: http://www.netl.doe.gov/research/coal/carbon-capture/post-combustion. [Accessed 8 August 2015].

[25] Global CCS Institute, "Large Scale CCS Projects," [Online]. Available: http://www.globalccsinstitute.com/projects/large-scale-ccs-projects. [Accessed 8 August 2015].

[26] C. K. Matthews and K. E. van Holde, Biochemistry, Redwood City, CA: Benjamin/Cummings Publishing Company, 1990.

[27] S. Milmo, "The enzyme makers," *Chem. Ind.,* vol. 76, no. 11, pp. 29-31, November 2012.

[28] S. Salmon and A. House, "Enzyme-catalyzed solvents for CO2 separation," in *Novel Materials for Carbon Dioxide Mitigation Technology*, F. Shi and B. Morreale, Eds., Amsterdam, Elsevier B.V., 2015, pp. 23-86. DOI: 10.1016/B978-0-444-63259-3.01001-6.

[29] M. E. Russo, G. Olivieri, A. Marzocchella, P. Salatino, P. Caramuscio and C. Cavaleiro, "Post-combustion carbon capture mediated by carbonic anhydrase," *Sep. Purif. Technol.,* vol. 107, pp. 331-339, 2013.

[30] A. C. Pierre, "Enzymatic carbon dioxide capture," *ISRN Chem. Eng.,* pp. 1-22, 2012, DOI:10.5402/2012/753687.

[31] J. M. Gonzalez and S. Z. Fisher, "Carbonic Anhydrases in Industrial Applications," in *Carbonic Anhydrase: Mechanism, Regulation, Links to Disease, and Industrial Applications,* S. C. Frost and R. McKenna, Eds., Dordrecht, Springer, 2014, pp. 405-426.

[32] R. Dilmore, C. Griffith, Z. Liu, Y. Soong and S. Hedges, "Carbonic anhydrase-facilitated CO2 absorption with polyacrylamide buffering bead capture," *Int. J. Greenh. Gas Con.,* vol. 3, pp. 401-410, 2009.

[33] O. Lacroix, "CO2 Capture Using Immobilized Carbonic Anhydrase in Robinson-Mahoney Basket and Packed Absorption Column Reactors," M.Sc. Thesis, Department de Genie Chemique, Université Laval Quebéc, Quebéc, 2008.

[34] C. K. Savile and J. J. Lalonde, "Biotechnology for the acceleration of carbon dioxide capture and sequestration," *Curr. Opin. Biotech.,* vol. 22, pp. 818-823, 2011.

[35] J. K. J. Yong, G. W. Stevens, F. Caruso and S. E. Kentish, "The use of carbonic anhydrase to accelerate carbon dioxide capture processes," *J. Chem. Technol. Biotechnol.,* vol. 90, pp. 3-10, 2015. DOI: 10.1002/jctb.4502.

[36] A. L. Kohl and R. B. Nielsen, Gas Purification, 5th ed., Houston, Texas: Gulf Professional Publishing, 1997.

[37] M. Wang, A. Lawal, P. Stephenson, J. Sidders and C. Ramshaw, "Post-combustion CO2 capture with chemical absorption: A state-of-the-art review," *Chem. Eng. Res. Des.,* vol. 89, pp. 1609-1624, 2011.

[38] H. F. Svendsen and E. T. M. T. Hessen, "Carbon dioxide capture by absorption, challenges and possibilities," *Chem. Eng. J.,* vol. 171, pp. 718-724, 2011.

[39] M. Trachtenberg, C. Tu, R. Landers, R. M. M. Wilson, P. Lapis, J. Kennedy, M. Paterson, D. Silverman, D. Thomas, R. Smith and F. Rudolph, "Carbon dioxide transport by proteic

and facilitated transport membranes," *Life Support Biosph. Sci.*, vol. 6, pp. 293-302, 1999.

[40] L. Bao and M. Trachtenberg, "Facilitated transport of CO2 across a liquid membrane: comparing enzyme, amine, and alkaline," *J. Membrane Sci.*, vol. 280, pp. 330-334, 2006.

[41] P. Saunders, S. Salmon, M. Borchert and L. P. Lessard, "Modular membrane reactor and process for carbon dioxide extraction". PCT Patent application WO 2010/014774, 4 February 2010.

[42] M. Leimbrink, T. Patzer and M. Skiborowski, "Process intensification of CO2 capture by means of membrane contactors and efficient biocatalysts," Euromembrane Conference 2015, Aachen, Germany, 8 September 2015.

[43] C.-H. Yu, C.-H. Huang and C.-S. Tan, "A review of CO2 capture by absorption and adsorption," *Aerosol Air Qual. Res.*, vol. 12, pp. 745-769, 2012. DOI: 10.4209/aaqr.2012.05.0132.

[44] A. Awtry, R. Sears and C. Andersen, "Progress update on the carbon-dioxide absorber retrofit equipment program (CARE)," NETL CO2 Capture Technology Meeting, Pittsburgh PA, 2014. [Online]. Available: http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/A-Awtry-NSG-Progress-Update-On-NSGs-CARE.pdf. [Accessed 8 August 2015].

[45] Y. Zheng, S. Kiil and J. E. Johnsson, "Experimental investigation of a pilot-scale jet bubbling reactor for wet flue gas desulphurisation," *Chem. Eng. Sci.*, vol. 58, pp. 4695-4703, 2003.

[46] M. A. Walsh, "Wet FGD types and fundamentals," Worldwide Pollution Control Association conference, Orlando, FL, 2008. [Online]. Available: http://wpca.info/pdf/presentations/Orlando_Dec2008/2-Wet%20FGD%20Types%20and%20Fundamentals%208-08.pdf. [Accessed 8 August 2015].

[47] Resodyn Acoustic Mixers, Inc., "Technical White Paper: Resonant Acoustic Mixing," [Online]. Available: http://www.resodynmixers.com/wp-content/uploads/2009/05/ram-technical-white-paper1.pdf. [Accessed 8 August 2015].

[48] Arisdyne Systems, Inc., "Controlled Flow Cavitation (CFC)," [Online]. Available: http://www.arisdyne.com/content/controlled-flow-cavitation-cfc%E2%84%A2. [Accessed 8 August 2015].

[49] M. Rahimi, N. Azimi and F. Parvizian, "Using microparticles to enhance micromixing in a high frequency continuous flow sonoreactor," *Chem. Eng. Proc.*, vol. 70, pp. 250-258, 2013.

[50] Y. Lu, M. Rostam-Abadi, X. Ye, S. Zhang, D. Ruhter, A. Khodayari and M. Rood, "Development and evaluation of a novel integrated vacuum carbonate absorption process," Final Report submitted by Illinois State Geological Survey, Prairie Research Institute, University of Illinois at Urbana-Champaign, to U.S. Department of Energy, National Energy Technology Laboratory for project DE-FC26-08NT0005498, 2012. [Online]. Available: http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/NT0005498-Final-Report-07-30-12.pdf.

[51] P. Danckwerts, "The absorption of gases in liquids," *Pure Appl Chem*, vol. 10, pp. 625-642, 1965.

[52] G. Graf, "Regenerative control of CO2 in the air by carboninc anhydrase," Technical Report No. AFFDL-TR-66-62, Department of Chemistry, Youngstown University, Youngstown, Ohio, 1966.

[53] C. Lippert, J. Landon, K. Liu, M. Sarma, R. Franca, R. Frimpong, G. Qi and K. Liu, "An advanced catalytic solvent for lower cost post-combustion CO2 capture in a coal-fired power plant," NETL CO2 Capture Technology Meeting, Pittsburgh, PA, 24 June 2015. [Online]. Available: http://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/C-Lippert-CAER-UK-Advanced-Catalytic-Solvent.pdf. [Accessed 8 August 2015].

[54] J. Thompson, H. Nikolic and K. Liu, "Application of a heat integrated post-combustion CO2 capture system with Hitachi advanced solvent into existing coal-fired power plant," NETL CO2 Capture Technology Meeting, Pittsburgh, PA, 24 June 2015. [Online]. Available: http://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/J-Thompson-CAER-UK-Heat-Integrated-Capture.pdf. [Accessed 8 August 2015].

[55] Y. Lu, M. Rostam-Abadi, X. Ye, Z. Zhang and T. Djukardi, "Development and evaluation of a novel integrated vacuum carbonate absorption process (DE-FC26-08NT0005498)," 2010 DOE/NETL CO2 Capture Technology Meeting, Pittsburgh, PA, 13-17 September 2010. [Online]. Available: http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/development-evaluation-novel-integrated-vacuum-sept2010.pdf. [Accessed 22 August 2015].

[56] Y. Khalil and A. Gerbino, "Simultaneous removal of SO2 and CO2 from flue gases at large coal-fired stationary sources," OLI's 24th User Conference, Morristown, NJ, 2007.

[57] U.S. Environmental Protection Agency, "Sulfur Oxides Control Technology Series: Flue Gas Desulfurization - Lime/Limestone Processes," EPA Summary Report No. 625/8-81-006, 1981. [Online]. Available: http://nepis.epa.gov/Exe/ZyNET.exe/9100Y8QP.TXT?ZyActionD=ZyDocument&Client=EPA&Index=1981+Thru+1985&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&.

[58] P. S. Nolan, "Flue gas desulfurization technologies for coal-fired power plants (presented by Michael X. Jiang)," Coal-Tech 2000 International Conference, Jakarta, Indonesia, November 13-14, 2000. [Online]. Available: http://www.babcock.com/library/Documents/br-1709.pdf. [Accessed 22 August 2015].

[59] D. Burk, "On the use of carbonic anhydrase in carbonate and amine buffers for CO2 exchange in manometric vessels, atomic submarines, and industrial CO2 scrubbers," *Annals New York Academy of Sciences,* pp. 372-400, 1961.

[60] E. Alper and W.-D. Deckwer, "Some aspects of gas absorption mechanism in slurry reactors," in *Mass Transfer with Chemical Reaction in Multiphase Systems*, E. Alper, Ed., Dordrecht, Springer Science & Business Media, 1983, pp. 199-224.

[61] G. M. Bond, J. Stringer, D. K. Brandvold, F. A. Simsek, M.-G. Medina and G. Egeland, "Development of integrated system for biomimetic CO2 sequestration using the enzyme carbonic anhydrase," *Energy & Fuels,* vol. 15, pp. 309-316, 2001.

[62] S. Bhattacharya, A. Nayak, M. Schiavone and S. K. Bhattacharya, "Solubilization and

concentration of carbon dioxide: Novel spray reactors with immobilized carbonic anhydrase," *Biotechnology and Bioengineering,* vol. 86, no. 1, pp. 37-46, 2004.

[63] M. C. Trachtenberg, R. M. Cowan, D. A. Smith and I. L. Sider, "Development of biomimetic membranes for near zero PC power plant emissions," Final Scientific/ Technical Report submitted by Carbozyme, Inc., to U.S. Department of Energy, National Energy Technology Laboratory for project DE-FC26-07NT43084, 2011. [Online]. Available: http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/final-43084FSRFG073109.pdf. [Accessed 8 August 2015].

[64] Y. Lu, X. Ye, Z. Zhang, A. Khodayari and T. Djukadi, "Development of a carbonate absorption-based process for post-combustion CO2 capture: the role of biocatalyst to promote CO2 absorption rate," *Energy Procedia,* vol. 4, pp. 1286-1293, 2011.

[65] O. Alvizo, L. J. Nguyen, C. K. Savile, J. A. Bresson, S. L. Lakhapatri, E. O. P. Solis, R. J. Fox, J. M. Broering, M. R. Benoit, S. A. Zimmerman, S. J. Novick, J. Liang and J. J. Lalonde, "Directed evolution of an ultrastable carbonic anhydrase for highly efficient carbon capture from flue gas," *PNAS,* vol. 111, no. 46, pp. 16436-16441, 18 November 2014, DOI: 10.1073/pnas.1411461111.

[66] A. Zaks and J. Reardon, "Advanced low energy enzyme catalyzed solvent for CO2 capture," Final Technical Report submitted by Akermin, Inc., to U.S. Department of Energy, National Energy Technology Laboratory for project DE-FE0004228, 2013. [Online]. Available: http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0004228-Final-Report-01-07-2014.pdf.

[67] R. D. Aines, "Polymer-encapsulated carbonate solvents for improved bicarbonate solids utilization with minimal liquid water," NETL CO2 Capture Technology Meeting, Pittsburgh PA, 2013. [Online]. Available: http://www.netl.doe.gov/File%20Library/events/2013/co2%20capture/R-Aines-LLNL-Catalytic-Improvement-of-CCS.pdf. [Accessed 8 August 2015].

[68] L. Fradette, J. Kay, J. Carley, S. Lefebvre, S. Fradette, F. Clerveau, N. Fiala, K. Leroux and J. Stanislowski, "Pilot testing of enzyme-accelerated CO2 capture," 14th Annual Conference on Carbon Capture, Utilization & Sequestration, Pittsburgh, PA, 29 April 2015. [Online]. Available: http://www.co2solutions.com/uploads/file/CCUS_2015_Pilot_Testing_of_Enzyme-Accelerated_CO2_Capture_v2.pdf. [Accessed 12 May 2015].

[69] S. Swaminathan, A. Kuczynska, S. Hume, V. Mulgundmath, C. Freeman, M. Bearden, J. Remias, B. Ambedkar, S. Salmon and A. House, "Preliminary technical and economic feasibility study on the integration of a process utilizing low-energy solvents for carbon dioxide capture enabled by a combination of enzymes and ultrasonics with a subcritical PC power plant," Topical Report for project DE-FE0007741, submitted to U.S. Department of Energy, National Energy Technology Laboratory, October 2012. [Online]. Available: http://www.netl.doe.gov/research/coal/carbon-capture/post-combustion/solvent-novozymes. [Accessed 8 August 2015].

[70] J. Slater, D. Fitzgerald, R. Vidal, T. Russell, C. Freeman, M. Bearden, G. Whyatt, K. Liu, R. Frimpong, K. Liu, S. Salmon, A. House and E. Yarborough, "Preliminary environmental, health and safety risk assessment on the integration of a process utilizing low-energy solvents for carbon dioxide capture enabled by a combination of enzymes and

vacuum regeneration with a subcritical PC power plant," Topical Report, submitted to U.S. Department of Energy, National Energy Technology Laboratory, 31 December 2014.

[71] J. Slater, D. Fitzgerald, R. Vidal, T. Russell, C. Freeman, M. Bearden, G. Whyatt, K. Liu, R. Frimpong, K. Liu, S. Salmon, A. House and E. Yarborough, "Technical and economic feasibility assessment of the integration of a process utilizing low-energy solvents for carbon dioxide capture enabled by a combination of enzymes and vacuum regeneration with a subcritical PC power plant," Topical Report, submitted to U.S. Department of Energy, National Energy Technology Laboratory, 14 August 2015.

[72] DOE/NETL, "Cost and Performance Baseline for Fossil Energy Plants - Volume 1: Bituminous Coal and Natural Gas to Electricity, DOE/NETL-2010/1397 Final Report, Rev. 2a," 2013. [Online]. Available: http://www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/OE/BitBase_FinRep_Rev2a-3_20130919_1.pdf.

[73] Y. Zhang, J. Ge and Z. Liu, "Enhanced activity of immobilized or chemically modified enzymes," *ACS Catalysis*, vol. 5, pp. 4503-4513, 2015.

[74] T. Bucholz, M. K. Hulvey, J. P. Reardon, B. M. Rambo, D. C. Pulvirenti, L. E. Weber and A. Zaks, "Development of an organosilica coating containing carbonic anhydrase for applications in CO2 capture," in *Novel Materials for Carbon Dioxide Mitigation*, F. Shi and B. Morreale, Eds., Amsterdam, Elsevier B.V., 2015, pp. 117-147. DOI: 10.1016/B978-0-444-63259-3.01001-6.

[75] C. Capasso, V. De Luca, V. Carginale, R. Cannio and M. Rossi, "Biochemical properties of a novel and highly thermostable bacterial alpha-carbonic anhydrase from Sulfurihydrogenibium yellowstonense YO3AOP1," *J. Enzym. Inhib. Med. Ch.*, vol. 27, pp. 892-897, 2012.

[76] Nomenclature Committee of the International Union of Biochemistry and Molecular Biology, Enzyme Nomenclature, E. C. Webb, Ed., San Diego, CA: Academic Press, Inc., 1992.

[77] C. T. Supuran, "Carbonic anhydrases: Catalytic and inhibition mechanisms, distribution and physiological roles," in *Carbonic Anhydrase: Its Inhibitors and Activators*, C. T. Supuran, A. Scozzafava and J. Conway, Eds., Boca Raton, FL: CRC Press LLC, 2004, pp. 1-23.

[78] R. G. Khalifah, "The carbon dioxide hydration activity of carbonic anhydrase," *J. Biol. Chem.*, vol. 246, pp. 2561-2573, 1971.

[79] J. Wilcox, Carbon Capture, New York, NY: Springer, 2012.

[80] D. W. Christianson and C. A. Fierke, "Carbonic anhydrase: Evolution of the zinc binding site by nature and by design," *Acc. Chem. Res.*, vol. 29, pp. 331-339, 1996.

[81] R. Mikulski, D. West, K. H. Sippel, B. S. Avvaru, M. Aggarwal, C. Tu, R. McKenna and D. N. Silverman, "Water networks in fast proton transfer during catalysis by human carbonic anhydrase II," *Biochemistry*, vol. 52, pp. 125-131, 2013.

[82] E. Y. Kenig, L. Kucka and A. Gorak, "Rigorous modeling of reactive absorption processes," *Chem. Eng. Technol.*, vol. 26, no. 6, pp. 631-646, 2003.

[83] J. Tosh, J. Field, H. Benson and W. Haynes, "Equilibrium study of the system potassium carbonate, potassium bicarbonate, carbon dioxide, and water," Bureau of Mines, Report of

Investigations, no. 5484, pp. 23, 1959.

[84] C. Goyet and A. Snover, "High accuracy measurements of total dissolved inorganic carbon in the ocean: comparison of alternate detection methods," *Mar. Chem.,* vol. 44, pp. 235-242, 1993.

[85] N. Matin, J. Remias, J. Neathery and K. Liu, "Facile method for determination of amine speciation in CO2 capture solutions," *Ind. Eng. Chem. Res.,* vol. 51, no. 19, pp. 6613-6618, 2012.

[86] O. Louisnard and F. Gomez, "Growth by rectified diffusion of strongly acoustically forced gas bubbles in nearly staurated liquids," *Phys. Rev. E,* vol. 67, no. 3, p. 37, 2003.

[87] D. Hsieh and M. Plesset, "Theory of rectified diffusion of mass into gas bubbles," *J. Acoust. Soc. Am.,* vol. 33, no. 2, pp. 206-215, 1961.

[88] A. Eller and H. Flynn, "Rectified diffusion during nonlinear pulsation of cavitation bubbles," *J. Acoust. Soc. Am.,* vol. 37, no. 3, pp. 493-503, 1965.

[89] P. Roberts and C. Wu, "On rectified diffusion and sonoluminescence," *Theor. Comp. Fluid Dyn.,* vol. 10, pp. 357-372, 1998.

[90] L. Crum, "Measurements of the growth of air bubbles by rectified diffusion," *J. Acoust. Soc. Am.,* vol. 68, pp. 203-211, 1980.

[91] L. A. Crum, "Acoustic Cavitation Studies," Final Report to the U.S. Office of Naval Research for Contract N00014-79-C-0404, University of Mississippi, Department of Physics and Astronomy, 1981. [Online]. Available: http://www.dtic.mil/dtic/tr/fulltext/u2/a104409.pdf. [Accessed 8 August 2015].

[92] L. Thompson and L. Doraiswamy, "Sonochemistry: Science and engineering," *Ind. Eng. Chem. Res.,* vol. 38, no. 4, pp. 1215-1249, 1999.

[93] T. Mason, L. Paniwnyk and J. Lorimer, "The uses of ultrasound in food technology," *Ultrason. Sonochem.,* vol. 3, pp. S253-S260, 1996.

[94] K. Suslick, Ultrasound: Its Chemical, Physical and Biological Effects, New York, NY: VCH Publishers, Inc., 1988.

[95] M. L. d. Castro and F. P. Capote, Analytical Applications of Ultrasound, Amsterdam: Elsevier B.V., 2007.

[96] O. Schlafer, M. Sievers, H. Klotzbucher and T. Onyeche, "Improvements in biological activity by low energy ultrasound assisted bioreactors," *Ultrasonics,* vol. 38, no. 1-8, pp. 711-716, 2000.

[97] D. Knorr, M. Zenker, V. Heinz and D.-U. Lee, "Applications and potential of ultrasonics in food processing," *Trends Food Sci. Technol.,* vol. 15, no. 5, pp. 261-266, 2004.

[98] K. Matsuura, M. Hirotsune, Y. Nunokawa, M. Satoh and K. Honda, "Acceleration of cell growth and ester formation by ultrasonic wave irradiation," *J. Ferment. Bioeng.,* vol. 77, no. 1, pp. 36-40, 1994.

[99] A. Patist and D. Bates, "Ultrasonic innovations in the food industry: From the laboratory to commercial production," *Innov. Food Sci. Emerg. Technol.,* vol. 9, pp. 147-154, 2008.

[100] Lloyd's Register Marine Services, "Ballast Water Treatment Technology: Current status," February 2010. [Online]. Available: http://www.psmfc.org/ballast/wordpress/wp-content/uploads/2010/06/Ballast-Water-Treatment-Technology_Feb-2010.pdf. [Accessed 8 August 2015].

[101] E. Alper, B. Wichtendahl and W.-D. Deckwer, "Gas absorption mechanism in catalytic slurry reactors," *Chem. Eng. Sci.*, vol. 35, pp. 217-222, 1980.

[102] B. Pinsent, L. Pearson and F. Roughton, "The kinetics of combination of carbon dioxide with hydroxide ions," *Trans. Faraday Soc.,* vol. 52, pp. 1512-1520, 1956, DOI: 10.1039/TF9565201512.

[103] E. Rickli, S. Ghazanfar, B. Gibbons and J. Edsall, "Carbonic anhydrases from human erythrocytes: Preparation and properties of two enzymes," *J. Biol. Chem.*, vol. 239, pp. 1065-1078, 1964.

[104] K. Wilbur and N. Anderson, "Electrometric and colorimetric determination of carbonic anhydrase," *J. Biol. Chem.*, vol. 176, pp. 147-154, 1948.

[105] S. Salmon, A. House and M. Whitener, "Compositions and methods for analysis of CO2 absorption". PCT Patent application WO2014/144264, 18 September 2014.

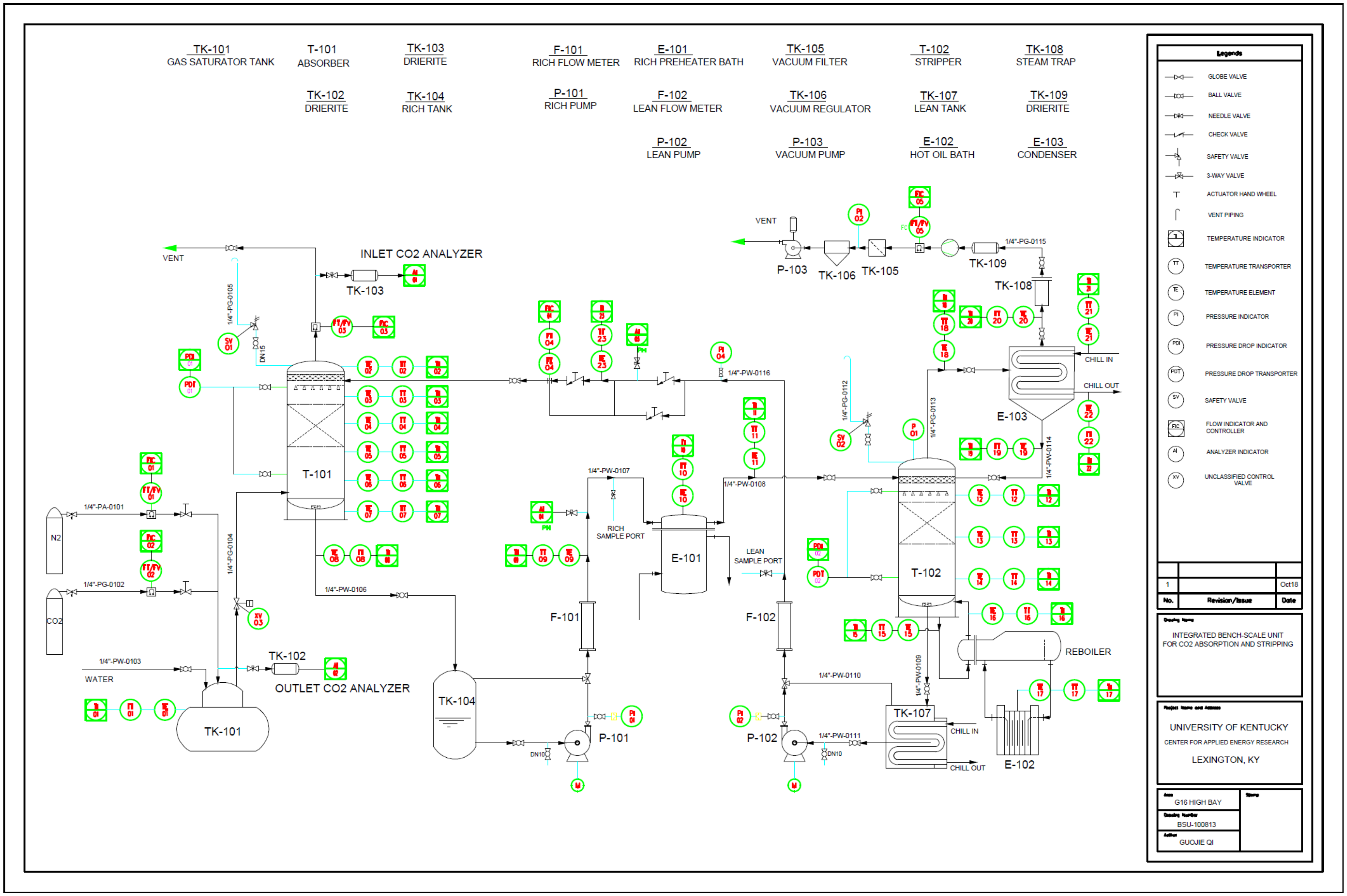
[106] DOE/NETL, "Cost and Performance Baseline for Fossil Energy Plants - Volume 1: Bituminous Coal and Natural Gas to Electricity, Rev. 1, DOE/NETL-2007/1281," August 2007.

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

[108] ACGIH Worldwide, "Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices," American Conference of Governmental Industrial Hygienists, 2003.

[109] B. A. Oyenekan and G. T. Rochelle, "Rate modeling of CO2 stripping from potassium carbonate promoted by piperazine," *Int. J. Greenhouse Gas Control,* vol. 3, pp. 121-132, 2009.

APPENDIX A – DETAILED PROCESS AND INSTRUMENTATION DIAGRAM (P&ID) OF BENCH-SCALE UNIT



APPENDIX B – OPERATION LIMITS TESTING RESULTS

Test A: 0.3 g/L CA, 40°C Absorber, 20 wt% K_2CO_3 (Table B.1)

Test results for high liquid flow rate (700 mL/min) and low stripper pressure (32 kPa(a)) with low enzyme dose, baseline absorber temperature and baseline potassium carbonate (20 wt%).

Enzyme Dosing	0.3g/l_CA					
Solvent Flow Rate, mL/min	700		700		700	
	DAY1		DAY2		DAY3	
Test Condition	Average	stdev	Average	stdev	Average	stdev
Ab.Gas IN. TC, °C	40.7	0.08	40.4	0.17	40.5	0.18
BP.TC, °C	76.9	0.43	77.0	0.64	78.7	1.16
Lean.TC, °C	40.3	0.40	40.8	0.40	40.6	0.54
Inlet Conc.CO_2_%	15.0		15.0		15.1	
Outlet Conc.CO_2_%	4.42	0.83	5.55	0.46	5.98	0.35
MFC.CO_2_LPM	4.46	0.00	4.46	0.00	4.46	0.00
MFC.N_2_LPM	25.4	0.00	25.4	0.00	25.4	0.00
Total Gas Flow_LPM	29.8		29.8		29.8	
Oil.Flowrate, LPM	10.1	0.03	10.1	0.01	10.2	0.01
REBOUT.TC, °C	89.7	0.24	89.8	0.31	90.4	0.40
REBIN.TC, °C	95.3	0.21	95.4	0.23	95.4	0.16
Rich.TC2, °C	66.1	0.18	66.0	0.28	66.1	0.22
Vacuum Pressure_kPaA	32.1		32.0		32.1	
Q, Reboiler, kW	1.49	0.04	1.49	0.04	1.35	0.12
Vacuum Pump, Watts	181	1.15	182	0.93	180	1.23
Corrected Vacuum Pump from bleed valve, kW	0.07		0.07		0.06	
Estimated heat loss (kW)	0.09		0.09		0.09	
Stripper Top Vap Temp (S.TC0)	70.3	1.14	69.4	0.35	67.6	1.43
Antifoam Dosing (vol%)	0.02		0.02		0.02	
CO_2 In, mmol/s	3.33		3.33		3.34	
CO_2 out, mmol/s	0.87		1.11		1.20	
Capture Efficiency (%)	73.8		66.7		64.1	
Energy Demand (kJ/mol CO_2 captured)	598		658		615	

Test B: 0.3 g/L CA, 30°C Absorber, 20 wt% K_2CO_3 (Table B.2)

Test results for high liquid flow rate (700 mL/min), low stripper pressure (32 kPa(a)) and low absorber temperature with low enzyme dose and baseline potassium carbonate (20 wt%).

Enzyme Dosing	0.3g/l_CA					
Solvent Flow Rate, mL/min	700		700		700	
	DAY4		DAY5		DAY6	
Test Condition	Average	stdev	Average	stdev	Average	stdev
Ab.Gas IN. TC, °C	29.2	1.11	31.3	0.09	30.8	0.31
BP.TC, °C	79.7	0.33	78.6	1.66	78.3	1.25
Lean.TC, °C	30.7	0.78	30.2	1.26	30.5	0.79
Inlet Conc.CO2_%	15.0		15.1		15.0	
Outlet Conc.CO2_%	8.43	0.29	7.43	0.86	7.49	0.53
MFC.CO_2_LPM	4.46	0.00	4.46	0.00	4.46	0.01
MFC.N_2_LPM	25.4	0.00	25.4	0.00	25.4	0.00
Total Gas Flow_LPM	29.8		29.8		29.8	
Oil.Flowrate, LPM	10.1	0.01	10.2	0.01	10.1	0.03
REBOUT.TC, °C	90.6	0.13	90.5	0.58	90.2	0.44
REBIN.TC, °C	95.1	0.06	95.4	0.10	95.2	0.10
Rich.TC2, °C	66.1	0.12	66.4	0.28	66.2	0.21
Vacuum Pressure_kPaA	31.9		32.1		32.0	
Q, Reboiler, kW	1.21	0.03	1.29	0.15	1.34	0.10
Vacuum Pump, Watts	181	0.66	181	1.00	181	1.62
Corrected Vacuum Pump from bleed valve, kW	0.05		0.06		0.05	
Estimated heat loss (kW)	0.09		0.09		0.09	
Stripper Top Vap Temp (S.TC0)	64.5	0.3	66.6	2.01	68.7	2.58
Antifoam Dosing (vol%)	0		0.02		0.02	
CO_2 In, mmol/s	3.33		3.36		3.33	
CO_2 out, mmol/s	1.74		1.51		1.53	
Capture Efficiency (%)	47.8		54.9		54.2	
Energy Demand (kJ/mol CO_2 captured)	731		679		718	

Test C: 1.5 g/L CA, 30°C Absorber, 20 wt% K_2CO_3 (Table B.3)

Test results for high liquid flow rate (700 mL/min), low stripper pressure (32 kPa(a)) and low absorber temperature with mid-range enzyme dose and baseline potassium carbonate (20 wt%).

Enzyme Dosing	1.5g/l_CA					
Solvent Flow Rate, mL/min	700		700		700	
	DAY1		DAY2		DAY3	
Test Condition	Average	stdev	Average	stdev	Average	stdev
Ab.Gas IN. TC, °C	33.1	1.44	31.3	0.09	31.1	0.06
BP.TC, °C	77.9	0.59	77.9	0.37	75.7	0.11
Lean.TC, °C	29.7	0.36	29.6	0.65	29.9	0.18
Inlet Conc.CO_2_%	14.9		15.2		15.0	
Outlet Conc.CO_2_%	1.60	0.15	2.19	0.22	3.15	0.21
MFC.CO_2_LPM	4.46	0.00	4.46	0.00	4.46	0.01
MFC.N_2_LPM	25.4	0.00	25.4	0.00	25.4	0.00
Total Gas Flow_LPM	29.8		29.8		29.8	
Oil.Flowrate, LPM	10.1	0.02	10.2	0.02	10.2	0.02
REBOUT.TC, °C	90.2	0.22	90.3	0.14	89.6	0.07
REBIN.TC, °C	95.5	0.06	95.4	0.06	95.4	0.05
Rich.TC2, °C	66.2	0.10	66.3	0.27	66.0	0.14
Vacuum Pressure_kPaA	32.9		32.8		32.0	
Q, Reboiler, kW	1.40	0.06	1.37	0.03	1.56	0.01
Vacuum Pump, Watts	178	0.39	181	0.98	178	0.60
Corrected Vacuum Pump from bleed valve, kW	0.09		0.09		0.08	
Estimated heat loss (kW)	0.09		0.09		0.09	
Stripper Top Vap Temp (S.TC0)	67.6	1.18	67.8	0.98	64.7	0.23
Antifoam Dosing (vol%)	0.02		2 x 0.02		0.02	
CO_2 In, mmol/s	3.30		3.37		3.34	
CO_2 out, mmol/s	0.31		0.42		0.61	
Capture Efficiency (%)	90.7		87.4		81.6	
Energy Demand (kJ/mol CO_2 captured)	466		464		566	

Test D: 3 g/L CA, 30°C Absorber, 20 wt% K_2CO_3 (Table B.4)

Test results for high liquid flow rate (700 mL/min), low stripper pressure (32 kPa(a)) and low absorber temperature with high enzyme dose and baseline potassium carbonate (20 wt%).

Enzyme Dosing	3g/l_CA					
Solvent Flow Rate, mL/min	700		700		700	
	DAY1		DAY2		DAY3	
Test Condition	Average	stdev	Average	stdev	Average	stdev
Ab.Gas IN. TC, °C	32.0	0.07	31.2	0.06	31.2	0.05
BP.TC, °C	78.2	0.11	77.6	0.36	77.5	0.31
Lean.TC, °C	29.9	0.19	29.9	0.24	30.9	0.67
Inlet Conc.CO_2_%	14.8		15.0		15.0	
Outlet Conc.CO_2_%	1.03	0.04	1.03	0.07	1.13	0.07
MFC.CO_2_LPM	4.46	0.00	4.46	0.01	4.46	0.00
MFC.N_2_LPM	25.4	0.00	25.4	0.00	25.4	0.00
Total Gas Flow_LPM	29.8		29.8		29.8	
Oil.Flowrate, LPM	10.2	0.02	10.2	0.02	10.2	0.02
REBOUT.TC, °C	90.3	0.06	90.1	0.16	90.2	0.12
REBIN.TC, °C	95.4	0.06	95.5	0.06	95.6	0.06
Rich.TC2, °C	66.2	0.09	65.6	0.23	66.4	0.28
Vacuum Pressure_kPaA	33.2		32.6		32.4	
Q, Reboiler, kW	1.39	0.00	1.43	0.03	1.44	0.03
Vacuum Pump, Watts	178.0	0.39	181	0.98	178	0.60
Corrected Vacuum Pump from bleed valve, kW	0.09		0.09		0.09	
Estimated heat loss (kW)	0.09		0.09		0.09	
Stripper Top Vap Temp (S.TC0)	69.6	0.44	69.2	0.27	69.9	0.37
Antifoam Dosing (vol%)	0.02		0.02		0.02	
CO_2 In, mmol/s	3.29		3.33		3.32	
CO_2 out, mmol/s	0.20		0.20		0.22	
Capture Efficiency (%)	94.0		94.1		93.5	
Energy Demand (kJ/mol CO_2 captured)	449		457		463	

Test E: 0.3 g/L CA, 30°C Absorber, 23.5 wt% K_2CO_3 (Table B.5)

Test results for high liquid flow rate (700 mL/min), low stripper pressure (32 kPa(a)), and low absorber temperature with low enzyme dose and increased concentration of potassium carbonate (23.5 wt%).

Enzyme Dosing	0.3 g/l_CA					
Solvent Flow Rate, mL/min	700		700		700	
	DAY1		DAY2		DAY3	
Test Condition	Average	stdev	Average	stdev	Average	stdev
Ab.Gas IN. TC, °C	31.4	0.11	31.1	0.41	31.9	0.68
BP.TC, °C	77.6	0.27	76.8	0.15	77.4	0.57
Lean.TC, °C	28.1	0.16	29.6	0.84	31.5	1.12
Inlet Conc.CO_2_%	15.1		15.0		14.4	
Outlet Conc.CO_2_%	3.01	0.29	4.45	0.50	5.28	0.38
MFC.CO_2_LPM	4.46	0.01	4.46	0.01	4.45	0.00
MFC.N_2_LPM	25.4	0.00	25.4	0.00	25.4	0.00
Total Gas Flow_LPM	29.8		29.8		29.8	
Oil.Flowrate, LPM	10.3	0.12	10.4	0.05	10.4	0.06
REBOUT.TC, °C	90.3	0.10	89.8	0.10	90.1	0.21
REBIN.TC, °C	95.7	0.06	95.2	0.12	95.4	0.07
Rich.TC2, °C	66.5	0.31	66.2	0.30	66.4	0.41
Vacuum Pressure_kPaA	32.1		32.1		32.0	
Q, Reboiler, kW	1.39	0.00	1.43	0.03	1.44	0.03
Vacuum Pump, Watts	178	0.39	181	0.98	178	0.60
Corrected Vacuum Pump from bleed valve, kW	0.08		0.07		0.07	
Estimated heat loss (kW)	0.09		0.09		0.09	
Stripper Top Vap Temp (S.TC0)	69.6	0.41	69.2	0.30	68.5	0.89
Antifoam Dosing (vol%)	0.02		0.02		0.02	
CO_2 In, mmol/s	3.34		3.32		3.19	
CO_2 out, mmol/s	0.59		0.88		1.05	
Capture Efficiency (%)	82.5		73.5		67.0	
Energy Demand (kJ/mol CO_2 captured)	500		578		660	

APPENDIX C – PARAMETRIC TEST PHASE II RESULTS

Results of Parametric Tests #1 – 2 (Table C.1)

	Parametric #1			Parametric #2	
Test Condition	Run 1	Run 2	Run 3	Run 1	Run 2
Liquid Flow Rate, mL/min	500	500	500	600	600
Ab.Gas IN. TC, ^oC	40.3	40.0	40.4	39.8	39.8
BP.TC, ^oC	75.8	76.8	77.2	77.9	77.8
Lean.TC, ^oC	39.5	39.7	40.2	40.0	39.9
Inlet Conc.CO_2_%	14.8	14.8	14.8	15.0	15.0
Outlet Conc.CO_2_%	2.01	1.80	1.95	2.45	2.46
Total Gas Flow_LPM	30.0	30.0	30.0	30.0	30.0
Oil.Flowrate, LPM	10.0	10.0	10.0	10.0	10.0
REBOUT.TC, ^oC	90.6	90.0	90.8	91.3	91.1
REBIN.TC, ^oC	94.8	94.2	95.2	95.2	95.2
Rich.TC2, ^oC	65.3	66.1	66.3	67.4	67.6
Q, Reboiler, KW	1.13	1.11	1.16	1.04	1.07
Corrected Vacuum Pump from bleed valve, kW	0.09	0.09	0.08	0.09	0.09
Estimated heat loss (kW)	0.09	0.09	0.09	0.09	0.09
Stripper Top (S.TC0)	67.6	70.5	70.6	67.4	67.6
Antifoam Dosing (vol%)	0.04	0.04	0.08	0.04	0.04
CO_2 In, mmol/s	3.31	3.32	3.31	3.31	3.31
CO_2 out, mmol/s	0.39	0.35	0.38	0.48	0.48
Capture Efficiency (%)	88.2	89.5	88.6	85.6	85.5
Energy Demand (kJ/mol CO_2 captured)	383	371	391	363	374
Stripper Pressure, kPaA	34.8	34.5	36.0	34.9	35.0
Replenishment (%)	15	15	15	15	15
Rich Carbon Loading (mol CO_2/kg)	2.34	2.35	2.32	2.39	2.38
Rich Alkalinity (mol/kg)	3.05	3.02	3.04	3.10	3.12
Rich Conversion	54%	55%	53%	54%	52%
Lean Carbon Loading (mol CO_2/kg)	2.05	2.08	2.12	2.16	2.18
Lean Alkalinity (mol/kg)	3.07	3.07	3.13	3.16	3.19
Lean Conversion	34%	35%	35%	37%	37%

Results of Parametric Test # 3 (Table C.2)

	Parametric #3		
Test Condition	Run 1	Run 2	Run 3
Liquid Flow Rate, mL/min	400	400	400
Ab.Gas IN. TC, ^{o}C	40.0	39.8	40.1
BP.TC, ^{o}C	77.7	78.6	77.9
Lean.TC, ^{o}C	39.3	40.1	39.4
Inlet Conc.CO_2_%	15.0	14.8	14.8
Outlet Conc.CO_2_%	2.25	2.69	2.42
Total Gas Flow_LPM	30.0	30.0	30.0
Oil.Flowrate, LPM	10.0	10.0	10.0
REBOUT.TC, ^{o}C	91.2	90.9	91.7
REBIN.TC, ^{o}C	95.3	94.5	95.5
Rich.TC2, ^{o}C	67.0	68.6	67.6
Q, Reboiler, KW	1.07	0.95	0.99
Corrected Vacuum Pump from bleed valve, kW	0.08	0.08	0.08
Estimated heat loss (kW)	0.09	0.09	0.09
Stripper Top (S.TC0)	71.6	70.4	70.3
Antifoam Dosing (vol%)	0.04	0.08	0.08
CO_2 In, mmol/s	3.31	3.31	3.31
CO_2 out, mmol/s	0.44	0.53	0.47
Capture Efficiency (%)	87%	84%	86%
Energy Demand (kJ/mol CO_2 captured)	367.3	335	344
Stripper Pressure, kPaA	35.1	34.6	34.8
Replenishment (%)	26	20	20
Rich Carbon Loading (mol CO_2/kg)	2.42	2.48	2.48
Rich Alkalinity (mol/kg)	3.19	3.17	3.21
Rich Conversion	52%	57%	55%
Lean Carbon Loading (mol CO_2/kg)	2.12	2.22	2.16
Lean Alkalinity (mol/kg)	3.24	3.23	3.25
Lean Conversion	31%	37%	33%

Results of Phase I Test and Parametric Test # 4 (Table C.3)

	Parametric Phase I		Parametric #4	
Test Condition	Run 1	Run 4	Run 1	Run 2
Liquid Flow Rate, mL/min	500	500	300	300
Ab.Gas IN. TC, ^{o}C	39.1	40.4	41.2	40.2
BP.TC, ^{o}C	75.9	76.0	77.0	76.0
Lean.TC, ^{o}C	40.1	40.2	40.2	40.5
Inlet Conc.CO_2_%	14.8	15.0	14.8	14.8
Outlet Conc.CO_2_%	2.64	2.87	3.28	3.22
Total Gas Flow_LPM	30.0	30.0	30.0	30.0
Oil.Flowrate, LPM	10.1	9.74	10.1	10.1
REBOUT.TC, ^{o}C	86.6	86.8	88.0	87.2
REBIN.TC, ^{o}C	90.0	89.9	90.7	90.2
Rich.TC2, ^{o}C	61.6	65.5	66.5	65.8
Q, Reboiler, KW	0.88	0.81	0.73	0.77
Corrected Vacuum Pump from bleed valve, kW	0.08	0.08	0.08	0.08
Estimated heat loss (kW)	0.09	0.09	0.09	0.09
Stripper Top (S.TC0)	61.4	64.9	68.0	68.2
Antifoam Dosing (vol%)	0.04	0.04	0.04	0.04
CO_2 In, mmol/s	3.31	3.31	3.31	3.31
CO_2 out, mmol/s	0.52	0.56	0.65	0.63
Capture Efficiency (%)	84.4	83.0	81%	81%
Energy Demand (kJ/mol CO_2 captured)	310	290	266	280
Stripper Pressure, kPaA	35.7	35.9	34.8	35.0
Replenishment (%)	-	15%	20%	20%
Enzyme Dosing (g/L)	2.5	2.5	2.5	2.5
Rich Carbon Loading (mol CO_2/kg)	2.41	2.49	2.48	2.48
Rich Alkalinity (mol/kg)	3.06	3.13	3.17	3.15
Rich Conversion	57%	59%	57%	57%
Lean Carbon Loading (mol CO_2/kg)	2.16	2.21	2.21	2.18
Lean Alkalinity (mol/kg)	3.09	3.16	3.23	3.18
Lean Conversion	40%	40%	37%	37%

Results of Parametric Tests # 5 and #6 (Table C.4)

	Parametric #5			Parametric #6	
Test Condition	Run 1	Run 2	Run 3	Run 1	Run 2
Liquid Flow Rate, mL/min	500	500	500	300	300
Ab.Gas IN. TC, ^{o}C	40.0	39.7	39.4	39.5	39.8
BP.TC, ^{o}C	76.2	75.9	75.9	76.6	75.8
Lean.TC, ^{o}C	40.5	40.1	40.5	40.3	40.1
Inlet Conc.CO_2_%	14.9	14.9	14.9	14.8	15.0
Outlet Conc.CO_2_%	2.41	3.11	3.07	2.67	2.62
Total Gas Flow_LPM	30.0	30.0	30.0	30.0	30.0
Oil.Flowrate, LPM	10.1	10.1	10.1	10.1	10.1
REBOUT.TC, ^{o}C	87.0	87.3	87.2	87.2	87.2
REBIN.TC, ^{o}C	90.2	90.2	90.2	90.1	90.2
Rich.TC2, ^{o}C	65.6	66.2	66.2	66.2	65.9
Q, Reboiler, KW	0.84	0.78	0.78	0.79	0.78
Corrected Vacuum Pump from bleed valve, kW	0.08	0.08	0.08	0.08	0.08
Estimated heat loss (kW)	0.09	0.09	0.09	0.09	0.09
Stripper Top (S.TC0)	65.2	64.8	65.6	65.0	65.5
Antifoam Dosing (vol%)	0.04	0.04	0.04	0.04	0.04
CO_2 In, mmol/s	3.31	3.32	3.31	3.31	3.31
CO_2 out, mmol/s	0.47	0.61	0.60	0.52	0.51
Capture Efficiency (%)	86%	82%	82%	84%	85%
Energy Demand (kJ/mol CO_2 captured)	290	281	282	276	274
Stripper Pressure, kPaA	35.2	34.5	34.8	34.8	34.6
Replenishment (%)	23%	22%	20%	20%	20%
Enzyme Dosing (g/L)	4	4	4	4	4
Rich Carbon Loading (mol CO_2/kg)	2.43	2.48	2.46	2.50	2.46
Rich Alkalinity (mol/kg)	3.23	3.20	3.15	3.16	3.15
Rich Conversion	50%	55%	56%	58%	56%
Lean Carbon Loading (mol CO_2/kg)	2.13	2.2	2.2	2.18	2.20
Lean Alkalinity (mol/kg)	3.23	3.22	3.17	3.19	3.20
Lean Conversion	32%	37%	39%	37%	37%

Results of Parametric Tests # 7 and #8 (Table C.5)

	Parametric #7		Parametric #8	
Test Condition	Run 1	Run 2	Run 1	Run 2
Liquid Flow Rate, mL/min	500	500	300	300
Ab.Gas IN. TC, ^{o}C	40.4	40.4	39.8	40.1
BP.TC, ^{o}C	75.9	76.3	77.1	76.8
Lean.TC, ^{o}C	40.2	39.9	39.8	40.5
Inlet Conc.CO_2_%	14.7	14.7	14.7	15.0
Outlet Conc.CO_2_%	4.64	4.81	4.93	5.33
Total Gas Flow_LPM	30.0	30.0	30.0	30.0
Oil.Flowrate, LPM	10.1	10.1	10.1	10.0
REBOUT.TC, ^{o}C	87.3	87.2	87.5	87.5
REBIN.TC, ^{o}C	90.3	90.2	90.2	90.2
Rich.TC2, ^{o}C	65.8	65.8	67.3	66.8
Q, Reboiler, KW	0.79	0.79	0.72	0.71
Corrected Vacuum Pump from bleed valve, kW	0.07	0.07	0.07	0.06
Estimated heat loss (kW)	0.09	0.09	0.09	0.09
Stripper Top (S.TC0)	64.4	64.4	66.2	66.2
Antifoam Dosing (vol%)	0.04	0.04	0.04	0.04
CO_2 In, mmol/s	3.31	3.31	3.31	3.31
CO_2 out, mmol/s	0.93	0.96	0.99	1.07
Capture Efficiency (%)	72%	71%	70%	68%
Energy Demand (kJ/mol CO_2 captured)	322	323	298	304
Stripper Pressure, kPaA	34.7	34.9	34.9	35.1
Replenishment (%)	20%	20%	20%	20%
Enzyme Dosing (g/L)	1	1	1	1
Rich Carbon Loading (mol CO_2/kg)	2.50	2.49	2.60	2.54
Rich Alkalinity (mol/kg)	3.18	3.18	3.16	3.14
Rich Conversion	57%	57%	64%	62%
Lean Carbon Loading (mol CO_2/kg)	2.31	2.31	2.28	2.28
Lean Alkalinity (mol/kg)	3.24	3.20	3.20	3.19
Lean Conversion	42%	44%	42%	43%

Results of Parametric Tests # 9 and #10 (Table C.6)

	Parametric #9		Parametric #10	
Test Condition	Run 1	Run 2	Run 1	Run 2
Liquid Flow Rate, mL/min	500	500	500	500
Ab.Gas IN. TC, ^{o}C	40.3	40.6	40.5	40.5
BP.TC, ^{o}C	75.4	75.9	76.4	76.5
Lean.TC, ^{o}C	40.2	40.3	40.4	40.6
Inlet Conc.CO_2_%	14.9	14.9	14.8	14.8
Outlet Conc.CO_2_%	12.4	12.5	12.4	12.4
Total Gas Flow_LPM	30.0	30.0	30.0	30.0
Oil.Flowrate, LPM	10.1	10.1	10.0	10.0
REBOUT.TC, ^{o}C	86.7	86.9	90.5	90.7
REBIN.TC, ^{o}C	90.2	90.1	94.6	94.8
Rich.TC2, ^{o}C	65.6	65.7	66.0	66.4
Q, Reboiler, KW	0.92	0.85	1.09	1.09
Corrected Vacuum Pump from bleed valve, kW	0.02	0.02	0.02	0.02
Estimated heat loss (kW)	0.09	0.09	0.09	0.09
Stripper Top (S.TC0)	70.3	70.3	71.3	71.3
Antifoam Dosing (vol%)	0.00	0.00	0.00	0.00
CO_2 In, mmol/s	3.31	3.31	3.31	3.31
CO_2 out, mmol/s	2.70	2.72	2.68	2.68
Capture Efficiency (%)	18.6	18.1	19.1	19.0
Energy Demand (kJ/mol CO_2 captured)	1371	1289	1612	1609
Stripper Pressure, kPaA	35.1	35.0	35.1	34.9
Rich Carbon Loading (mol CO_2/kg)	2.14	2.35	2.30	2.28
Rich Alkalinity (mol/kg)	2.94	3.19	3.21	3.20
Rich Conversion	45%	47%	43%	42%
Lean Carbon Loading (mol CO_2/kg)	2.10	2.28	2.22	2.22
Lean Alkalinity (mol/kg)	2.96	3.20	3.18	3.20
Lean Conversion	42%	42%	40%	39%

APPENDIX D – THRESHOLD LIMIT VALUES® FOR AIRBORNE ULTRASOUND

The Occupational Safety and Health Administration (OSHA) adopted the American Conference of Governmental Industrial Hygienists® (ACGIH®) Threshold Limit Values® (TLVs®) for airborne ultrasound in 2003 [108]. The TLVs® are set at the middle frequencies of the one-third octave bands from 10 kHz to 50 kHz and are designed to prevent possible hearing loss caused by the sub-harmonics of the set frequencies, rather than the ultrasonic sound itself. The TLVs® represent conditions under which it is believed that nearly all workers may be repeatedly exposed without adverse effect on their ability to hear and understand normal speech.

TLVs® for Ultrasound

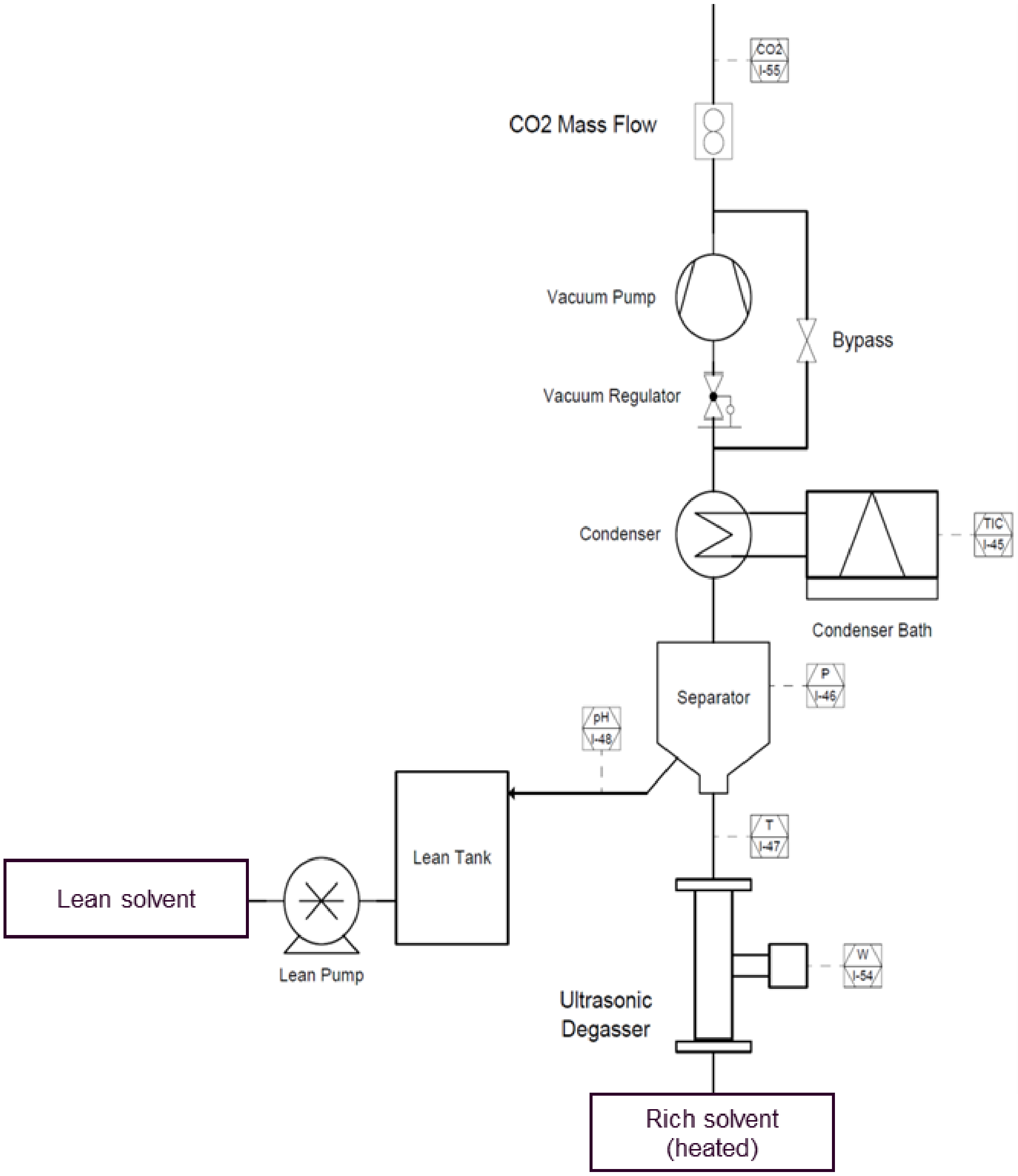
	One-third Octave-Band Level		
	Measured in Air in dB re: 20 μ Pa; Head in Air		Measured in Water in dB re: 1 μ Pa; Head in Water
Mid-Frequency of Third-Octave Band (kHz)	**Ceiling Values**	**8-Hour TWA**	**Ceiling Values**
10	105[A]	88[A]	167
12.5	105[A]	89[A]	167
16	105[A]	92[A]	167
20	105[A]	94[A]	167
25	110[B]	--	172
31.5	115[B]	--	177
40	115[B]	--	177
50	115[B]	--	177
63	115[B]	--	177
80	115[B]	--	177
100	115[B]	--	177

[A] *Subjective annoyance and discomfort may occur in some individuals at levels between 75 and 105 dB for the frequencies from 10 kHz to 20 kHz especially if they are tonal in nature. Hearing protection or engineering controls may be needed to prevent subjective effects. Tonal sounds in frequencies below 10 kHz might also need to be reduced to 80 dB.*

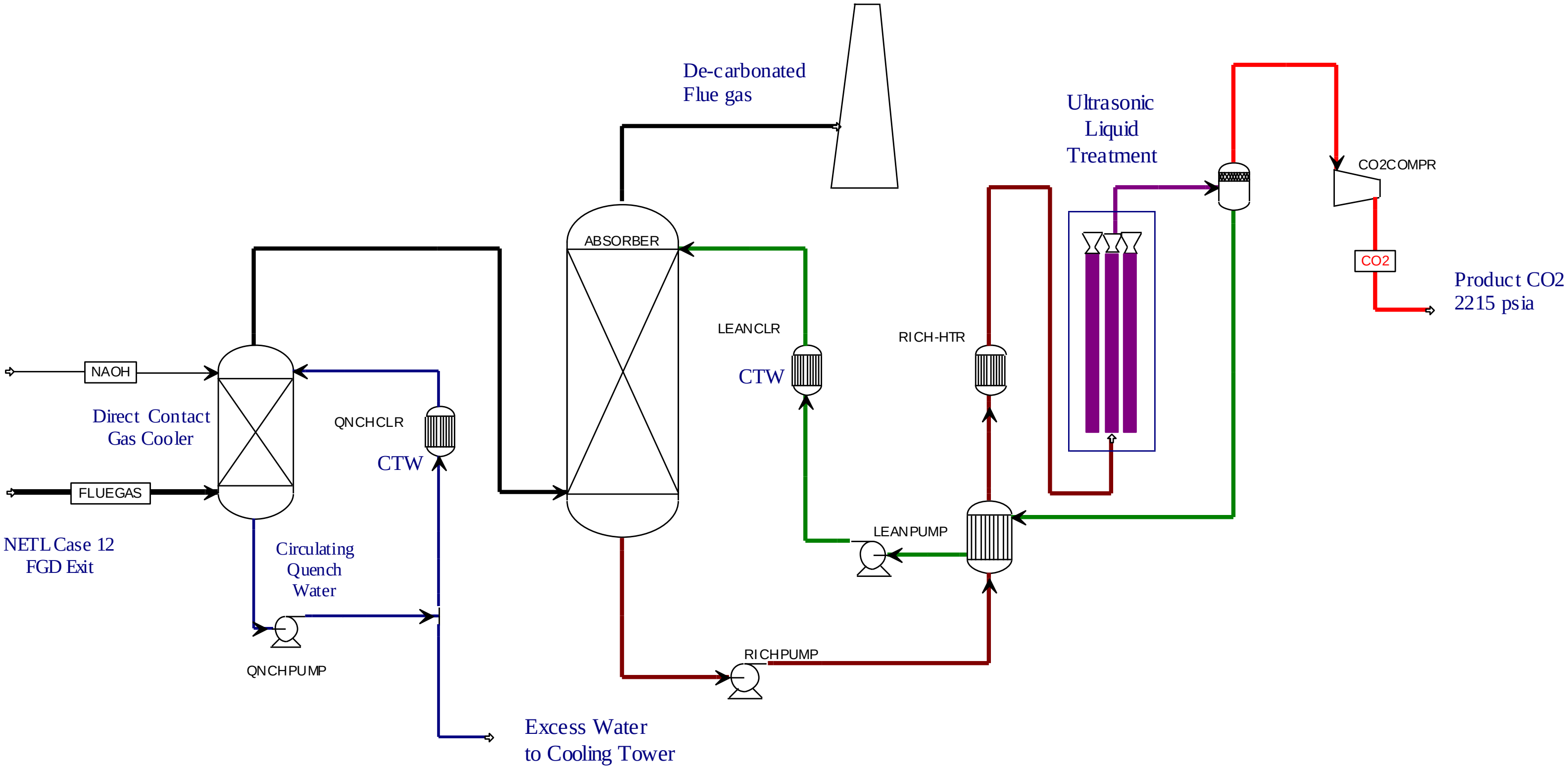
[B] *These values assume that human coupling with water or other substrate exists. These thresholds may be raised by 30 dB when there is no possibility that the ultrasound can couple with the body by touching water or some other medium. [When the ultrasound source directly contacts the body, the values in the table do not apply. The vibration level at the mastoid bone must be used.] Acceleration Values 15 dB above the reference of 1g rms should be avoided by reduction of exposure or isolation of the body from the coupling source. (g = acceleration due to the force of gravity, 9.80665 meters/second; rms = root-mean-square).*

Source: ACGIH® Worldwide. 2003 TLVs® and BEIs®: Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices, p.107.

APPENDIX E – FLOW-THROUGH ULTRASONIC REGENERATOR MODULE

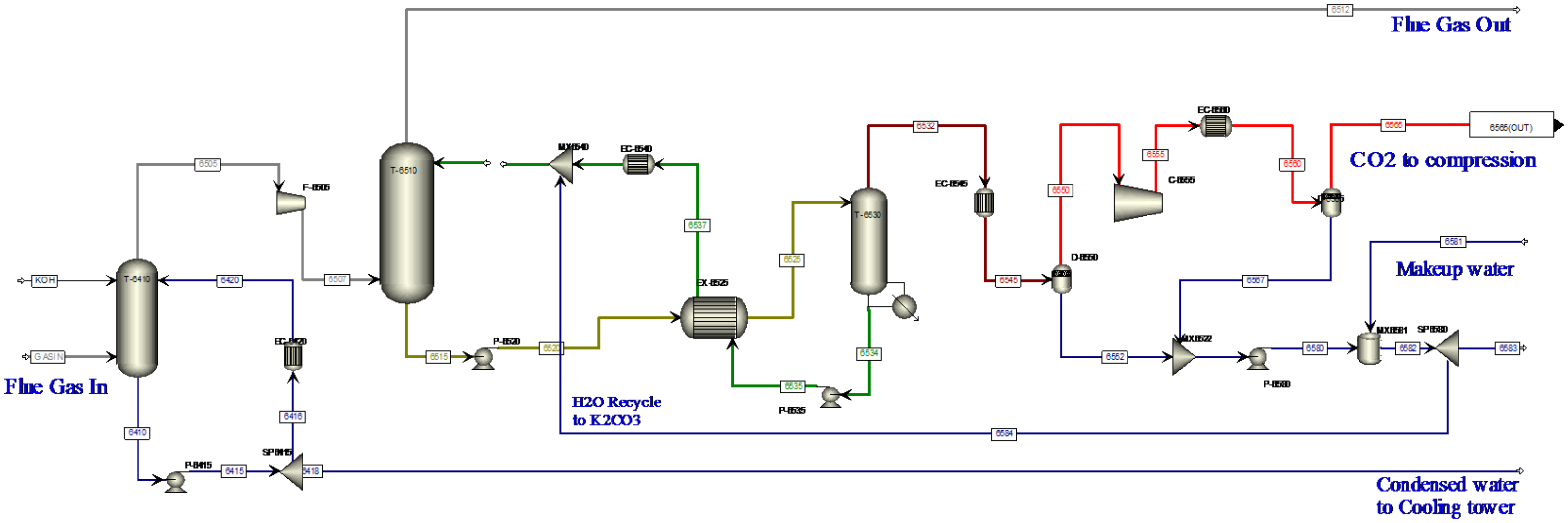


APPENDIX F – CONCEPTUAL PROCESS DESIGN FOR ULTRASONIC REGENERATION



Advantages	Challenges
- Low enthalpy, benign solvent (catalyzed aq. 20% K_2CO_3) - Potential for ~50% regeneration energy vs. MEA	- Demonstrate atmospheric regeneration at 70°C - Demonstrate overall techno-economic feasibility (energy demand and enzyme requirement)

APPENDIX G – PCC PROCESS CONCEPT FOR LOW TEMPERATURE VACUUM REGENERATION



Advantages	Challenges
• Low enthalpy, benign solvent (catalyzed aq. 20% K_2CO_3) ○ K_2CO_3 ΔH_{rxn} 27 kJ/mol CO_2 ○ MEA ΔH_{rxn} 83 kJ/mol CO_2 • Potential for ~20% reduction in energy penalty vs. MEA	• Demonstrate low temperature vacuum regeneration • Demonstrate overall techno-economic feasibility ○ energy demand ○ enzyme requirement

APPENDIX H – STATE POINT DATA TABLE FOR SOLVENT BASED SYSTEM

	Units	Measured/ Estimated Performance	Projected Performance
Pure "Solvent" (Chemical)			
Molecular Weight (K_2CO_3)	mol^{-1}	138.21	138.21
Solubility in water	g/100mL	112 (20°C) 156 (100°C)	112 (20°C) 156 (100°C)
Molecular Weight ($KHCO_3$)	mol^{-1}	100.12	100.12
Solubility in water	g/100mL	33.7 (20°C) 60 (60°C)	33.7 (20°C) 60 (60°C)
Normal Boiling point	°C	Not relevant	Not relevant
Normal Freezing Point	°C	Not relevant	Not relevant
Vapor Pressure @ 15 °C	Bar	Not relevant	Not relevant
Working Solution (aq. K_2CO_3)			
Concentration (K_2CO_3)	kg/kg	0.20 (20%)	0.20
Concentration (enzyme)	kg/kg	0.003	<0.003
Specific Gravity (15°C/15°C)	-	1.16	1.16
Specific Heat Capacity @ STP[c]	kJ/kg-K	4.35	4.35
Viscosity @ STP	cP	1.88	1.88
Surface Tension @ STP	dyn/cm	84.4 (20°C)	84.4 (20°C)
Absorption			
Pressure (total)	Bar	1.03[a]	1.03[a]
Temperature	°C	30-50	30-50
Steady-state CO_2 loading (rich)	mol CO_2/mol K_2CO_3	0.67	0.67
Heat of Absorption	kJ/mol CO_2	27	27
Solution Viscosity	cP	1.4 (30°C) 1.2 (40°C) 0.8 (50°C)	1.4 (30°C) 1.2 (40°C) 0.8 (50°C)
Desorption			
Pressure (total)	Bar	1.03[b]	1.03[b]
Temperature	°C	70	70
Steady-state CO_2 loading (lean)	mol CO_2/mol K_2CO_3	0.3	0.3
Heat of Desorption	kJ/mol CO_2	≈ same as absorption	≈ same as absorption

[a] where partial pressure of CO_2 is 0.14 bar assuming 14% CO_2 in inlet flue gas.

[b] ultrasonic effect equivalent to 0.41 bar with bulk vacuum.

[c] Standard Temperature and Pressure (15°C, 1 atm).

APPENDIX I – FULL TECHNICAL AND ECONOMIC ASSESSMENT

Following this page is appended the full Technical and Economic Feasibility Assessment on the Integration of a Process Utilizing Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration with a Subcritical PC Power Plant, prepared as a Topical Report deliverable under Task 7.1 of Award No. DE-FE0007741.

The report comprises: a title page, notices, abstract, table of contents, abbreviations, list of exhibits, executive summary (numbered pages 1-6), main report (numbered pages 7-110), and references (numbered pages 111-112).

TECHNICAL AND ECONOMIC FEASIBILITY ASSESSMENT ON THE INTEGRATION OF A PROCESS UTILIZING LOW-ENERGY SOLVENTS FOR CARBON DIOXIDE CAPTURE ENABLED BY A COMBINATION OF ENZYMES AND VACUUM REGENERATION WITH A SUBCRITICAL PC POWER PLANT

TOPICAL REPORT

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Abstract

The results of the technical and economic feasibility assessment for a carbonic anhydrase (CA) enzyme-activated potassium carbonate (K_2CO_3) solution post-combustion CO_2 capture (PCC) plant, incorporating vacuum regeneration and integrated with a subcritical pulverized coal (PC) power plant, are presented. A key finding is that, a system utilizing commercially available equipment and process technologies, together with the environmentally benign CA enzyme-activated K_2CO_3 based solvent, leads to a model predicted plant COE performance 9% higher than NETL Case 10 [1]. However, there is a likelihood of a lower environmental impact and potential for further process improvements, particularly with regards to enzyme development, that could result in a model predicted reduction of 1% in COE compared to NETL Case 10 [1].

Four cases utilizing the CA enzyme-activated solvent are compared, using vacuum regeneration at different pressures with different sources of steam, against NETL Case 10 [1]. The expected full-scale plant technical and economic performance have been estimated utilizing models of the PCC plant developed with Pacific Northwest National Laboratory in AspenTech's AspenPlus® software, bench scale test results from the University of Kentucky, and industrial experience of PCC plants utilizing amine based solvents.

A review of process performance, capital costs and operational costs for each case was undertaken to identify system conditions that would give the best plant economic performance with the highest confidence in immediate technical feasibility using currently available technologies, based on the bench scale test results and process model predictions. A cost of electricity (COE) and levelized cost of electricity (LCOE) assessment was performed showing the costs of the options assessed in the study. Key factors impacting the LCOE were identified as dissolved CA enzyme make-up rate and the technical capability and economy of the regeneration process. An important aspect of the feasibility assessment was the establishment of a dissolved enzyme replenishment approach, including spent enzyme removal, providing a straightforward means for maintaining system performance.

A sensitivity study focused on reducing enzyme make-up rate resulted in a projected performance for the enzyme-activated K_2CO_3 system that could, with improvements in enzyme longevity at elevated temperatures, be slightly better than the NETL base Case 10. The small potential COE reduction versus the reference Case was established in the present assessment, and a number of potential process improvements identified, that should be investigated further.

The further enzyme and process developments outlined could result in economically favorable operating parameters for the enzyme-activated process that would provide an alternative process option to the MEA approach with potential environmental advantages.

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Abbreviations

AACE – Association for the Advancement of Cost Engineering International
AEO – Annual energy outlook
BEC – Bare erected cost
Btu/lb – British thermal units per pound
CA – Carbonic Anhydrase
CF – Capacity factor
CCF – Capital charge factors
cfm – Cubic feet per minute
cm – Centimeter
COE – Cost of electricity
DC – Direct current
DCC – Direct contact cooler
DCS – Distributed control system
DOE – Department of Energy
EIA – Energy Information Administration
Econamine – Fluor Econamine FG Plus^{SM}
EPA – Environmental Protection Agency
EPC – Engineering, procurement and construction
EPCM – Engineering, procurement and construction management
EPRI – Electric Power Research Institute
FD – Forced draft
FGD – Flue gas desulfurization
FOAK – First of a kind
FRP – Fiberglass-reinforced plastic
ft – Foot, feet
GDP – Gross domestic product
GJ – Gigajoules
gpm – Gallons per minute
Hg – Mercury
HHV – Higher heating value
hp – Horse power
HP – High pressure
HSS – Heat stable salts
Hz – Hertz
ID – Induced draft
IEA – International Energy Agency
IOU – Investor-owned utility
IP – Intermediate pressure
K_2CO_3 – Potassium Carbonate
kg – Kilogram

kJ – Kilojoules
kV – Kilovolt
kWe – Kilowatt electric
kWh – Kilowatt-hour
kW$_{th}$ – Kilowatt thermal
lb – Pound
lb/MMBtu – Pounds per million British thermal units
LCOE – Levilized cost of electricity
LF – Levilization factors
LNB – Low NOx burners
LP – Low pressure
lpm – Liters per minute
m – Meter
MCR – Maximum continuous rating
md – Milidarcy
mills/kWh – Tenths of a cent per kilowatt hour
mm – Milimeter
MMBTU – Million British thermal units (also shown as 10^6 BTU)
MPa – Megapascal
MWe – Megawatt electric
MWh – Megawatt-hour
N/A – Not applicable
NETL – National Energy Technology Laboratory
NOAK – nth of a kind
NSPS – New Source Performance Standards
O&GJ – Oil and Gas Journal
O&M – Operation and maintenance
OEM – Original equipment manufacturer
OFA – Over fired air
PA – Primary air
PC – Pulverized coal
PCC – Post combustion carbon capture
ppmv – Parts per million volume
ppmd – Parts per million dry
PSFM – Power systems financial model
psia – Pounds per square inch absolute
psig – Pounds per square inch gauge
QGESS – Quality guidelines for energy system studies
RH – Reheater
SCR – Selective catalytic reduction
SS – Stainless steel
TASC – Total as spent capital

TOC – Total overnight cost
Ton – Short ton (907 kg)
Tonne – Metric ton (1000 kg)
TPC – Total plant cost
tph – Tons per hour
TS&M – Transport, storage and monitoring
U.S. – United States
VLP – Very low pressure
WG – Water gauge
wt% – Weight percent
°C – Degrees Celsius
°F – Degrees Fahrenheit
$/MWh – Dollars per megawatt-hour

List of Exhibits

Executive Summary

A project team, led by Novozymes North America, Inc. in collaboration with Pacific Northwest National Laboratory, University of Kentucky and Doosan Babcock Limited, was awarded DE-FE0007741 to conduct bench-scale tests of a novel K_2CO_3 based post-combustion capture (PCC) process. Aspects of the process include the application of a dissolved CA enzyme catalyst to promote CO_2 absorption in a low enthalpy K_2CO_3 based solvent and the incorporation of a vacuum stripping process to release CO_2 at a moderate temperature to determine the potential energy benefit of the process. Exposure of the prototype CA enzyme to thermal stress, even at moderate temperatures such as 70°C, results in degradation of the enzyme and a loss in performance that requires removal and replacement of degraded enzyme.

Using information gathered from the bench scale unit, validated kinetic data, PCC plant predictive models and industrial experience of PCC plant design and cost estimation, the process and cost performance of several cases were analyzed and compared to NETL baseline Case 9 and Case 10 to judge relative performance. Four cases utilizing the enzyme-activated solvent and one case with solvent containing no enzyme were compared, using vacuum regeneration at different pressures with different sources of steam, against the NETL Case 10 [1] as follows:

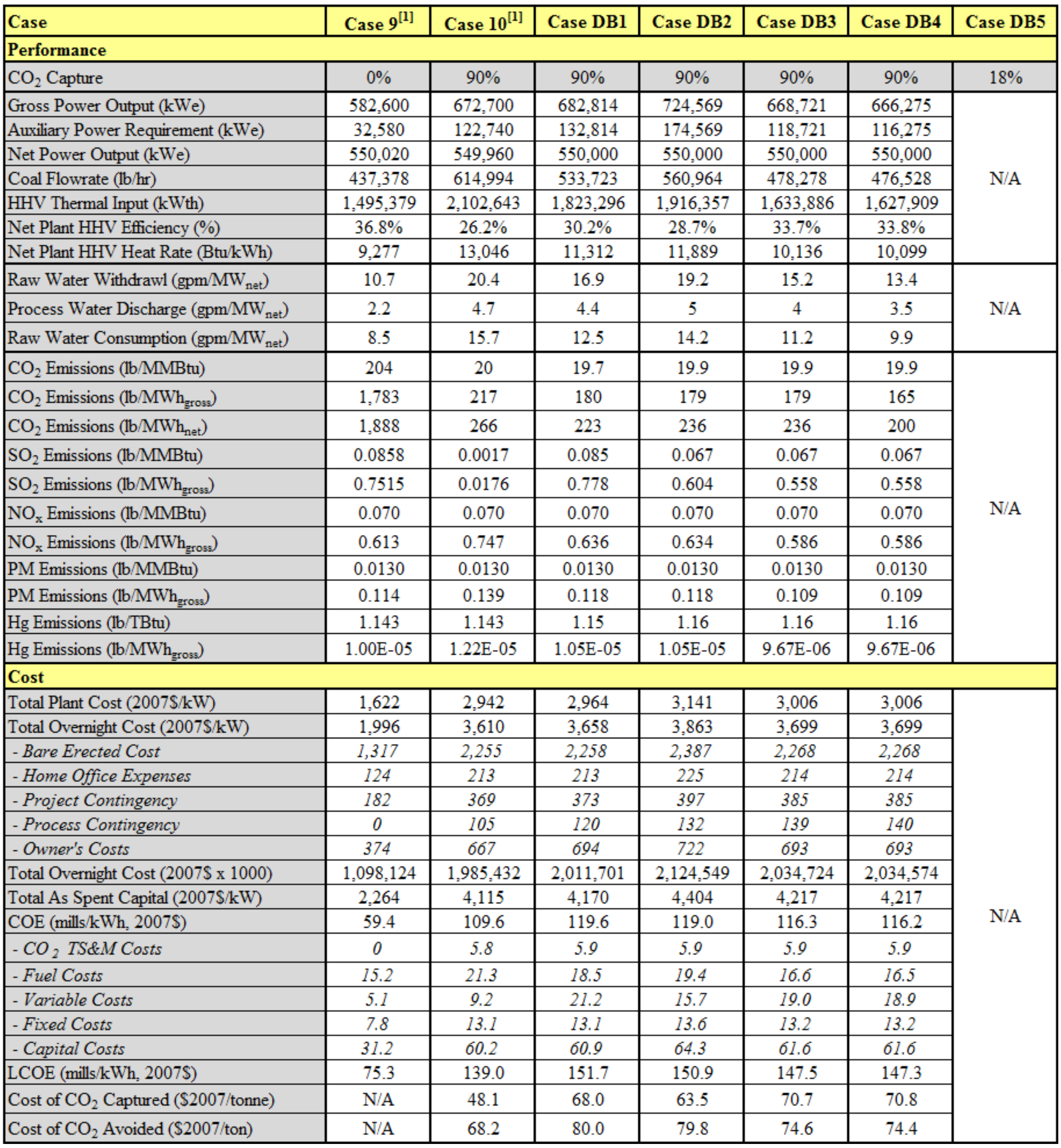
Case	Description
DB1	Enzyme-activated reaction kinetics with a stripper pressure of 6 psia and low pressure (LP) steam (73.5 psia, 570°F) utilized for reboiler duty. The bulk stripper temperature is 70°C.
DB2	Enzyme-activated reaction kinetics with a stripper pressure of 3 psia and LP (73.5 psia, 570°F)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

Case DB1, the best case in terms of minimized technical risk, was found to have a poorer COE performance than the NETL MEA PCC base Case 10. However, a potential benefit of the enzyme-activated K_2CO_3 solvent over MEA is the fact that the solvent and solvent degradation products are benign and therefore pose no significant environmental, health or safety concerns and are compliant with U.S. Federal legislation concerning environment, health and safety [24].

Case DB5 was modelled with no enzyme present, and used default kinetic parameters for K_2CO_3. The model predicted results show that the presence of enzyme, simulated using modified and validated kinetic parameters, has a significant effect on the performance of the solvent resulting in 90% CO_2 capture observed in Case DB3 rather than the maximum 18% CO_2 capture observed in Case DB5.

Performance and cost results

The full tabulated performance and cost summary of NETL Cases 9 and 10, and Cases DB1-5 is as follows:



Case	**Case 9[1]**	**Case 10[1]**	**Case DB1**	**Case DB2**	**Case DB3**	**Case DB4**	**Case DB5**
Performance							
CO_2 Capture	0%	90%	90%	90%	90%	90%	18%
Gross Power Output (kWe)	582,600	672,700	682,814	724,569	668,721	666,275	N/A
Auxiliary Power Requirement (kWe)	32,580	122,740	132,814	174,569	118,721	116,275	
Net Power Output (kWe)	550,020	549,960	550,000	550,000	550,000	550,000	
Coal Flowrate (lb/hr)	437,378	614,994	533,723	560,964	478,278	476,528	
HHV Thermal Input (kWth)	1,495,379	2,102,643	1,823,296	1,916,357	1,633,886	1,627,909	
Net Plant HHV Efficiency (%)	36.8%	26.2%	30.2%	28.7%	33.7%	33.8%	
Net Plant HHV Heat Rate (Btu/kWh)	9,277	13,046	11,312	11,889	10,136	10,099	
Raw Water Withdrawl (gpm/MW_{net})	10.7	20.4	16.9	19.2	15.2	13.4	N/A
Process Water Discharge (gpm/MW_{net})	2.2	4.7	4.4	5	4	3.5	
Raw Water Consumption (gpm/MW_{net})	8.5	15.7	12.5	14.2	11.2	9.9	
CO_2 Emissions (lb/MMBtu)	204	20	19.7	19.9	19.9	19.9	N/A
CO_2 Emissions (lb/MWh_{gross})	1,783	217	180	179	179	165	
CO_2 Emissions (lb/MWh_{net})	1,888	266	223	236	236	200	
SO_2 Emissions (lb/MMBtu)	0.0858	0.0017	0.085	0.067	0.067	0.067	
SO_2 Emissions (lb/MWh_{gross})	0.7515	0.0176	0.778	0.604	0.558	0.558	
NO_x Emissions (lb/MMBtu)	0.070	0.070	0.070	0.070	0.070	0.070	
NO_x Emissions (lb/MWh_{gross})	0.613	0.747	0.636	0.634	0.586	0.586	
PM Emissions (lb/MMBtu)	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	
PM Emissions (lb/MWh_{gross})	0.114	0.139	0.118	0.118	0.109	0.109	
Hg Emissions (lb/TBtu)	1.143	1.143	1.15	1.16	1.16	1.16	
Hg Emissions (lb/MWh_{gross})	1.00E-05	1.22E-05	1.05E-05	1.05E-05	9.67E-06	9.67E-06	
Cost							
Total Plant Cost (2007$/kW)	1,622	2,942	2,964	3,141	3,006	3,006	N/A
Total Overnight Cost (2007$/kW)	1,996	3,610	3,658	3,863	3,699	3,699	
- Bare Erected Cost	*1,317*	*2,255*	*2,258*	*2,387*	*2,268*	*2,268*	
- Home Office Expenses	*124*	*213*	*213*	*225*	*214*	*214*	
- Project Contingency	*182*	*369*	*373*	*397*	*385*	*385*	
- Process Contingency	*0*	*105*	*120*	*132*	*139*	*140*	
- Owner's Costs	*374*	*667*	*694*	*722*	*693*	*693*	
Total Overnight Cost (2007$ x 1000)	1,098,124	1,985,432	2,011,701	2,124,549	2,034,724	2,034,574	
Total As Spent Capital (2007$/kW)	2,264	4,115	4,170	4,404	4,217	4,217	
COE (mills/kWh, 2007$)	59.4	109.6	119.6	119.0	116.3	116.2	
- CO_2 TS&M Costs	*0*	*5.8*	*5.9*	*5.9*	*5.9*	*5.9*	
- Fuel Costs	*15.2*	*21.3*	*18.5*	*19.4*	*16.6*	*16.5*	
- Variable Costs	*5.1*	*9.2*	*21.2*	*15.7*	*19.0*	*18.9*	
- Fixed Costs	*7.8*	*13.1*	*13.1*	*13.6*	*13.2*	*13.2*	
- Capital Costs	*31.2*	*60.2*	*60.9*	*64.3*	*61.6*	*61.6*	
LCOE (mills/kWh, 2007$)	75.3	139.0	151.7	150.9	147.5	147.3	
Cost of CO_2 Captured ($2007/tonne)	N/A	48.1	68.0	63.5	70.7	70.8	
Cost of CO_2 Avoided ($2007/ton)	N/A	68.2	80.0	79.8	74.6	74.4	

Case DB4 gave the best performance with a COE of 116.2 mills/kWh (2007$), a 6.0% increase on the equivalent MEA PCC NETL Case 10 [1]. Case DB3 shows a similar result with a COE of 116.3 mills/kWh (2007$). Without enzyme present, Case DB5, the levels of CO_2 capture only reached 18%, far below the 90% capture target, and clearly illustrating why non-activated K_2CO_3 solvent has not been considered viable for ambient pressure flue gas scrubbing applications. Case DB2 shows that the application of a deeper vacuum in the stripper has a small benefit with a slight reduction in COE when compared to Case DB1.

Despite Cases DB2, DB3 and DB4 showing the best COE result based on the bench scale test data and process model predictions, Case DB1 is considered to be the most practical solution. The basis for Case DB1 is considered to have the lowest inherent technical risk with the highest confidence in physical system performance, utilizing commercially available equipment and related process technologies. Cases DB2, DB3 and DB4 each consider equipment requirements or operation at or beyond the limit of current available technology, and therefore provide a greater degree of uncertainty.

Case DB1 shows a COE of 119.6 mills/kWh (2007$) which represents a 9.1% increase on the equivalent MEA case, NETL Case 10 [1].

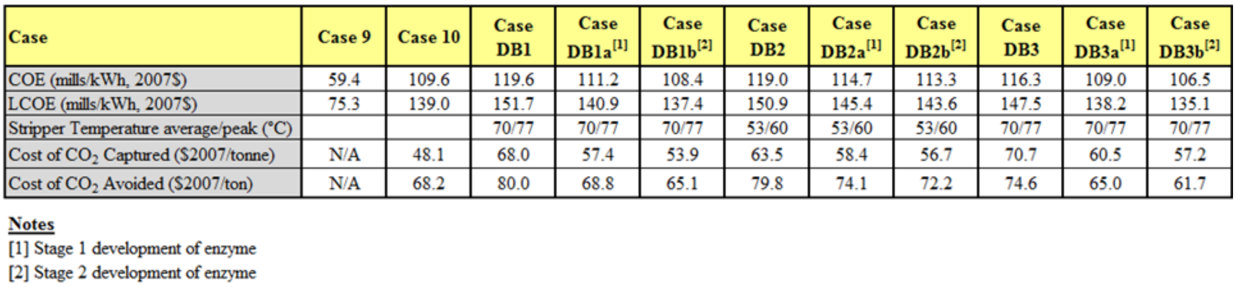
Cases DB3 and DB4 show a relatively lower auxiliary power requirement compared to the other cases. This is due to the additional power output generated from the VLP turbine when producing VLP steam from the LP steam extracted from the power plant turbine. The additional power output means that a smaller PC plant, PCC plant and turbine are required to produce the net 550MWe output. However, this benefit is slightly offset by the corresponding additional capital costs of installing the VLP turbine, but overall still delivers the best economic performance in terms of COE.

Potential performance and cost improvements

The performance and cost summary shows that variable costs are the key differentiator in COE performance between the enzyme-activated cases and NETL Case 10. In Case DB1 the variable costs contribution to COE is more than double that of NETL Case 10. Exposure of the prototype CA enzyme to thermal stress, even at moderate temperatures such as 70°C, results in degradation of the enzyme and a loss in performance that requires removal and replacement of degraded enzyme. The high enzyme make-up rate required to maintain system performance results in a significant operating cost that is reflected in the increased variable costs and ultimately the COE.

Using Novozymes' expertise it has been determined that the longevity of the enzyme could be improved from the current prototype in two stages of commercial development. The first stage could involve a combination of further enzyme-solvent dose optimization and selection among known CA variants with favorable longevity characteristics at the required process conditions compared to the prototype enzyme used in the present study. The second stage could involve a variety of different approaches, such as protein engineering, chemical modification and enzyme-immobilization, used alone or in combination to achieve further enzyme longevity improvements, resulting in reduced replenishment rates and corresponding cost reductions. As supported by findings published in the literature [25], the probability of success for both stage 1 and stage 2 enzyme developments are deemed by Novozymes to be high.

The predicted results of application of these potential enzyme developments to Cases DB1, DB2 and DB3 are shown here:



Case	Case 9	Case 10	Case DB1	Case DB1a[1]	Case DB1b[2]	Case DB2	Case DB2a[1]	Case DB2b[2]	Case DB3	Case DB3a[1]	Case DB3b[2]
COE (mills/kWh, 2007$)	59.4	109.6	119.6	111.2	108.4	119.0	114.7	113.3	116.3	109.0	106.5
LCOE (mills/kWh, 2007$)	75.3	139.0	151.7	140.9	137.4	150.9	145.4	143.6	147.5	138.2	135.1
Stripper Temperature average/peak (°C)			70/77	70/77	70/77	53/60	53/60	53/60	70/77	70/77	70/77
Cost of CO_2 Captured ($2007/tonne)	N/A	48.1	68.0	57.4	53.9	63.5	58.4	56.7	70.7	60.5	57.2
Cost of CO_2 Avoided ($2007/ton)	N/A	68.2	80.0	68.8	65.1	79.8	74.1	72.2	74.6	65.0	61.7

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

The result, when stage 1 development of enzyme is applied to Case DB1, is a reduction in COE from 119.6 mills/kWh (2007$) to 111.2 mills/kWh (2007$) representing a 1.5% (rather than 9.1%) increase compared to NETL Case 10. The results of applying the stage 2 enzyme development are a further reduction in COE to 108.4 mills/kWh (2007$), a performance that represents an improvement of 1.1% compared to NETL Case 10. Application of the stage 2 enzyme development to Case DB3 results in a COE of 106.5 mills/kWh (2007$), which represents an improvement of 2.8% on NETL Case 10. For all cases it should be noted that further enzyme-related improvements do not have as great an effect on the COE since other factors such as CAPEX become more dominant than OPEX.

Cases DB3 and DB4 were found to have an almost identical performance in all aspects despite having differing reaction kinetics specified in the stripper. The stripper simulation for Case DB3 utilizes enzyme-catalyzed reaction kinetics based on the validated bench scale models; whereas Case DB4 uses Aspen default reaction kinetics; meaning, Case DB4 simulates the stripper performance absent of any kinetic contribution by enzyme. The observed slightly better performance of Case DB4 compared to DB3 is likely to be due to small differences in the convergence of the respective process models. Since the results of the two cases can be considered identical within process modelling tolerances, they suggest that the enzyme has limited effect on the regeneration stage under the process conditions considered. The regeneration stage could potentially be equilibrium-limited with respect to CO_2 gas release from the liquid and therefore may not benefit from the effect of enzyme increasing the rate of bicarbonate conversion to dissolved CO_2. However, these results are based only on process models and should be tested on plant, both at bench scale and larger, to determine the process performance of the regeneration stage with no kinetic contribution from the enzyme. If the limited model predicted effect of the enzyme on the regeneration stage is observed in plant tests then further economic improvement could potentially be made by redesigning the process to localize the enzyme to the absorption stage. As the absorption stage operates at a lower temperature than the stripper, there would be a significant improvement in the enzyme longevity and an increased flexibility in the stripper stage to use the optimal combination of heat and pressure conditions without concern for enzyme degradation. For example, with enzyme localized to the absorption stage, low temperature vacuum stripping would not necessarily be required. Elimination of vacuum operation would reduce capital costs, reduce auxiliary power consumption and hence require a smaller PC boiler and associated equipment to achieve 550MWe net output. These cost reductions would be offset to some extent by the cost of restraining the enzyme in the absorber by some means, such as immobilization, and the impact on process performance would have to be assessed. Given the results observed in Case DB4 it is certainly possible that such a solution could result in a COE a few percent lower than that of NETL Case 10, however the performance of the configuration where enzyme is localized to the absorption stage and the effect of vacuum regeneration and non-vacuum regeneration on such a case would have to be assessed through practical demonstration.

All the results presented in this report are based on bench scale data and process models. The limitations of predicting full scale plant performance from such data have been noted. It is recommended that further work on a larger scale test unit be carried out to reduce the level of uncertainty, by validating performance on a larger scale, particularly with regards to vacuum performance, enzyme longevity and enzyme kinetics. A number of potential process improvements have been determined from the results presented in this report and these should be investigated further to determine the best possible operating parameters for the enzyme-activated process. A notable and practical aspect of the bench scale to full scale feasibility assessment was establishment of a dissolved enzyme replenishment approach, including spent enzyme removal via a continuous slipstream, offering a straightforward means for maintaining system performance. This approach, supported by both lab and bench scale data, provided the basis for determining the projected enzyme make-up rates.

Conclusions

- Case DB1 is considered to be the most practical solution. Case DB1 shows a COE of 119.6 mills/kWh (2007$) which represents a 9.1% increase on the equivalent MEA based NETL Case 10.
- Case DB5 was modelled with no enzyme present, utilizing default kinetic parameters for K_2CO_3. The model predicted results show that with a non-enzyme-activated K_2CO_3 solvent a maximum capture rate of 17.7% was achieved. The presence of enzyme has a significant effect on the performance of the solvent and clearly illustrates why non-activated K_2CO_3 solvent has not been considered viable for ambient pressure flue gas scrubbing applications.
- Case DB2 shows that the application of a deeper vacuum in the stripper has a small benefit with a slight reduction in COE when compared to Case DB1. The small increase in predicted performance is considered insufficient when compared to the greater uncertainty and technical risks associated with employing a deeper vacuum.
- Case DB4 gave the best performance with a COE of 116.2 mills/kWh (2007$), a 6.0% increase on NETL Case 10 [1]. Case DB3 shows a similar result with a COE of 116.3 mills/kWh (2007$).
- Predicted variable costs are the key differentiator in COE performance between the enzyme-activated cases and NETL Case 10. Exposure of the prototype CA enzyme to thermal stress, even at moderate temperatures such as 70°C, results in degradation of the enzyme and a loss in performance that requires removal and replacement of degraded enzyme. The high enzyme make-up rate required to maintain system performance results in a significant operating cost that is reflected in the increased variable costs and ultimately the COE.
- The longevity of the enzyme could be improved from the current prototype in two stages of commercial development.
- First stage enzyme development can be achieved through a combination of further enzyme-solvent dose optimization and selection among known CA variants with favorable longevity characteristics at the required process conditions. The result, when stage 1 development of enzyme is applied to Case DB1, is a reduction in COE from 119.6 mills/kWh (2007$) to 111.2 mills/kWh (2007$) representing a 1.5% (rather than 9.1%) increase when compared to NETL Case 10.

- Second stage enzyme development could involve a variety of different approaches, such as protein engineering, chemical modification and enzyme-immobilization, used alone or in combination to achieve further enzyme longevity improvements, resulting in reduced replenishment rates and corresponding cost reductions. The result of applying the stage 2 enzyme development to Case DB1 is a further reduction in COE to 108.4 mills/kWh (2007$), a performance that represents an improvement of 1.1% when compared to NETL Case 10.
- The further enzyme and process developments outlined could result in economically favorable operating parameters for the enzyme-activated process that would provide an alternative process option to the MEA approach with potential environmental advantages.

Future developments

Further aspects and improvements to be investigated include:

- Process and cost performance with enzyme localized in the absorber stage and utilizing vacuum regeneration with low enthalpy K_2CO_3 based solvent.
- Process and cost performance with enzyme localized in the absorber stage and utilizing non-vacuum regeneration, to avoid the additional capital costs and auxiliary power consumption associated with the construction and operation of vacuum systems.
- Utilization of heat sources from outside the PC plant steam cycle to provide heating in the reboiler, such as process waste heat or low grade steam, and determine cost and process performance.
- Utilization of less costly materials of construction that could be compatible with K_2CO_3, or other bicarbonate based solvents.
- Utilization of alternative solvents or mixed solvents that could provide higher CO_2 loading capacity and reduced recirculation rates to reduce equipment sizing and minimize pumping energy and reboiler duty.
- Development of enzymes with improved longevity, especially improved longevity at elevated temperature conditions. Such longevity improvements could also be possible by developing modified enzymes. The modification of enzymes could include utilizing enzymes in combination with physical matrices, such as particles, or through chemical modifications.
- Development of enzymes or modified enzymes with reduced dosage requirement to minimize initial fill and replenishment costs. Reduced dosage could, for example, be achieved by increasing the enzyme activity per unit amount or by localizing the enzyme to the gas-liquid interface.

Further investigation of the cases presented herein or potential improvements to these should be validated on a larger scale PCC test plant utilizing enzyme-activated K_2CO_3 solvent to reduce uncertainties and confirm the predicted process and cost performance for implementation at full scale.

1 Introduction

1.1 Project Overview

The U.S. Department of Energy's National Energy Technology Laboratory (NETL) issued Funding Opportunity Announcement DE-FOA-000403 – "Bench-Scale and Slipstream Development and Testing of Post Combustion Carbon Dioxide Capture and Separation Technology for Application to Existing Coal-Fired Power Plants" to provide financial support to promising CO_2 capture technologies. Sixteen projects were awarded in August 2011 totaling $41million. A project team, led by Novozymes North America, Inc. in collaboration with Pacific Northwest National Laboratory, University of Kentucky and Doosan Babcock Limited, was awarded DE-FE0007741 to conduct bench-scale tests and techno-economic assessment of a novel potassium carbonate (K_2CO_3) based post-combustion CO_2 capture (PCC) process.

Aspects of the process include the application of a soluble carbonic anhydrase enzyme catalyst to promote CO_2 absorption in a low enthalpy K_2CO_3 based solvent and the incorporation of a vacuum stripping process to release CO_2 at a moderate temperature to determine the potential energy benefit of a low temperature regeneration process. Exposure of the prototype CA enzyme to thermal stress, even at moderate temperatures such as 70°C, results in its degradation and a loss in performance that requires removal and replacement of degraded enzyme.

1.2 Report Objectives

The aim of this report is to present a technical and economic feasibility assessment of an enzyme-activated K_2CO_3 solution PCC plant integrated with a subcritical pulverized coal (PC) power plant. Due to the nature of the process, the focus of the investigation has been the CO_2 capture plant, keeping the rest (boiler and CO_2 compression) of the plant identical to the configuration provided in NETL Case 10 [1].

1.2.1 *Case Descriptions*

The cases investigated are shown below:

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

2 Plant Description

Five cases consisting of a subcritical PC fired power plant with different PCC plant configurations were evaluated. The design of each PC plant is based on a PC steam generator firing Illinois No. 6 coal and a steam turbine. The entire coal-fired power plant, including the integrated PCC plant, has been modelled and optimized for 550 MWe net output to allow for a meaningful comparison among the five cases and the baseline cases of NETL Case 9 (subcritical PC boiler without CO_2 capture) and NETL Case 10 (subcritical PC boiler with amine based CO_2 capture) [1].

Each design is based on market-ready technology that is assumed to be commercially available for the plant startup date. To maintain consistency with the NETL baseline Cases in [1] the following single-reheat steam conditions were used in all cases:

16.5MPa/566°C/566°C (2,400 psig/1,050°F/1,050°F)

The steam conditions were selected based on a survey of boiler and steam turbine original equipment manufacturers (OEM), who were asked for the most advanced steam conditions that they would guarantee for a commercial project in the US with a subcritical PC unit rated at nominal 550 MWe net capacity and firing Illinois No. 6 coal as reported in [1].

2.1 PC Common Process Areas

A general outline of the common process areas has been highlighted in this section. The case-specific process areas and performance results of both the common and case-specific process areas are presented in the case-specific sections. To ensure that a meaningful comparison can be made the design basis used in the NETL report [1] for the common process areas has been maintained and is outlined in the following sections.

2.1.1 Coal and Limestone Sorbent Receiving and Storage

The function of the coal receiving and storage system for PC plants is to provide the equipment required for unloading, conveying, preparing, and storing the fuel delivered to the plant. The scope of the system is from the trestle bottom dumper and coal receiving hoppers up to the coal storage silos. The system is designed to support short-term operation at the 5 percent over pressure/valves wide open condition (16 hours) and long-term operation of 90 days or more at the maximum continuous rating (MCR).

The scope of the limestone sorbent receiving and storage system includes truck roadways, turnarounds, unloading hoppers, conveyors and the day storage bin for the purpose of supplying limestone sorbent to the FGD scrubber.

The coal is delivered to the site by 100-car unit trains comprising 91 tonne (100 ton) rail cars. The unloading is done by a trestle bottom dumper, which unloads the coal into two receiving hoppers. Coal from each hopper is fed directly into a vibratory feeder. The 8 cm x 0 (3" x 0) coal from the feeder is discharged onto a belt conveyor. Two conveyors with an intermediate transfer tower are assumed to convey the coal to the coal stacker, which transfer the coal to either the long-term storage pile or to the reclaim area. The conveyor passes under a magnetic plate separator to remove tramp iron and then to the reclaim pile.

Coal from the reclaim pile is fed by two vibratory feeders, located under the pile, onto a belt conveyor, which transfers the coal to the coal surge bin located in the crusher tower. The coal is reduced in size to 2.5 cm x 0 (1" x 0) by the coal crushers. The coal is then transferred by conveyor to the transfer tower. In the transfer tower the coal is routed to the tripper that loads the coal into one of the six boiler silos.

Limestone sorbent is delivered to the site using 23 tonne (25 ton) trucks. The trucks empty into a below grade hopper where a feeder transfers the limestone sorbent to a conveyor for delivery to the storage pile. Limestone sorbent from the storage pile is transferred to a reclaim hopper and conveyed to a day bin.

2.1.2 Steam Generator and Ancillaries

The steam generator for the subcritical PC plant considered in all cases includes the following:

- Drum-type evaporator
- Economizer
- Water-cooled dry bottom furnace
- Two-stage superheater
- Reheater (RH)
- Spray type desuperheater
- Soot blower system
- Forced draft (FD) fans

- Primary air (PA) fans
- Induced draft (ID) fans
- Ljungstrom type air preheaters
- Coal feeders and pulverizers
- Low NOx coal burners (LNB) and light oil igniters/warm-up system
- Over fired air (OFA) system

It has been assumed that the power plant is designed to be operated as a base-loaded unit but with some consideration given for daily or weekly cycling.

The steam generator operates as follows:

Feedwater and Steam

Feedwater enters the economizer, recovers heat from the combustion gases exiting the steam generator, and then passes to the boiler drum, from where it is distributed to the water wall circuits enclosing the furnace. After passing through the lower and upper furnace circuits and steam drum in sequence, the steam passes through the convection enclosure circuits to the primary superheater and then to the secondary superheater.

The steam then exits the steam generator en route to the high pressure (HP) turbine. Steam from the HP turbine returns to the steam generator as cold reheat steam and returns to the intermediate pressure (IP) turbine as hot reheat steam.

Air and Combustion Products

Combustion air from the FD fans is heated in Ljungstrom type air preheaters, recovering heat energy from the exhaust gases exiting the boiler. This air is distributed to the burner windbox as secondary air. Air for conveying PC to the burners is supplied by the PA fans. This air is heated in the Ljungstrom type air preheaters to permit drying of the PC, and a portion of the air from the PA fans bypasses the air preheaters to be used for regulating the coal/air temperature leaving the mills through injection at the mill inlet.

The PC and air mixture flows to the coal nozzles at various elevations of the furnace. The hot combustion products rise to the top of the boiler and pass through the superheater and reheater sections. The gases then pass through the economizer and air preheater. The gases exit the steam generator at this point and flow to the selective catalytic reduction (SCR) reactor, fabric filter, ID fan, flue gas desulfurization (FGD) system, and PCC process where applicable, before leaving through the stack.

Fuel Feed

The crushed Illinois No. 6 bituminous coal is fed through feeders to each of the mills (pulverizers), where its size is reduced to approximately 72 percent passing 200 mesh and less than 0.5 percent remaining on 50 mesh. The PC exits each mill via the pulverized fuel piping and is distributed to the coal nozzles in the furnace walls using transport air supplied by the PA fans.

Ash Removal

The furnace bottom comprises several hoppers, with a clinker grinder under each hopper. The hoppers are of welded steel construction, lined with refractory. The hopper design incorporates a water-filled seal trough around the upper periphery for cooling and sealing. Water and ash discharged from the hopper pass through the clinker grinder to an ash sluice system for conveyance to a dewatering bin, where the ash is dewatered before it is transferred to trucks for offsite disposal. The description of the balance of the bottom ash handling system is presented in Section 2.1.9. The steam generator incorporates fly ash hoppers under the economizer outlet and air heater outlet.

Burners

A boiler of a capacity to give 550MWe net output employs approximately 24 to 36 coal nozzles arranged at multiple elevations. Each burner is designed with staging of the coal combustion to minimize NO_x formation. In addition, OFA nozzles are provided to further stage combustion and thereby minimize NO_x formation.

Oil-fired pilot torches are provided for each coal burner for ignition, warm-up and flame stabilization at startup and low loads.

Air Preheaters

Each steam generator is furnished with two vertical-shaft Ljungstrom regenerative type air preheaters. These units are driven by electric motors through gear reducers.

Soot Blowers

The soot-blowing system utilizes an array of 50 to 150 retractable nozzles and lances that clean the furnace walls and convection surfaces with jets of HP steam. The blowers are sequenced to provide an effective cleaning cycle depending on the coal quality and design of the furnace and convection surfaces. Electric motors drive the soot blowers through their cycles.

2.1.3 NO_x Control System

The plant is designed to achieve the environmental target of 0.07 lb NO_x/MMBtu utilizing two measures to reduce the NO_x. The first is a combination of LNBs and the introduction of OFA in the boiler. The LNBs and OFA reduce the emissions to approximately 0.5 lb/MMBtu.

The second measure to reduce the NO_x emissions is the installation of a SCR system prior to the air heater. The SCR system uses ammonia and a catalyst to reduce NO_x to N_2 and H_2O.

The SCR system consists of three subsystems, a reactor vessel, ammonia storage and injection, and gas flow control.

The reactor vessel is designed to allow a sufficient residence time for the ammonia to contact the NO_x in the boiler exhaust gas. Ammonia is injected into the gas immediately prior to entering the reactor vessel and the catalyst contained in the reactor vessel enhances the reaction between the ammonia and the NO_x in the gas. Catalysts consist of various active materials such as titanium dioxide, vanadium pentoxide, and tungsten trioxide. The operating range for vanadium/titanium-based catalysts is 260°C (500°F) to 455°C (850°F). The boiler is equipped with an economizer bypass to provide flue gas to the reactors at the desired temperature during periods of operation at a low flow rate, such as during low load operation. Also included with the reactor vessel is soot-blowing equipment used for cleaning the catalyst.

The ammonia storage and injection system consists of the unloading facilities, bulk storage tank, vaporizers, dilution air skid, and injection grid.

The FG flow control consists of ductwork, dampers, and flow straightening devices required to route the boiler exhaust to the SCR reactor and then to the air heater. The economizer bypass and associated dampers for low load temperature control are also included.

The SCR system is designed to achieve 86 percent NO_x reduction with 2 ppmv ammonia slip at the end of the catalyst life. This, in conjunction with the LNBs, achieves the required NO_x emission limit of 0.07 lb/MMBtu. The SCR capital costs are included with the boiler costs, as is the cost for the initial load of catalyst.

2.1.4 Particulate Control

The fabric filter (or baghouse) consists of two separate single-stage, in-line, multi-compartment units. Each unit is of high (0.9-1.5 m/min [3-5 ft/min]) air-to-cloth ratio design with a pulse-jet on-line cleaning system. The ash is collected on the outside of the bags, which are supported by steel cages and the dust cake is removed by a pulse of compressed air. The bag material is polyphenylensulfide with an intrinsic Teflon Polytetrafluoroethylene coating and are rated for a continuous temperature of 180°C (356°F) and a peak temperature of 210°C (410°F). Each compartment contains a number of gas passages with filter bags, and heated ash hoppers supported by a rigid steel casing. The fabric filter is provided with necessary control devices, inlet gas distribution devices, insulators, inlet and outlet nozzles, expansion joints, and other items as required.

2.1.5 Flue Gas Desulfurization

The FGD system is a wet limestone, forced oxidation, positive pressure absorber non-reheat unit, with wet-stack, and gypsum production. The function of the FGD system is to scrub the boiler exhaust gases to remove SO_2 prior to release to the environment, or entering into the PCC plant. Sulfur removal efficiency is 98 percent in the FGD unit for all cases in this report. For NETL Case 10 [1], the SO_2 content of the scrubbed gases must be further reduced to approximately 10 ppmv to minimize formation of amine heat stable salts (HSS) during the CO_2 absorption process. As the enzyme-activated K_2CO_3 PCC process is not affected by SO_2 there is no requirement for further SO_2 removal within the PCC plant. Thus, for NETL Case 10 the PCC unit includes a polishing scrubber to reduce the flue gas SO_2 concentration from approximately 44 ppmv at the FGD exit to the required 10 ppmv prior to the PCC absorber, but for Cases DB1 – DB5, no such polishing scrubber is included.

The FGD system is divided into three sections:

- Limestone Handling and Reagent Preparation
- FGD Scrubber
- Byproduct Dewatering

Limestone Reagent Preparation System

The function of the limestone reagent preparation system is to grind and slurry the limestone delivered to the plant. The scope of the system is from the day bin up to the limestone feed system. The system is designed to support continuous base load operation.

Each day bin supplies a 100 percent capacity ball mill via a weigh feeder. The wet ball mill accepts the limestone and grinds the limestone to 90 to 95 percent passing 325 mesh (44 microns). Water is added at the inlet to the ball mill to create a limestone slurry. The reduced limestone slurry is then discharged into a mill slurry tank. Mill recycle pumps, two per tank, pump the limestone water slurry to an assembly of hydrocyclones and distribution boxes. The slurry is classified into several streams, based on suspended solids content and size distribution.

The hydrocyclone underflow with oversized limestone is directed back to the mill for further grinding. The hydrocyclone overflow with correctly sized limestone is routed to a reagent storage tank. Reagent distribution pumps direct slurry from the tank to the absorber module.

FGD Scrubber

The flue gas exiting the air preheater section of the boiler passes through one of two parallel fabric filter units, then through the ID fans and into the one 100 percent capacity FGD absorber module. The absorber module is designed to operate with counter-current flow of gas and reagent. Upon entering the bottom of the absorber vessel, the gas stream is subjected to an initial quenching spray of reagent. The gas flows upward through the spray zone, which provides enhanced contact between gas and reagent. Multiple spray elevations with header piping and nozzles maintain a consistent reagent concentration in the spray zone. Continuing upward, the reagent-laden gas passes through several levels of moisture separators. These consist of chevron-shaped vanes that direct the gas flow through several abrupt changes in direction, separating the entrained droplets of liquid by inertial effects. The scrubbed flue gas exits at the top of the absorber vessel and is routed to the stack in NETL Case 9 or the PCC process for all other cases.

The scrubbing slurry falls to the lower portion of the absorber vessel, which contains a large inventory of liquid. Oxidation air is added to promote the oxidation of calcium sulfite contained in the slurry to calcium sulfate (gypsum). Multiple agitators operate continuously to prevent settling of solids and enhance mixture of the oxidation air and the slurry. Recirculation pumps recirculate the slurry from the lower portion of the absorber vessel to the spray level. Spare recirculation pumps are provided to ensure the availability of the absorber.

The chemical equilibrium in the absorber is maintained by a continuous makeup of fresh reagent, and a blowdown of byproduct solids via the bleed pumps. A spare bleed pump is provided to ensure the availability of the absorber. The byproduct solids are routed to the byproduct dewatering system. The circulating slurry is monitored for pH and density.

The FGD system is designed for wet stack operation. Scrubber bypass or reheat, to ensure the exhaust gas temperature is above the saturation temperature, is not employed in the reference plant design because new scrubbers have improved mist eliminator efficiency, and detailed flow modeling of the flue interior enables the placement of gutters and drains to intercept moisture that may be present and convey it to a drain. Consequently, raising the exhaust gas temperature above the FGD discharge temperature is not considered necessary.

Byproduct Dewatering

The function of the byproduct dewatering system is to dewater the bleed slurry from the FGD absorber modules. The dewatering process selected for this plant is gypsum dewatering producing wallboard grade gypsum.

The recirculating reagent in the FGD absorber vessel accumulates dissolved and suspended solids on a continuous basis as byproducts from the SO_2 absorption process. Maintenance of the quality of the recirculating slurry requires that a portion be withdrawn and replaced by fresh reagent. This is accomplished on a continuous basis by the bleed pumps pulling off byproduct solids and the reagent distribution pumps supplying fresh reagent to the absorber.

Gypsum (calcium sulfate) is produced by the injection of oxygen into the calcium sulfite in the absorber tower sump. The bleed from the absorber contains approximately 20 wt% gypsum. The absorber slurry is pumped by an absorber bleed pump to a primary dewatering hydrocyclone cluster. The primary hydrocyclone performs two process functions. The first function is to dewater the slurry from 20 wt% to 50 wt% solids. The second function of the primary hydrocyclone is to perform a $CaCO_3$ and $CaSO_4•2H_2O$ separation. This process ensures a limestone stoichiometric ratio in the absorber vessel of 1.10 and an overall limestone stoichiometric ratio of 1.05. This system reduces the overall operating cost of the FGD system. The underflow from the hydrocyclone flows into the filter feed tank, from which it is pumped to a horizontal belt vacuum filter. Two 100 percent filter systems are provided to allow for redundant capacity.

The scope of the byproduct dewatering system is from the bleed pump discharge connections to the gypsum storage pile.

Hydrocyclones

Multiple hydrocyclones are used to process the bleed stream from the absorber. The hydrocyclones are configured in a cluster with a common feed header. The system has two hydrocyclone clusters, each with five 15 cm (6 inch) diameter units. Four cyclones are used to continuously process the bleed stream at design conditions, and one cyclone is spare.

Cyclone overflow and underflow are collected in separate launders. The overflow from the hydrocyclones still contains about 5 wt% solids, consisting of gypsum, fly ash, and limestone residues and is sent back to the absorber. The underflow of the hydrocyclones (20 to 50 wt% solids) flows into the filter feed tank from where it is pumped to the horizontal belt vacuum filters.

Horizontal Vacuum Belt Filters

The secondary dewatering system consists of horizontal vacuum belt filters. The pre-concentrated gypsum slurry (50 wt%) is pumped to an overflow pan through which the slurry flows onto the vacuum belt. As the vacuum is pulled, a layer of cake is formed. The cake is dewatered to approximately 90 wt% solids as the belt travels to the discharge. At the discharge end of the filter, the filter cloth is turned over a roller where the solids are dislodged from the filter cloth. This cake falls through a chute onto the pile prior to the final byproduct uses. The required vacuum is provided by a vacuum pump. The filtrate is collected in a filtrate tank that provides surge volume for use of the filtrate in grinding the limestone. Filtrate that is not used for limestone slurry preparation is returned to the FGD scrubber.

2.1.6 Mercury Removal

Mercury removal is based on a coal Hg content of 0.15 ppmd. The combination of pollution control technologies used in the PC plant, SCR, fabric filters and FGD; result in significant co-benefit capture of mercury. The SCR promotes the oxidation of elemental mercury, which in turn enhances the mercury removal capability of the fabric filter and FGD unit. The mercury co-benefit capture is assumed to be 90 percent for this combination of control technologies. Co-benefit capture alone is sufficient to meet current New Source Performance Standards (NSPS) mercury limits so no activated carbon injection is included.

2.1.7 PCC Process

This section provides a sufficiently detailed process description of the PCC technology utilized in the enzyme-activated K_2CO_3 solvent process to allow a good understanding of the main components. NETL Case 10 [1] utilizes a CO_2 absorption/stripping/solvent reclaim process based on the Fluor Econamine FG Plus^{SM} (Econamine) technology. The bulk removal of CO_2 from gases by the use of chemical absorbents is a well-established technique as used for the “sweetening” of fuel gas throughout the petrochemical industry. This conventional amine based process has been adapted with the application of K_2CO_3 solvent, CA enzyme and vacuum stripping technologies.

Exhibit 1 provides a simplified process flow diagram to describe the flue gas and solvent paths in the enzyme-activated K_2CO_3 solvent process.

The CO_2 is absorbed from the flue gases into an aqueous 23.5 wt% K_2CO_3-based chemical solvent containing dissolved CA enzyme within the CO_2 absorber column removing 90% of the incoming CO_2 with the remaining off-gas discharged to atmosphere through a stack. The CA enzyme accelerates the inter-conversion between dissolved CO_2 and bicarbonate ions and K_2CO_3 in the solvent provides sufficient alkalinity and loading capacity (alternatively called "buffering" capacity) to absorb CO_2 in the form of bicarbonate. The CO_2-laden solvent collected at the bottom of the absorber tower, termed 'rich' solvent, is passed to a regeneration section where the application of heat reverses the inter-conversion between dissolved CO_2 and bicarbonate ions and releases the CO_2 as gas. The gaseous CO_2 is removed from the vacuum stripper and passed to a compression and dehydration system prior to being dispatched for storage or utilized in enhanced oil recovery. The now relatively CO_2-free solvent, termed 'lean' solvent, is returned to the absorber column. Fresh CA enzyme-containing solvent is added to the system as needed via the solvent supply/storage system, and can be metered using conventional liquid handling systems.

An additional feature of the system is the inclusion of a solvent and CA enzyme reclaimer unit which serves to maintain system performance by continuously withdrawing a slipstream of lean solvent and allowing separation of deactivated CA enzyme, which can agglomerate to form suspended solids in the solvent. Replenishment with fresh dissolved CA enzyme makes up for the amount of inactivated CA enzyme withdrawn and the combination of spent CA enzyme removal; together with fresh CA enzyme replenishment keeps the amount of active CA enzyme in the system at the correct level to maintain stable performance. Also, if needed, these systems can be used to increase or decrease the level of active CA enzyme in the system, for example to accommodate fluctuations in flue gas feed or composition of the gas stream. These features use conventional liquid dosing and solid-liquid separation technologies to achieve straightforward, flexible process control.

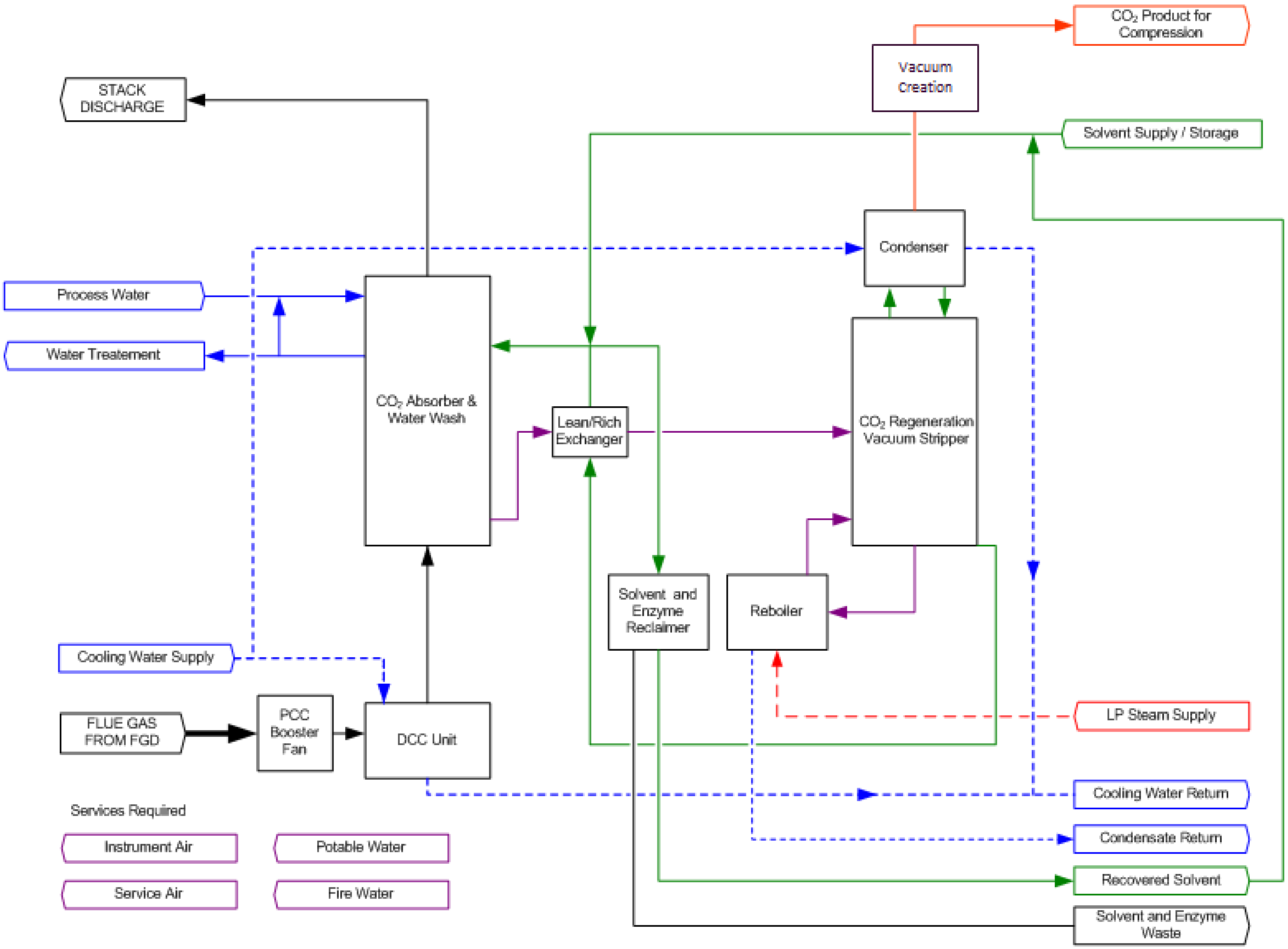


Exhibit 1 **Simplified Process Flow Diagram of PCC Plant**

Flue Gas Conditioning

Flue gas is created by the subcritical PC process, where coal and primary air are introduced into the boiler through wall-fired burners. Prior to the PCC process NO_x emissions are controlled through the use of low NO_x burners and over-fired air. The flue gas exits the boiler through a SCR unit that further reduces the flue gas NO_x concentration before passing through a pulse jet fabric filter to control particulate emissions. An ID fan provides the motive force for the flue gas to pass through a wet limestone forced oxidation scrubber to control SO_2 with a removal efficiency of 98 percent. The wet limestone scrubber calcium sulfate by-product is dewatered before being sold as a plaster constituent. Co-benefit mercury capture in the bag filter and FGD results in a 90 percent reduction of mercury emissions. The conditioned flue gas is then passed to the PCC process for further conditioning.

In a conventional amine-based absorption/stripping process, such as NETL Case 10 [1], in addition to reacting with CO_2, the solvent reacts with O_2 and acid gases such as NO_2, SO_2 and SO_3 contained in the flue gas along with any pipework system corrosion products to produce degradation products such as complex salts. The reactions with acid gases and O_2 form HSS that cannot be thermally regenerated. Thus, an additional FGD polisher is required to mitigate HSS formation.

In the proposed CA enzyme-activated K_2CO_3 process, the enzyme is not susceptible to degradation by SO_x and NO_x and, therefore, an additional PCC plant FGD polisher is not required upstream of the absorption section.

Booster Fan

The PCC system requires a booster fan to overcome the pressure drop of the ducting and all components in the flue gas path (direct contact cooler (DCC) and absorber).

Circulating Water System

Cooling water is provided from the PC plant cooling water system and returned to the PC plant cooling tower. The PCC plant requires a significant amount of cooling water for flue gas cooling, water wash cooling, reflux condenser duty, the lean solvent cooler, and CO_2 compression interstage cooling. Water requirements of the PCC process are minimized by the re-use of water removed from the incoming flue gas produced through cooling in the PCC plant.

Direct Contact Cooler

In order to achieve optimal CO_2 capture performance, the flue gas temperature entering the CO_2 absorber unit should be reduced from 57°C, as per NETL Case 10 PCC plant flue gas inlet temperature, to the practical optimum value of approximately 40°C to be passed directly to the carbon capture plant absorber. Without additional gas cooling, the PCC efficiency and economic performance may be compromised. The flue gas is passed through the DCC, which is a packed column where flue gas is contacted with re-circulating cooling water flowing in a counter-current arrangement. The arrangement also provides additional gas cleaning capabilities by removing undesirable soluble species from the incoming flue gas.

The cooling water is introduced at the top of the single packed section through a liquid distributor system. The DCC water system consists of a direct cooling loop with heat exchanger banks used to reject heat to the power plant's cooling water circuit. The potential for acidic build-up in the DCC water loop is controlled by utilizing a constant make-up to, and bleed from, the loop. The initial fill of the circuit is provided from the process water supply. During operation the DCC unit will generate an excess of water resulting from the condensation of flue gas moisture due to the reduction in flue gas temperature. The water level in the sump at the base of the column is maintained by discharging water to the station water treatment plant before being forwarded to the make-up systems for the CO_2 capture process and PC plant, therefore contributing towards maintaining the water balance in the PC plant.

CO_2 Absorber Column

The absorber column is designed to remove 90% of the CO_2 from the flue gas by absorption into the enzyme-activated K_2CO_3 based solvent. In the absorber, lean solvent solution, having been discharged from the regeneration section and reduced to a suitable temperature by cooling, is introduced to the structured packing section by means of a liquid distribution system, which avoids splashing/droplet formation and ensures the even flow of the solvent onto the packing material. The cooled flue gas from the DCC unit enters the bottom of the absorber column horizontally through a special gas inlet nozzle to minimize liquid entrainment above the liquid sump before flowing upwards through the column packed section.

The solvent solution flows down by gravity over Sulzer Mellapak^{TM} 350.Y type metal structured packing with a modelled surface area of 107.6 sqft/cuft (353 m^2/m^3) and comes into contact in a counter-current fashion with the flue gas flowing upwards within the column. The column consists of four packed sections in total, consisting of three absorption sections and one wash section. To ensure even distribution throughout the total height of the absorber column, solvent collection and re-distribution between each section of packing material is utilized. The 'rich' solvent collected at the base of the absorber column is pumped by the rich solvent pump through heat exchangers to the regeneration section in order to facilitate solvent regeneration by the combined application of heat and reduced pressure to remove the captured CO_2.

The remaining flue gas passes upwards through a chimney tray into the water wash section where any potential enzyme-activated K_2CO_3 solvent carryover and any impurities are intercepted and removed from the gas stream before the off-gas leaves the absorber through a stack.

Water Wash Section

The purpose of the water wash section is to minimize solvent losses due to mechanical entrainment and evaporation. The flue gas from the top of the CO_2 absorption section is contacted with a re-circulating stream of water for the removal of any potential K_2CO_3 solvent carryover or enzyme-containing solvent aerosols. The scrubbed gases, along with any unrecovered solvent, exit the top of the wash section for discharge to atmosphere via the vent stack. A slipstream of the water exiting the absorber wash section is discharged to the PC plant water treatment plant, with the remainder recycled to the water wash inlet and mixed with fresh make-up water.

Lean / Rich Heat Exchangers

The rich solvent stream from the bottom of the CO_2 absorber is passed through the lean/rich heat exchangers, where heat is recovered from the hot lean solvent leaving the base of the CO_2 regeneration section. The heat exchangers use hot CO_2-lean solvent solution from the lean solvent header to partially heat the CO_2-rich solvent solution leaving the absorber column before it enters the regeneration section.

CO_2 Regeneration Section

The CO_2 absorption by chemical reaction that occurred in the absorber column is reversed by the application of heat within the vacuum stripping column. A vacuum stripping column is utilized to lower the vaporization temperature and allow a lower reboiler operating temperature to prolong enzyme life, as the CA enzyme is susceptible to thermal deactivation. The vacuum in the regeneration section is created by a radial-type vacuum blower.

The CO_2-rich solvent from the lean/rich heat exchanger is introduced into the stripper section where it is evenly distributed across the packed column cross section by means of a liquid distribution system. Hot vapor generated in the stripper reboiler, consisting of predominantly water and released CO_2, flows up the stripper section and exchanges heat with the falling rich solvent liquid thereby stripping (releasing) the CO_2 as gas and simultaneously regenerating the solvent as it flows down the Sulzer Mellapak^{TM} 350.Y type metal structured packing.

The vapor leaving the top of the stripper containing CO_2 and steam is partially condensed in the reflux condenser with cooling water. The partially condensed stream then flows to the CO_2 product separator where the gas and liquid are separated. The CO_2-rich gas is then delivered to the CO_2 product compressor.

Solvent Reboiler

The reboiler is used to generate a hot vapor stream from the CO_2-lean solvent that is collected at the bottom of the stripper column. It is a plate type heat exchanger using LP or VLP steam extracted from the turbine. The steam condensate generated is returned to the power plant for recovery in the appropriate condensate system.

Solvent and Enzyme Reclaimer

The enzyme degrades thermally, loses its catalytic activity and needs to be replenished. The deactivation of the enzyme decreases the solvent effectiveness and increases the energy consumption of the capture process. Therefore, a slipstream of the lean solvent is extracted from the system and is passed to a centrifuge separator where the deactivated enzyme, which forms suspended solids in the solvent, is removed as a moist sludge along with some of the solvent. The remaining 'cleaned' solvent is then recirculated back into the make-up system via a recovered solvent storage tank. It is envisaged that solvent make-up consists of fresh solvent and enzyme combined with recovered solvent. The fresh make-up solvent is required to maintain the solvent balance and ensure a constant solvent effectiveness i.e. enzyme activity. Fresh K_2CO_3, including make-up enzyme, is introduced upstream of the absorber in the CO_2-lean solvent line.

The solid waste removed in the reclamation process is a bio-degradable solid waste product that can be used for composting or as a fertilizer.

The longevity of the prototype CA enzyme was derived by Novozymes at lab-scale mimicking the Case DB1 and Case DB2 stripper temperatures and solvent residence times at the stripper temperatures. Tests were performed to determine the relationship between solids removal efficiency in the modeled system and the required CA enzyme replenishment rate. A 20% difference between the insoluble dry solids measured in University of Kentucky's bench-unit test samples and the solids predicted by full-scale simulation utilizing Novozymes' lab data was observed. The difference may be attributable to several factors, including uncertainties in antifoam interaction with solvent components in the bench-unit system, and also sample-to-sample variability among bench-unit samples. A correction factor was applied to correct for the 20% difference observed and close the mass balance. The correction is considered to be well within acceptable uncertainty, although it is noted that this aspect of the process should be evaluated more rigorously upon further development and demonstration of the technology.

Gas Compression and Dehydration

Since the stripper in the enzyme-activated K_2CO_3 solution PCC process operates under vacuum conditions, an additional single-stage geared compression system is necessary to achieve the desired downstream CO_2 pressure target in order to meet the required input operating conditions for the main CO_2 compression and dehydration process.

In the main compression section, the CO_2 is compressed to 15.3 MPa (2,215 psia) by a six-stage centrifugal compressor. The discharge pressures of the stages were balanced to give reasonable power distribution and discharge temperatures across the various stages as shown in Exhibit 2.

The power consumption for this large compressor was estimated assuming a polytropic efficiency of 86 percent and a mechanical efficiency of 98 percent for all stages.

The virtually moisture-free super critical CO_2 stream is delivered to the plant battery limit as a sequestration ready CO_2 product. CO_2 transport, storage and monitoring (TS&M) costs were estimated and included in levelized cost of electricity (LCOE) and cost of electricity (COE) calculations as described in Section 3.4.

Exhibit 2 CO_2 Compressor Interstage Pressures

Stage	**Outlet Pressure, MPa (psia)**
1	0.36 (52)
2	0.78 (113)
3	1.71 (248)
4	3.76 (545)
5	8.27 (1,200)
6	15.3 (2,215)

2.1.8 Power Generation

The steam turbine is designed for long-term operation (90 days or more) at MCR with throttle control valves 95 percent open. It is also capable of a short-term 5 percent over pressure/valves wide open condition (16 hours).

The steam turbine is a tandem compound type, consisting of HP-IP-two LP (double flow) sections enclosed in three casings, designed for condensing single reheat operation, and equipped with non-automatic extractions and four-flow exhaust. For Cases DB1 and DB2 LP steam is extracted from the IP-LP crossover to supply the reboiler, with the condensate returned to the condenser. For Cases DB3 – 5, in which VLP steam is utilized in the reboiler, an additional let-down turbine has been included. LP steam is taken from the IP-LP crossover and passed through a separate let down turbine, producing an amount of electricity and quantity of VLP steam, with condensate returned to the condenser. Instead of having a separate let-down turbine it may be possible to take an additional turbine bleed from one of the last stages in the main turbine.

The turbine drives a hydrogen-cooled generator. The turbine has direct current (DC) motor-operated lube oil pumps, and main lube oil pumps, which are driven off the turbine shaft [2]. The exhaust pressure is 50.8 cm (2 in) Hg in the single pressure condenser. There are seven extraction points. The condenser is two-shell, transverse, single pressure with divided waterbox for each shell.

Turbine bearings are lubricated by a closed-loop, water-cooled pressurized oil system. Turbine shafts are sealed against air in-leakage or steam blowout using a labyrinth gland arrangement connected to a LP steam seal system. The generator stator is cooled with a closed-loop water system consisting of circulating pumps, shell and tube or plate and frame type heat exchangers, filters, and deionizers, all skid-mounted. The generator rotor is cooled with a hydrogen gas recirculation system using fans mounted on the generator rotor shaft.

The turbine stop valves, control valves, reheat stop valves, and intercept valves are controlled by an electro-hydraulic control system. Main steam from the boiler passes through the stop valves and control valves and enters the turbine at 16.5 MPa/566°C (2,400 psig/1,050ºF). The steam initially enters the turbine near the middle of the HP span, flows through the turbine, and returns to the boiler for reheating. The reheat steam flows through the reheat stop valves and intercept valves and enters the IP section at 566°C (1,050ºF). After passing through the IP section, the steam enters a crossover pipe, which transports the steam to the two LP sections. The steam divides into four paths and flows through the LP sections exhausting downward into the condenser. The turbine is designed to operate at constant inlet steam pressure over the entire load range.

2.1.9 Balance of Plant

The balance of plant components consist of the condensate, feedwater, main and reheat steam, extraction steam, ash handling, ducting and stack, waste treatment and miscellaneous systems as described below. An overview of the condensate, feed heating and steam system is shown in Exhibit 22 for Case DB1.

Condensate

The function of the condensate system is to pump condensate from the condenser hotwell to the deaerator, through the gland steam condenser and the LP feedwater heaters. Each system consists of one main condenser; two variable speed electric motor-driven vertical condensate pumps each sized for 50 percent capacity; one gland steam condenser; four LP heaters; and one deaerator with storage tank that feeds the boiler feed pumps.

Condensate is delivered to a common discharge header through two separate pump discharge lines, each with a check valve and a gate valve. A common minimum flow recirculation line discharging to the condenser is provided downstream of the gland steam condenser to maintain minimum flow requirements for the gland steam condenser and the condensate pumps.

LP feedwater heaters 1 through 4 are 50 percent capacity, parallel flow, and are located in the condenser neck. All remaining feedwater heaters are 100 percent capacity shell and U-tube heat exchangers. Each LP feedwater heater is provided with inlet/outlet isolation valves and a full capacity bypass. LP feedwater heater drains cascade down to the next lowest extraction pressure heater and finally discharge into the condenser. Pneumatically actuated control valves are used to control normal drain levels in the heaters. High heater level dump lines discharging to the condenser are provided for each heater for turbine water induction protection.

Feedwater

The function of the feedwater system is to pump the feedwater from the deaerator storage tank through the HP feedwater heaters to the economizer. One turbine-driven boiler feedwater pump sized at 100 percent capacity is provided to pump the feedwater through the

HP feedwater heaters. One 25 percent motor-driven boiler feedwater pump is provided for startup. The pumps are provided with inlet and outlet isolation valves, and individual minimum flow recirculation lines discharging back to the deaerator storage tank. The recirculation flow is controlled by a combination of check valves in the main line and in the bypass, bypass control valve, and a flow sensing element. The suction of the boiler feed pump is equipped with startup strainers, which are utilized during initial startup and following major outages or system maintenance.

Each HP feedwater heater is provided with inlet/outlet isolation valves and a full capacity bypass. Feedwater heater drains cascade down to the next lowest extraction pressure heater and finally discharge into the deaerator. Pneumatic level control valves control normal drain level in the heaters. High heater level dump lines discharging to the condenser are provided for each heater for turbine water induction protection. Dump line flow is controlled by pneumatic level control valves.

The deaerator is a horizontal, spray tray type with internal direct contact stainless steel (SS) vent condenser and storage tank. The boiler feed pump turbine is driven by main steam up to 60 percent plant load. Above 60 percent load, extraction from the IP-LP crossover (1.05 MPa/395°C [153 psig/743°F]) provides steam to the boiler feed pump steam turbine.

Main and Reheat Steam

The function of the main steam system is to convey main steam from the boiler superheater outlet to the HP turbine stop valves. The function of the reheat system is to convey steam from the HP turbine exhaust to the boiler reheater and from the boiler reheater outlet to the IP turbine stop valves. Main steam exits the boiler superheater through a motor-operated stop/check valve and a motor-operated gate valve and is routed in a single line feeding the HP turbine. A branch line off the IP turbine exhaust feeds the boiler feed water pump turbine during unit operation starting at approximately 60 percent load.

Cold reheat steam exits the HP turbine, flows through a motor-operated isolation gate valve and a flow control valve, and enters the boiler reheater. Hot reheat steam exits the boiler reheater through a motor-operated gate valve and is routed to the IP turbine. A branch connection from the cold reheat piping supplies steam to feedwater heater 7.

Extraction Steam

The function of the extraction steam system is to convey steam from turbine extraction points through the following routes and shown in Exhibit 22:

- From HP turbine exhaust (cold reheat) to feedwater heater 7
- From IP turbine extraction to feedwater heater 6 and the deaerator (heater 5)
- From LP turbine extraction to feedwater heaters 1, 2, 3, and 4

The turbine is protected from overspeed on turbine trip, from flash steam reverse flow from the heaters through the extraction piping to the turbine. This protection is provided by positive closing, balanced disc non-return valves located in all extraction lines except the lines to the LP feedwater heaters in the condenser neck. The extraction non-return valves are located only in horizontal runs of piping and as close to the turbine as possible.

The turbine trip signal automatically trips the non-return valves through relay dumps. The remote manual control for each heater level control system is used to release the non-return valves to normal check valve service when required to restart the system.

Circulating Water System

It is assumed that the plant is serviced by a public water facility and has access to groundwater for use as makeup cooling water with minimal pretreatment. All filtration and treatment of the circulating water are conducted on site. A mechanical draft, wood frame, counter-flow cooling tower is provided for the circulating water heat sink. Two 50 percent cooling water pumps are provided. The cooling water system provides cooling water to the condenser, the auxiliary cooling water system, and the PCC plant.

The auxiliary cooling water system is a closed loop system. Plate and frame heat exchangers with circulating water as the cooling medium are provided. This system provides cooling water to the lube oil coolers, turbine generator, boiler feed pumps, etc. All pumps, vacuum breakers, air release valves, instruments, controls, etc. are included for a complete operable system.

Ash Handling System

The function of the ash handling system is to provide the equipment required for conveying, preparing, storing, and disposing of the fly ash and bottom ash produced on a daily basis by the boiler. The scope of the system is from the baghouse hoppers, air heater and economizer hopper collectors, and bottom ash hoppers to the hydrobins (for bottom ash) and truck filling stations (for fly ash). The system is designed to support short-term operation at the 5 percent over pressure/valves wide open condition (16 hours) and long-term operation at the 100 percent guarantee point (90 days or more).

The fly ash collected in the baghouse and the air heaters is conveyed to the fly ash storage silo. A pneumatic transport system using LP air from a blower provides the transport mechanism for the fly ash. Fly ash is discharged through a wet unloader, which conditions the fly ash and conveys it through a telescopic unloading chute into a truck for disposal.

The bottom ash from the boiler is fed into a clinker grinder. The clinker grinder is provided to break up any clinkers that may form. From the clinker grinders the bottom ash is sluiced to hydrobins for dewatering and offsite removal by truck.

Ash from the economizer hoppers and pyrites (rejected from the coal pulverizers) is conveyed using water to the economizer/pyrites transfer tank. This material is then sluiced on a periodic basis to the hydrobins.

Ducting and Stack

One stack is provided with a single fiberglass-reinforced plastic (FRP) liner. The stack is constructed of reinforced concrete. The stack is 152 m (500 ft) high to allow for adequate particulate dispersion.

Waste Treatment/Miscellaneous Systems

An onsite water treatment facility treats all runoff, cleaning wastes, blowdown, and backwash to within the U.S. Environmental Protection Agency (EPA) standards for suspended solids, oil and grease, pH, and miscellaneous metals. Waste treatment equipment is housed in a separate building. The waste treatment system consists of a water collection basin, three raw waste pumps, an acid neutralization system, an oxidation system, flocculation, clarification/thickening, and sludge dewatering. The water collection basin is a synthetic-membrane-lined earthen basin, which collects rainfall runoff, maintenance cleaning wastes, and backwash flows.

The raw waste is pumped to the treatment system at a controlled rate by the raw waste pumps. The neutralization system neutralizes the acidic wastewater with hydrated lime in a two-stage system, consisting of a lime storage silo/lime slurry makeup system, dry lime feeder, lime slurry tank, slurry tank mixer, and lime slurry feed pumps.

The oxidation system consists of an air compressor, which injects air through a sparger pipe into the second-stage neutralization tank. The flocculation tank is fiberglass with a variable speed agitator. A polymer dilution and feed system is also provided for flocculation. The clarifier is a plate-type, with the sludge pumped to the dewatering system. The sludge is dewatered in filter presses and disposed offsite. Trucking and disposal costs are included in the cost estimate. The filtrate from the sludge dewatering is returned to the raw waste sump.

Miscellaneous systems consisting of fuel oil, service air, instrument air, and service water are provided. A storage tank provides a supply of fuel oil used for startup and for a small auxiliary boiler. Fuel oil is delivered by truck. All truck roadways and unloading stations inside the fence area are provided.

Buildings and Structures

Foundations are provided for the support structures, pumps, tanks, and other plant components. The following buildings are included in the design basis:

- Fuel oil pump house, pump house and electrical equipment building
- Boiler and steam turbine buildings
- Coal crusher building
- Runoff water pump house
- Administration and service building
- Continuous emissions monitoring building
- Industrial waste treatment building
- Makeup water and pretreatment building
- FGD system buildings

2.1.10 Accessory Electric Plant

The accessory electric plant consists of switchgear and control equipment, generator equipment, station service equipment, conduit and cable trays, and wire and cable. It also includes the main power transformer, required foundations, and standby equipment.

2.1.11 Instrumentation and Control

An integrated plant-wide control and monitoring distributed control system (DCS) is provided. The DCS is a redundant microprocessor-based, functionally distributed system. The control room houses an array of multiple video monitor and keyboard units. The monitor/keyboard units are the primary interface between the generating process and operations personnel. The DCS incorporates plant monitoring and control functions for all the major plant equipment. The DCS is designed to provide 99.5 percent availability. The plant equipment and the DCS are designed for automatic response to load changes from minimum load to 100 percent. Startup and shutdown routines are implemented as supervised manual routines, with operator selection of modular automation routines available.

2.2 Key System Assumptions

System assumptions for NETL Cases 9 and 10 [1], subcritical PC power plant with and without CO_2 capture and the five cases considered with enzyme-activated K_2CO_3 PCC plant are compiled in Exhibit 3.

Exhibit 3 Subcritical PC Plant Study Configuration Matrix

	Case 9 w/o CO2 Capture [1]	Case 10 w/CO2 Capture [1]	Case DB1	Case DB2	Case DB3	Case DB4	Case DB5
Steam Cycle, MPa/°C/°C (psig/°F/°F)	16.5/566/566 (2400/1050/1050)	16.5/566/566 (2400/1050/1050)	16.5/566/566 (2400/1050/1050)	16.5/566/566 (2400/1050/1050)	16.5/566/566 (2400/1050/1050)	16.5/566/566 (2400/1050/1050)	16.5/566/566 (2400/1050/1050)
Coal	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6
Condenser pressure, mm Hg (in Hg)	50.8 (2)	50.8 (2)	50.8 (2)	50.8 (2)	50.8 (2)	50.8 (2)	50.8 (2)
Boiler Efficiency, %	88	88	88	88	88	88	88
Cooling water to condenser, °C (°F)	16 (60)	16 (60)	16 (60)	16 (60)	16 (60)	16 (60)	16 (60)
Cooling water from condenser, °C (°F)	27 (80)	27 (80)	27 (80)	27 (80)	27 (80)	27 (80)	27 (80)
Stack temperature, °C (°F)	57 (135)	32 (89)	40 (104)	40 (104)	40 (104)	40 (104)	40 (104)
SO_2 Control	Wet Limestone Forced Oxidation	Wet Limestone Forced Oxidation	Wet Limestone Forced Oxidation	Wet Limestone Forced Oxidation	Wet Limestone Forced Oxidation	Wet Limestone Forced Oxidation	Wet Limestone Forced Oxidation
FGD Efficiency, % (A)	98	98 (B, C)	98	98	98	98	98
NOx Control	LNB w/OFA and SCR	LNB w/OFA and SCR	LNB w/OFA and SCR	LNB w/OFA and SCR	LNB w/OFA and SCR	LNB w/OFA and SCR	LNB w/OFA and SCR
SCR Efficiency, % (A)	86	86	86	86	86	86	86
Ammonia Slip (end of catalyst life), ppmv	2	2	2	2	2	2	2
Particulate Control	Fabric Filter	Fabric Filter	Fabric Filter	Fabric Filter	Fabric Filter	Fabric Filter	Fabric Filter
Fabric Filter efficiency, % (A)	99.8	99.8	99.8	99.8	99.8	99.8	99.8
Ash Distribution, Fly/Bottom	80% / 20%	80% / 20%	80% / 20%	80% / 20%	80% / 20%	80% / 20%	80% / 20%
Mercury Control	Co-benefit Capture	Co-benefit Capture	Co-benefit Capture	Co-benefit Capture	Co-benefit Capture	Co-benefit Capture	Co-benefit Capture
Mercury removal efficiency, % (A)	90	90	90	90	90	90	90
CO_2 Control	N/A	Econamine	Enzyme-Activated K_2CO_3	Enzyme-Activated K_2CO_3	Enzyme-Activated K_2CO_3	Enzyme-Activated K_2CO_3	K_2CO_3
Overall CO_2 Capture (A)	N/A	90%	90%	90%	90%	90%	18%
CO_2 Sequestration	N/A	Off-site Saline Formation	Off-site Saline Formation	Off-site Saline Formation	Off-site Saline Formation	Off-site Saline Formation	Off-site Saline Formation

A. Removal efficiencies are based on the FG species content
B. An SO_2 polishing step is included to meet more stringent SOx content limits in the FG (< 10 ppmv) to reduce formation of amine HSS during the CO_2 absorption process
C. SO_2 exiting the post-FGD polishing step is absorbed in the CO_2 capture process making stack emissions negligible

Balance of Plant

The balance of plant assumptions are common to all cases and are presented in Exhibit 4.

Exhibit 4 Balance of Plant Assumptions

Cooling system	Recirculating Wet Cooling Tower
Fuel and Other storage	
Coal	30 days
Ash	30 days
Gypsum	30 days
Limestone	30 days
Plant Distribution Voltage	
Motors below 1 hp	110/220 volt
Motors between 1 hp and 250 hp	480 volt
Motors between 250 hp and 5,000 hp	4,160 volt
Motors above 5,000 hp	13,800 volt
Steam and GT generators	24,000 volt
Grid Interconnection voltage	345 kV
Water and Waste Water	
Makeup Water	The water supply is 50 percent from a local publically owned treatment works and 50 percent from groundwater, and is assumed to be in sufficient quantities to meet plant makeup requirements. Makeup for potable, process, and de-ionized water is drawn from municipal sources.
Process Wastewater	Storm water that contacts equipment surfaces is collected and treated for discharge through a permitted discharge.
Sanitary Waste Disposal	Design includes a packaged domestic sewage treatment plant with effluent discharged to the industrial wastewater treatment system. Sludge is hauled off site. Packaged plant is sized for 5.68 cubic meters per day (1,500 gallons per day).
Water Discharge	Most of the process wastewater is recycled to the cooling tower basin. Blowdown will be treated for chloride and metals, and discharged.

2.2.1 Sparing Philosophy

Single trains are used throughout the design with exceptions where equipment capacity requires an additional train. There is no redundancy other than normal sparing of rotating equipment. The plant design consists of the following major subsystems:

- One dry-bottom, wall-fired PC subcritical boiler (1 x 100%).
- Two SCR reactors (2 x 50%).
- Two single-stage, in-line, multi-compartment fabric filters (2 x 50%).

- One wet limestone forced oxidation positive pressure SO_2 absorber (1 x 100%).
- One steam turbine (1 x 100%).
- For NETL Case 10, two parallel Econamine CO_2 absorption systems, with each system consisting of two absorbers, strippers and ancillary equipment (2 x 50%).
- For all enzyme-activated K_2CO_3 PCC cases, two parallel CO_2 absorption systems, with each system consisting of two absorbers, strippers and ancillary equipment (2 x 50%) are considered.

3 Evaluation Basis

For each Cases DB1 to DB5 an Aspen Plus® software model has been developed to generate material and energy balances to create a design basis for the major equipment. These models and equipment sizing were then used as the basis for generating the capital and operating cost estimates relating to the process. Equipment performance estimates to replicate model results were based on information obtained from vendors, performance data from design/build utility projects, and/or best engineering judgment. The capital and operational costs were based on simulation results, scaled estimates from previous design projects and vendor information.

This section documents the design basis common to all cases with the specific design covered in the case-specific sections. Ultimately a COE was calculated for each of the cases and is reported as the revenue requirement figure-of-merit.

3.1 Key Assumptions

3.1.1 Site Characteristics

This study assumes that the plant is to be located at a generic site in Midwestern U.S., with ambient conditions and site characteristics as presented below. The ambient conditions are the same as ISO conditions.

Elevation, (ft)	0
Barometric Pressure, MPa (psia)	0.10 (14.696)
Design Ambient Temperature, Dry Bulb, °C (°F)	15 (59)
Design Ambient Temperature, Wet Bulb,°C, (°F)	11 (51.5)
Design Ambient Relative Humidity, %	60

Location	Greenfield, Midwestern USA
Topography	Level
Size, acres	300
Transportation	Rail
Ash/Slag Disposal	Off Site
Water	Municipal (50%) / Groundwater (50%)
Access	Land locked, having access by rail and highway
CO_2 Storage	Compressed to 15.3 MPa (2,215 psia), transported 80 kilometers (50 miles) and sequestered in a saline formation at a depth of 1,239 m (4,055 ft)

The land area assumes 30 acres are required for the plant proper and the balance provides a buffer of approximately 0.25 miles to the fence line and provide for a rail loop if required. In all cases it was assumed that the PC boiler and steam turbine are enclosed in a boiler house and turbine building respectively.

The following design parameters are considered site-specific, and are not quantified for this study. Allowances for normal conditions and construction are included in the cost estimates.

- Flood plain considerations
- Existing soil/site conditions
- Water discharges and reuse
- Rainfall/snowfall criteria
- Seismic design
- Buildings/enclosures
- Local code height requirements
- Noise regulations – Impact on site and surrounding area

3.1.2 Coal Characteristics

The design coal is Illinois No. 6 with characteristics presented in Exhibit 5. The coal properties are from NETL's Coal Quality Guidelines [3].

The Power Systems Financial Model (PSFM) was used to derive the capital charge factors (CCF) and levelization factors (LF) for this study [4]. The PSFM requires that all cost inputs have a consistent cost year basis. Because the capital and operating cost estimates are in June 2007 dollars, the fuel costs must also be in June 2007 dollars.

The coal cost used in this study is $1.55/GJ ($1.64/MMBtu) (cost of coal in June 2007). This cost was determined using the following information from the Energy Information Administration (EIA) 2008 annual energy outlook (AEO):

- The 2007 minemouth cost of Illinois No. 6 in 2006 dollars, $32.66/tonne ($29.63/ton), was obtained from Supplemental Table 112 of the EIA's 2008 AEO for eastern interior high-sulfur bituminous coal.
- The cost of Illinois No. 6 coal was escalated to 2007 dollars using the gross domestic product (GDP) chain-type price index from AEO 2008, resulting in a price of $33.67/tonne ($30.55/ton) [5].
- Transportation costs for Illinois No. 6 were estimated to be 25 percent of the minemouth cost based on the average transportation rate of the respective coals to the surrounding regions [1]. The final delivered costs for Illinois No. 6 coal used in the calculations is $42.09/tonne ($38.18/ton) or $1.55/GJ ($1.64/MMBtu).

Exhibit 5 Design Coal

Rank	**Bituminous**	
Seam	**Illinois No. 6 (Herrin)**	
Source	**Old Ben Mine**	
Proximate Analysis (weight %) (Note A)		
	As Received	**Dry**
Moisture	11.12	0.00
Ash	9.70	10.91
Volatile Matter	34.99	39.37
Fixed Carbon	44.19	49.72
Total	100.00	100.00
Sulfur	2.51	2.82
HHV, kJ/kg	27,113	30,506
HHV, Btu/lb	11,666	13,126
LHV, kJ/kg	26,151	29,544
LHV, Btu/lb	11,252	12,712
Ultimate Analysis (weight %)		
	As Received	**Dry**
Moisture	11.12	0.00
Carbon	63.75	71.72
Hydrogen	4.50	5.06
Nitrogen	1.25	1.41
Chlorine	0.29	0.33
Sulfur	2.51	2.82
Ash	9.70	10.91
Oxygen (Note B)	6.88	7.75
Total	100.00	100.00

Notes:
A. The proximate analysis assumes sulfur as volatile matter
B. By difference

3.1.3 Raw Water Withdrawal and Consumption

A water balance was performed for each case on the major water consumers in the process. The total water demand for each subsystem was determined through process modelling and internal recycle water available from various sources like boiler feedwater blowdown and condensate from flue gas in CO_2 capture cases was applied to offset the water demand. The difference between demand and recycle is raw water withdrawal. Raw water withdrawal is the water removed from the ground or diverted from a surface-water source for use in the plant. Raw water consumption is also accounted for as the portion of the raw water withdrawn that is evaporated, transpired, incorporated into products or otherwise not returned to the water source it was withdrawn from. Consumption represents the net impact of the process on the water source.

Raw water makeup was assumed to be provided 50 percent by a publicly owned treatment works and 50 percent from groundwater. Raw water withdrawal is defined as the water metered from a raw water source and used in the plant processes for any and all purposes, such as cooling tower makeup, boiler feedwater makeup, slurry preparation makeup, ash handling makeup and FGD system makeup.

The largest consumer of raw water in all cases is cooling tower makeup. It was assumed that all cases utilized a mechanical draft, evaporative cooling tower, and all process blowdown streams were assumed to be treated and recycled to the cooling tower.

The design ambient wet bulb temperature of 11°C (51.5°F) was used to achieve a cooling water temperature of 16°C (60°F) using an approach of 5°C (8.5°F). The cooling water range was assumed to be 11°C (20°F). The cooling tower makeup rate was determined through process modelling.

The water balances presented in subsequent sections include the water demand of the major water consumers within the process, the amount provided by internal recycle, the amount of raw water withdrawal by difference, the amount of process water returned to the source and the raw water consumption, again by difference.

3.2 Modelling Approach

Aspen Plus® software has been used in the study as a tool for modelling the process. This computational platform for rigorous calculations of physical and thermodynamic properties of water, steam and multi-component mixtures was used to produce material and energy balances around each unit operation in the steam cycle and CO_2 capture system.

The processes for NETL Cases 9 and 10 [1] were simulated to ensure that comparable results were achieved to ensure the models were created on a similar basis. The NETL Case 9 model was then adapted to include the CA enzyme-activated K_2CO_3 solvent PCC plant. Part of the adaptation was the use of derived reaction kinetics to simulate the enzyme's action on absorption and desorption of CO_2. The University of Kentucky's bench scale unit was modelled using Aspen Plus® software by Pacific Northwest National Laboratory. The model was then validated using the bench scale system test data and the CA enzyme-activated solvent reaction kinetics to be used in the full scale models were derived.

Once the model for Case DB1 had been setup and converged, an iterative step was required to determine the target operating point at which an overall CO_2 capture of 90% was achieved with a net power output of 550MWe.

The remaining cases were carried out as above with different sensitivities applied such as a deeper vacuum in the stripper, the utilization of very low pressure steam for reboiler heating duty or the use of non-enzyme-activated kinetics. The resulting performance parameters of the optimized PCC plant cases were used to calculate the power and equipment size requirements of the process for cost estimation.

The five cases considered were:

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

Model to Plant Differences and Effects

A number of differences between the bench scale system testing and process models were noted as a result of the scale up and these result in changes between measured and predicted performance. The model to plant difference that is most apparent is the reboiler heat duty, which was measured at approximately 350 kJ/molCO_2 in the bench scale tests. The model predicted reboiler heat duty in Case DB1 is 126 kJ/molCO_2. Part of this difference could be attributed to general uncertainties when making predictions for a 300,000-fold (based on solvent inventory) scale-up from bench to full scale, however, more specific explanations could account for the difference in reboiler heat duty, as outlined below.

The kinetic model developed by PNNL to simulate enzyme–activated stripper kinetics has a significant influence on the simulated reboiler duty, meaning that reboiler duty was higher in the absence of enzyme-activated stripper kinetics. Furthermore, incorporation of enzyme-activated kinetics led to a predicted reboiler duty that was much lower when compared to the reboiler duty observed by UKCAER during operation of the bench-scale unit. Information from the kinetic simulation was incorporated in the full feasibility model, resulting in the reboiler duty presented and benefits from the favorable stripper kinetics predicted by the enzyme-activated model. The measured bench-scale data shows a much higher reboiler duty than predicted by the enzyme–activated model and it is likely that the full scale model is currently over-predicting system performance.

The ratio of the liquid solvent recirculation rate to flue gas flow into the absorber is commonly known as the L/G ratio. In the bench-scale unit the measured L/G ratio on a mass basis was approximately 18, the model predicted L/G ratio to meet the CO_2 capture requirements was approximately 8. A number of factors influence the predicted L/G ratio, the increased absorption residence time and contact area in the full scale models result in a higher solvent CO_2 loading and therefore a lower circulation rate required to achieve 90% CO_2 capture. The result of a lower circulation rate also reduces the amount of solvent required to be heated in the stripper and hence reduces the reboiler heat duty.

The approach temperature measured in the lean-rich heat exchanger on the bench-scale unit was approximately 10°C. In the model, the approach temperature was set at 5°C as this is understood to be the minimum practical approach temperature to provide optimal performance, within practical equipment sizing constraints. The improved heat recovery in the model would reduce sensible heat requirements in the stripper and further reduce reboiler heat duty.

A final factor that also could contribute to reduced reboiler duty is the plant arrangements employed. In the bench-scale unit the condensate removed from CO_2 product leaving the top of the stripper in the product gas condenser is returned to the stripper column. This returned condensate is then subject to heating in the reboiler adding to the reboiler heat duty. In the process model the product gas condensate is routed to the absorber and therefore, does not add to the reboiler heat duty.

All of these factors could contribute the lower reboiler heat duty predicted by the model but it is recommended that plant tests that reflect the absorption and reboiler residence times, L/G ratio, heat exchanger approach temperatures and plant configuration are carried out to validate the model predicted performance and reduce uncertainties.

Comparison with MEA

The 126 kJ/molCO_2 reboiler heat duty observed in Case DB1 is better than that of MEA, which is unexpected given that the CO_2 loading capacity of MEA is higher than the CA enzyme-activated K_2CO_3 solvent. This results in a lower L/G ratio requirement of approximately 4 to achieve 90% CO_2 capture with similarly sized equipment. Given the lower circulation rate it would be expected that a reduced reboiler heat duty would be observed. However, the NETL Case 10 [1] predicted reboiler heat duty is 156 kJ/molCO_2. One reason the predicted reboiler heat duty for Case DB1 could be lower than MEA Case 10 is that Case 10 utilizes pressurized stripping, whereas the CA enzyme-activated K_2CO_3 cases consider vacuum stripping, which reduces the saturation temperature and so reduces the reboiler heat duty requirement. Therefore for a fair comparison the stripper system energy penalty needs to be taken into account i.e. the energy required to create the vacuum for Case DB1 also needs to be considered.

3.3 Cost Estimation Methodology

The estimating methodologies for capital costs, operations and maintenance costs, and CO_2 TS&M costs are described below. The finance structure, basis for the discounted cash flow analysis, and first-year COE cost calculations are also described.

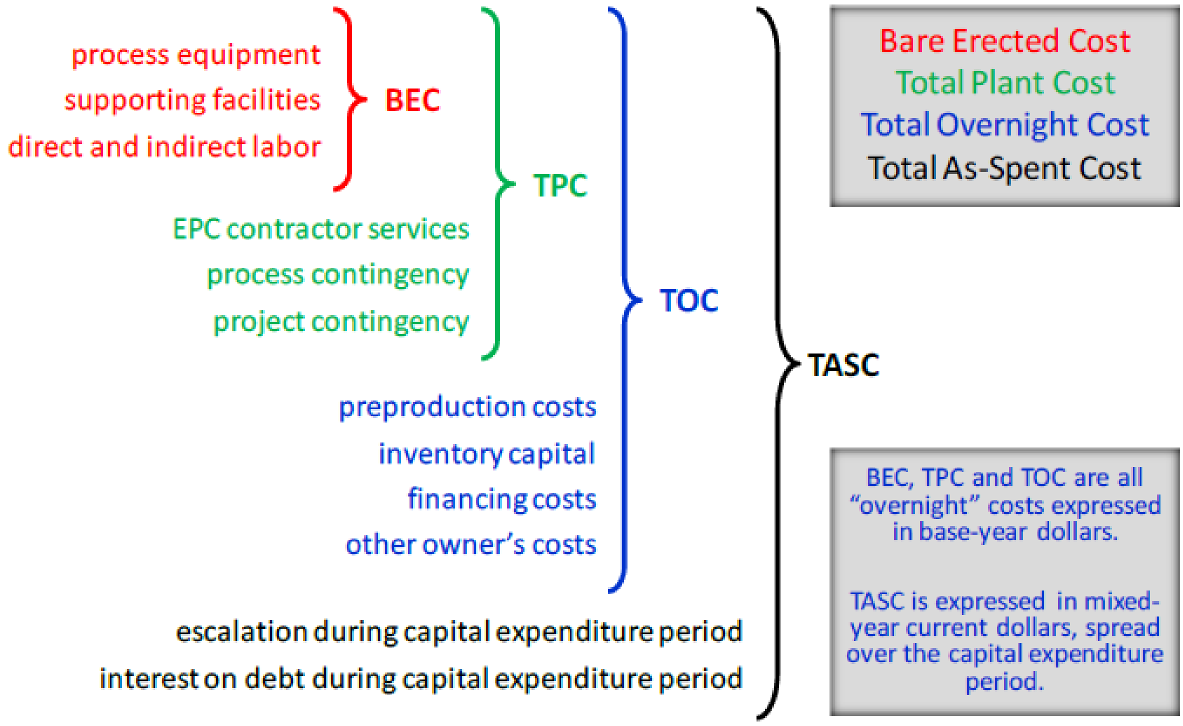
To ensure a fair comparison with NETL Cases 9 and 10 [1] all non PCC common plant costs such as the boiler and ancillaries have been scaled, where applicable, from Case 10 costs using the methodology outlined in DOE/NETL Capital Cost Scaling Methodology Quality Guidelines for Energy System Studies (QGESS) [6]. The scaling parameters were determined from the results of the Aspen Plus® software model outputs for the individual cases to achieve a 550MWe net plant output.

For the PCC process a 2007$ cost for an MEA based PCC plant sized as per NETL Case 10 [1] was calculated using vendor data and capital cost estimates, scaled where applicable, from previous Doosan Babcock design projects. This was then compared to the NETL Case 10 PCC plant cost estimate to provide an adjustment factor between Doosan Babcock and NETL derived cost estimates. Where applicable, the derived factor was directly applied to the plant costs for the enzyme-activated K_2CO_3 solvent cases to allow for a fair relative estimate of the PCC plant costs to be obtained.

3.3.1 Capital Costs

As illustrated in Exhibit 6, this study reports capital cost at four levels: Bare Erected Cost (BEC), Total Plant Cost (TPC), Total Overnight Cost (TOC) and Total As-spent Capital (TASC). BEC, TPC and TOC are “overnight” costs and are expressed in “base-year” dollars. The base year is the first year of capital expenditure, which for this study is assumed to be 2007. TASC is expressed in mixed-year, current-year dollars over the entire capital expenditure period, which is assumed to last five years (2007 to 2012).

Exhibit 6 Capital Cost Levels and their Elements



The BEC comprises the cost of process equipment, on-site facilities and infrastructure that support the plant (e.g., shops, offices, labs, road), and the direct and indirect labor required for its construction and/or installation. The cost of engineering, procurement and construction (EPC) services and contingencies is not included in BEC. BEC is an overnight cost expressed in base-year (2007) dollars.

The TPC comprises the BEC plus the cost of services provided by the engineering, procurement and construction (EPC) contractor and project and process contingencies. EPC services include: detailed design, contractor permitting (i.e., those permits that individual contractors must obtain to perform their scopes of work, as opposed to project permitting, which is not included here), and project/construction management costs. TPC is an overnight cost expressed in base-year (2007) dollars.

The TOC comprises the TPC plus owner’s costs. TOC is an “overnight” cost, expressed in base-year (2007) dollars and does not include escalation or interest during construction.

The TASC is the sum of all capital expenditures as they are incurred during the capital expenditure period including their escalation. TASC also includes interest during construction. Accordingly, TASC is expressed in mixed, current-year dollars over the capital expenditure period.

Cost Estimate Basis and Classification

The TPC and operation and maintenance (O&M) costs for each of the cases in the study were estimated using an in-house database populated with a combination of adjusted vendor-furnished and actual cost data from recent Doosan Babcock design projects.

Recommended Practice 18R-97 of the Association for the Advancement of Cost Engineering International (AACE) describes a Cost Estimate Classification System as applied in Engineering, Procurement and Construction for the process industries [7].

This techno-economic study has been carried out as an AACE Class 4 Cost Estimate. Exhibit 7 describes the characteristics of the cost estimate and are expected to have an accuracy range of -15%/+30%.

Exhibit 7 Features of an AACE Class 4 Cost Estimate

Project Definition	Typical Engineering Completed	Expected Accuracy
1 to 15%	plant capacity, block schematics, indicated layout, process flow diagrams for main process systems, and preliminary engineered process and utility equipment lists	-15% to -30% on the low side, and +20% to +50% on the high side

System Code-of-Accounts

The costs are grouped according to a process/system oriented code of accounts. This type of code-of-account structure has the advantage of grouping all reasonably allocable components of a system or process so they are included in the specific system account.

Plant Maturity

Cost estimates in this report reflect nth-of-a-kind (NOAK) costs for plants that only contain fully mature technologies which have been widely deployed at commercial scale, e.g., PC power plants without CO_2 capture. The cost of such plants has dropped over time due to the "learning by doing" and risk reduction benefits that result from serial deployments as well as from continuing R&D.

Cost estimates in this report reflect the cost of the next commercial offering for plants that include technologies that are not yet fully mature and/or which have not yet been serially deployed in a commercial context, e.g., plants with CO_2 capture. These cost estimates for next commercial offerings do not include the unique cost premiums associated with first-of-a-kind (FOAK) plants that must demonstrate emerging technologies and resolve the cost and performance challenges associated with initial iterations. However, these estimates do utilize currently available cost bases for emerging technologies with associated process contingencies applied at the appropriate subsystem levels.

Cost estimates for all of the plants, regardless of technology maturity, are based on many design assumptions that affect costs, including the use of a favorable site with no unusual characteristics that make construction more costly. The primary value of this report lies not in the absolute accuracy of cost estimates for the individual cases (estimated to be -15%/+30%), but in the fact that all cases were evaluated using a common methodology with a consistent set of technical and economic assumptions.

This consistency of approach allows meaningful comparisons of relative costs among the cases to be evaluated.

Contracting Strategy

The estimates are based on an engineering, procurement, construction management (EPCM) approach utilizing multiple subcontracts. This approach provides the Owner with greater control of the project, while minimizing, if not eliminating, most of the risk premiums typically included in an EPC contract price.

In a traditional lump sum EPC contract, the Contractor assumes all risk for performance, schedule, and cost. However, as a result of current market conditions, EPC contractors appear more reluctant to assume that overall level of risk. Rather, the current trend appears to be a modified EPC approach where much of the risk remains with the Owner. Where Contractors are willing to accept the risk in EPC type lump-sum arrangements, it is reflected in the project cost. In today's market, Contractor premiums for accepting these risks, particularly performance risk, can be substantial and increase the overall project costs dramatically.

The EPCM approach used as the basis for the estimates here is anticipated to be the most cost effective approach for the Owner. While the Owner retains the risks, the risks become reduced with time, as there is better scope definition at the time of contract award(s).

Estimate Scope

The estimates represent a complete power plant facility on a generic site. The plant boundary limit is defined as the total plant facility within the "fence line" including coal receiving and water supply system, but terminating at the high voltage side of the main power transformers. TS&M cost is not included in the reported capital cost or O&M costs, but is treated separately and added to the COE.

This study assumes that each new plant would be dispatched any time it is available and would be capable of generating maximum capacity when online. An availability of 85% (capacity factor (CF) 0.85) was used in this study and it has been assumed that the addition of CO_2 capture does not impact the CF. This assumption was made to enable a comparison based on the impact of capital and variable operating costs only. Any reduction in assumed CF would further increase the COE for the CO_2 capture cases.

Capital Cost Assumptions

The capital cost estimates for each case were developed using simulation results, scaled estimates from previous design projects and vendor information. This approach utilized power plant design experience for similar equipment in Doosan Babcock's range of power and process projects. A reference bottom-up estimate for each major component provided the data for the estimating models.

Other key estimate considerations where used as per NETL Case 10 [1] as follows:

- Labor costs are based on Midwest, Merit Shop. The estimating models are based on U.S. Gulf Coast and the labor has been factored to Midwest. The basis for the factors is the PAS, Inc. (PAS) "Merit Shop Wage & Benefit Survey," which is published annually. Based on the data provided in PAS, the weighted average payroll plus fringe rate for a standard craft distribution as developed for the estimating models was used.

  PAS presents information for eight separate regions. For this study, Region 5 (IL, IN, MI, MN, OH, and WI) was selected.

- The estimates are based on a competitive bidding environment, with adequate skilled craft labor available locally.
- Labor is based on a 50-hour work-week. No additional incentives such as per-diems or bonuses have been included to attract craft labor.
- While not included at this time, labor incentives may ultimately be required to attract and retain skilled labor depending on the amount of competing work in the region, and the availability of skilled craft in the area at the time the projects proceed to construction.
- The estimates are based on a greenfield site.
- The site is considered to be Seismic Zone 1, relatively level, and free from hazardous materials, archeological artifacts, or excessive rock. Soil conditions are considered adequate for spread footing foundations. The soil bearing capability is assumed adequate such that piling is not needed to support the foundation loads.
- Costs are limited to within the "fence line," terminating at the high voltage side of the main power transformers with the exception of costs included for TS&M, which are added to the plant costs to determine the COE.
- Engineering and Construction Management are estimated at 8-10 percent of BEC. These costs consist of all home office engineering and procurement services as well as field construction management costs. Site staffing generally includes a construction manager, resident engineer, scheduler, and personnel for project controls, document control, materials management, site safety, and field inspection.

Price Fluctuations

During the course of this study, the prices of equipment and bulk materials have fluctuated quite substantially. Some reference quotes pre-dated the 2007 year cost basis while others were received post-2007. All vendor quotes used to develop these estimates were adjusted to June 2007 dollars accounting for the price fluctuations.

Exclusions

The capital cost estimate includes all anticipated costs for equipment and materials, installation labor, professional services (Engineering and Construction Management), and contingency. The following items are excluded from the capital costs:

- All taxes, with the exception of payroll and property taxes (property taxes are included with the fixed O&M costs).
- Site specific considerations – including, but not limited to, seismic zone, accessibility, local regulatory requirements, excessive rock, piles, laydown space, etc.
- Additional premiums associated with an EPC contracting approach.

Contingency

Process and project contingencies are included in estimates to account for unknown costs that are omitted or unforeseen due to a lack of complete project definition and engineering. Contingencies are added because experience has shown that such costs are likely, and expected, to be incurred even though they cannot be explicitly determined at the time the estimate is prepared.

Capital cost contingencies do not cover uncertainties or risks associated with:

- Scope changes.
- Changes in labor availability or productivity.
- Delays in equipment deliveries.
- Changes in regulatory requirements.
- Unexpected cost escalation.
- Performance of the plant after startup (e.g., availability, efficiency).

Process Contingency

Process contingency is intended to compensate for uncertainty in cost estimates caused by performance uncertainties associated with the development status of a technology. Process contingencies are applied to each plant section based on its current technology status. As shown in Exhibit 8, AACE International Recommended Practice 16R-90 [8] provides guidelines for estimating process contingencies based on Electric Power Research Institute‘s (EPRI) philosophy.

Process contingencies have been applied to the estimates in this study as follows:

- PCC Plant – 20 percent on all cases utilizing PCC plant to account for the fact that the post-combustion capture process is unproven at commercial scale for power plant applications.
- Instrumentation and Controls – 5 percent on the cases with PCC plant to allow for potential integration issues.

Exhibit 8 AACE Guidelines for Process Contingency

Technology Status	Process Contingency (% of Associated Process Capital)
New concept with limited data	40+
Concept with bench-scale data	30-70
Small pilot plant data	20-35
Full-sized modules have been operated	5-20
Process is used commercially	0-10

Project Contingency

AACE 16R-90 [8] states that project contingency for a “budget-type” estimate (AACE Class 4 or 5) should be 15 to 30 percent of the sum of BEC, EPC fees and process contingency. This was used as a general guideline, for the estimates in this report.

Owner’s Costs

Exhibit 9 explains the estimation method for owner’s costs. With some exceptions, the estimation method follows guidelines in Sections 12.4.7 to 12.4.12 of AACE International Recommended Practice No. 16R-90 [8]. EPRI’s “Technical Assessment Guide (TAG®) – Power Generation and Storage Technology Options” [26] also has guidelines for estimating owner’s costs. The EPRI and AACE guidelines are very similar. In instances where they differ, this study has sometimes adopted the EPRI approach.

Interest during construction and escalation during construction are not included as owner’s costs but are factored into the COE and are included in TASC. These costs vary based on the capital expenditure period and the financing scenario. For the cases with PCC plant the finance structure is a high risk investor-owned utility (IOU) with a capital expenditure period of five years. In these cases the ratio of TASC/TOC determined from the PSFM of 1.140 was used to account for escalation and interest during construction.

Exhibit 9 Owner's Costs Included in TOC

Owner's Cost	Estimate Basis
Prepaid Royalties	Any technology royalties are assumed to be included in the associated equipment cost, and thus are not included as an owner's cost.
Preproduction (Start-Up) Costs	• 6 months operating labor • 1 month maintenance materials at full capacity • 1 month non-fuel consumables at full capacity • 1 month waste disposal • 25% of one month's fuel cost at full capacity • 2% of TPC Compared to AACE 16R-90 [8], this includes additional costs for operating labor (6 months versus 1 month) to cover the cost of training the plant operators, including their participation in startup, and involving them occasionally during the design and construction. AACE 16R-90 [8] and EPRI TAG® [26] differ on the amount of fuel cost to include; this estimate follows EPRI.
Working Capital	Although inventory capital (see below) is accounted for, no additional costs are included for working capital.
Inventory Capital	• 0.5% of TPC for spare parts • 60 day supply (at full capacity) of fuel. Not applicable for natural gas. • 60 day supply (at full capacity) of non-fuel consumables (e.g., chemicals and catalysts) that are stored on site. Does not include catalysts and adsorbents that are batch replacements such as SCR catalyst. AACE 16R-90 [8] does not include an inventory cost for fuel, but EPRI TAG® [26] does.
Land	• $3,000/acre (300 acres considered for PC)
Financing Cost	• 2.7% of TPC This financing cost (not included by AACE 16R-90 [8]) covers the cost of securing financing, including fees and closing costs but not including interest during construction (or allowance for funds used during construction). The "rule of thumb" estimate (2.7% of TPC) is based on NETL report [1].

Owner's Cost	**Estimate Basis**
Other Owner's Costs	• 15% of TPC This additional lumped cost is not included by AACE 16R-90 [8] or EPRI TAG® [26]. The "rule of thumb" estimate (15% of TPC) is based on NETL report [1]. Significant deviation from this value is possible as it is very site and owner specific. The lumped cost includes: - Preliminary feasibility studies, including a Front-End Engineering Design (FEED) study - Economic development (costs for incentivizing local collaboration and support) - Construction and/or improvement of roads and/or railroad spurs outside of site boundary - Legal fees - Permitting costs - Owner's engineering (staff paid by owner to give third-party advice and to help the owner oversee/evaluate the work of the EPC contractor and other contractors) - Owner's contingency (Sometimes called "management reserve", these are funds to cover costs relating to delayed startup, fluctuations in equipment costs, unplanned labor incentives in excess of a five-day/ten-hour-per-day work week. Owner's contingency is NOT a part of project contingency.) This lumped cost does NOT include: - EPC Risk Premiums (Cost estimates are based on an Engineering Procurement Construction Management approach utilizing multiple subcontracts, in which the owner assumes project risks for performance, schedule and cost) - Transmission interconnection: the cost of interconnecting with power transmission infrastructure beyond the plant busbar. - Taxes on capital costs: all capital costs are assumed to be exempt from state and local taxes. - Unusual site improvements: normal costs associated with improvements to the plant site are included in the bare erected cost, assuming that the site is level and requires no environmental remediation. Unusual costs associated with the following design parameters are excluded: flood plain considerations, existing soil/site conditions, water discharges and reuse, rainfall/snowfall criteria, seismic design, buildings/enclosures, fire protection, local code height requirements, noise regulations.

3.3.2 Operational & Maintenance Costs

The production costs or operating costs and related maintenance expenses (O&M) pertain to those charges associated with operating and maintaining the power plants over their expected life.

These costs include:

- Operating labor
- Maintenance – material and labor
- Administrative and support labor
- Consumables
- Fuel
- Waste disposal
- Co-product or by-product credit (that is, a negative cost for any by-products sold)

There are two components of O&M costs; fixed O&M, which is independent of power generation, and variable O&M, which is proportional to power generation.

Operating Labor

Operating labor cost was determined based on of the number of operators required for each specific case. The average base labor rate used to determine annual cost is $34.65/hour. The associated labor burden is estimated at 30 percent of the base labor rate. Taxes and insurance are included as fixed O&M costs totaling 2 percent of the TPC.

Maintenance Material and Labor

Maintenance cost was evaluated on the basis of relationships of maintenance cost to initial capital cost. This represents a weighted analysis in which the individual cost relationships were considered for each major plant component or section.

Administrative and Support Labor

Labor administration and overhead charges are assessed at a rate of 25 percent of the burdened O&M labor.

Consumables

The cost of consumables, including fuel, was determined on the basis of individual rates of consumption, the unit cost of each specific consumable commodity, and the plant annual operating hours.

Quantities for major consumables such as fuel and sorbent were taken from heat and mass balance diagrams developed by process models for each case. Other consumables were evaluated on the basis of the quantity required using reference data and plant models.

The quantities for initial fills and daily consumables were calculated on a 100 percent operating capacity basis. The annual cost for the daily consumables was then adjusted to incorporate the annual plant operating basis, or CF.

Initial fills of the consumables, fuels and chemicals, are different from the initial chemical loadings, which are included with the equipment pricing in the capital cost, for example SCR catalyst.

Waste Disposal

Waste quantities and disposal costs were determined and evaluated similarly to the consumables. Fly ash and bottom ash are considered a waste with a disposal cost of \$17.89/tonne (\$16.23/ton).

Co-Products and By-Products

By-product quantities were also determined similarly to the consumables. However, due to the variable marketability of gypsum, no credit was taken for its potential salable value. Likewise the wet solids waste from the CA enzyme-activated PCC cases can potentially be used as a compost or fertilizer, but the marketability for the quantities produced has not be determined and so no credit has been taken for their potential salable value.

It should be noted that by-product credits and/or disposal costs could potentially be an additional determining factor in the choice of technology for some companies and in selecting some sites. A high local value of the product can establish whether or not added capital should be included in the plant costs to produce a particular co-product. Ash is a potential by-product in certain markets, and in the absence of activated carbon injection the fly ash would remain uncontaminated and have potential marketability. However, as stated above, the ash is considered waste in this study with a concomitant disposal cost.

3.3.3 CO_2 Transport, Storage & Monitoring

For those cases that feature carbon sequestration, the capital and operating costs for CO_2 TS&M were taken from independent estimates by NETL [1]. Those costs were converted to a TS&M COE increment that was included in the plant COE.

CO_2 TS&M was modeled based on the following assumptions:

- CO_2 is supplied to the pipeline at the plant fence line at a pressure of 15.3 MPa (2,215 psia). The CO_2 product gas composition for all cases is expected to meet the specification described in Exhibit 10 [9]. A glycol dryer located near the mid-point of the compression train is used to meet the moisture specification.

Exhibit 10 CO_2 Pipeline Specification

Parameter	Units	Parameter Value
Inlet Pressure	MPa (psia)	15.3 (2,215)
Outlet Pressure	MPa (psia)	10.4 (1,515)
Inlet Temperature	°C (°F)	35 (95)
N_2 Concentration	ppmv	< 300
O_2 Concentration	ppmv	< 40
Ar Concentration	ppmv	< 10
H_2O Concentration	ppmv	< 150

- The CO_2 is transported 80 km (50 miles) via pipeline to a geologic sequestration field for injection into a saline formation.
- The CO_2 is transported and injected as a super critical fluid in order to avoid two-phase flow and achieve maximum efficiency [10]. The pipeline is assumed to have an outlet pressure above the supercritical pressure of 8.3 MPa (1,200 psia) with no recompression along the way. Accordingly, CO_2 flow in the pipeline was modeled to determine the pipe diameter that results in a pressure drop of 6.9 MPa (1,000 psi) over the 80 km (50 mile) pipeline length [11] (although not explored in this study, the use

of boost compressors and a smaller pipeline diameter could possibly reduce capital costs for sufficiently long pipelines.) The diameter of the injection pipe will be of sufficient size that frictional losses during injection are minimal and no booster compression is required at the well-head in order to achieve an appropriate down-hole pressure, with hydrostatic head making up the difference between the injection and reservoir pressure.

- The saline formation is at a depth of 1,236 m (4,055 ft) and has a permeability of 22 millidarcy (md) (22 μm^2) and formation pressure of 8.4 MPa (1,220 psig) [12]. This is considered an average storage site and requires roughly one injection well for each 9,360 tonnes (10,320 tons) of CO_2 injected per day [12]. The assumed aquifer characteristics are tabulated in Exhibit 11.

The cost metrics utilized in this study provide a best estimate of TS&M costs for a "favorable" sequestration project, and may vary significantly based on variables such as terrain to be crossed by the pipeline, reservoir characteristics, and number of land owners from which sub-surface rights must be acquired. Raw capital and operating costs are derived from detailed cost metrics found in the literature, escalated to June 2007-year dollars using appropriate price indices. These costs were then verified against values quoted by industrial sources where possible. Where regulatory uncertainty exists or costs are undefined, such as liability costs and the acquisition of underground pore volume, analogous existing policies were used for representative cost scenarios.

Exhibit 11 Deep, Saline Aquifer Specification

Parameter	Units	Base Case
Pressure	MPa (psi)	8.4 (1,220)
Thickness	m (ft)	161 (530)
Depth	m (ft)	1,236 (4,055)
Permeability	md	22
Pipeline Distance	km (miles)	80 (50)
Injection Rate per Well	tonne (ton) CO_2/day	9,360 (10,320)

The following sections describe the sources and methodologies used for each metric.

TS&M Capital Costs

TS&M capital costs include both a 20 percent process contingency and 30 percent project contingency.

In several areas, such as Pore Volume Acquisition, Monitoring, and Liability, cost outlays occur over a longer period, up to 100 years. In these cases a capital fund is established based on the net present value of the cost outlay, and this fund is then levelized similar to the other costs.

Transport Costs

CO_2 transport costs are broken down into three categories: pipeline costs, related capital expenditures, and O&M costs.

Pipeline costs used from the NETL report [1] are derived from data published in the Oil and Gas Journal's (O&GJ) annual Pipeline Economics Report for existing natural gas, oil, and petroleum pipeline project costs from 1991 to 2003. These costs are expected to be analogous to the cost of building a CO_2 pipeline, as noted in various studies [10, 12, 13]. The University of California performed a regression analysis to generate cost curves from the

O&GJ data: (1) Pipeline Materials, (2) Direct Labor, (3) Indirect Costs, and (4) Right-of-way acquisition, with each represented as a function of pipeline length and diameter [13]. These cost curves were escalated to the June 2007 year dollars used in this study.

Related capital expenditures were based on the findings of a previous study funded by DOE/NETL, Carbon Dioxide Sequestration in Saline Formations – Engineering and Economic Assessment [12]. This study utilized a similar basis for pipeline costs (O&GJ Pipeline cost data up to the year 2000), but added a CO_2 surge tank and pipeline control system to the project.

Transport O&M costs were assessed using metrics published in a second DOE/NETL sponsored report entitled Economic Evaluation of CO_2 Storage and Sink Enhancement Options [10]. This study was selected due to the reporting of O&M costs in terms of pipeline length, whereas the other studies mentioned above either (a) do not report operating costs, or (b) report them in absolute terms for one pipeline, as opposed to as a length- or diameter-based metric.

Storage Costs

Storage costs were divided into five categories: (1) Site Screening and Evaluation, (2) Injection Wells, (3) Injection Equipment, (4) O&M Costs, and (5) Pore Volume Acquisition. With the exception of Pore Volume Acquisition, all of the costs were obtained from Economic Evaluation of CO_2 Storage and Sink Enhancement Options [10]. These costs include all of the costs associated with determining, developing, and maintaining a CO_2 storage location, including site evaluation, well drilling, and the capital equipment required for distributing and injecting CO_2.

Pore Volume Acquisition costs are the costs associated with acquiring rights to use the sub-surface volume where the CO_2 will be stored, i.e., the pore space in the geologic formation. These costs were based on research by Carnegie Mellon University, which examined existing sub-surface rights acquisition as it pertains to natural gas storage [14]. The regulatory uncertainty in this area combined with unknowns regarding the number and type (private or government) of property owners, require a number of “best engineering judgment” decisions to be made. In this study it was assumed that long-term lease rights were acquired from the property owners in the projected CO_2 plume growth region for a nominal fee, and that an annual “rent” was paid when the plume reached each individual acre of their property for a period of up to 100 years from the injection start date. The present value of the life cycle pore volume costs are assessed at a 10 percent discount rate and a capital fund is set up to pay for these costs over the 100 year rent scenario.

Liability Protection

Liability Protection addresses the fact that if damages are caused by injection and long-term storage of CO_2, the injecting party may bear financial liability. Several types of liability protection schemes have been suggested for CO_2 storage, including Bonding, Insurance, and Federal Compensation Systems combined with either tort law (as with the Trans-Alaska Pipeline Fund), or with damage caps and pre-emption, as is used for nuclear energy under the Price Anderson Act [15]. However, at present, a specific liability regime has yet to be dictated either at a Federal or (to our knowledge) State level. However, certain state governments have enacted legislation, which assigns liability to the injecting party, either in perpetuity (Wyoming) or until ten years after the cessation of injection operations, pending reservoir integrity certification, at which time liability is turned over to the state (North Dakota and Louisiana) [16,17,18]. In the case of Louisiana, a trust fund totaling five million dollars is established over the first ten years (120 months) of injection operations for each injector. This fund is then used by the state for CO_2 monitoring and, in the event of an at-fault incident, damage payments.

Liability costs assume that a bond must be purchased before injection operations are permitted in order to establish the ability and good will of an injector to address damages where they are deemed liable. A figure of five million dollars was used for the bond based on the Louisiana fund level. This bond level may be conservatively high, in that the Louisiana fund covers both liability and monitoring, but that fund also pertains to a certified reservoir where injection operations have ceased, having a reduced risk compared to active operations.

Monitoring Costs

Monitoring costs were evaluated based on the methodology set forth in the International Energy Agency (IEA) Greenhouse Gas R&D Programme's Overview of Monitoring Projects for Geologic Storage Projects report [19]. In this scenario, operational monitoring of the CO_2 plume occurs over 30 years (during plant operation) and closure monitoring occurs for the following fifty years (for a total of eighty years). Monitoring is via electromagnetic survey, gravity survey, and periodic seismic survey; electromagnetic and gravity surveys are ongoing while seismic survey occurs in years 1, 2, 5, 10, 15, 20, 25, and 30 during the operational period, then in years 40, 50, 60, 70, and 80 after injection ceases.

3.3.4 Finance Structure

The global economic assumptions are listed in Exhibit 12.

Finance structures were chosen based on the assumed type of developer/owner (IOU or independent power producer) and the assumed risk profile of the plant being assessed (low-risk or high-risk). For this study the owner/developer was assumed to be an IOU. All cases with CO_2 capture were considered high risk. The non-capture PC case was considered low risk. Exhibit 13 describes the low-risk IOU and high-risk IOU finance structures that were assumed for this study. These finance structures were recommended in a 2008 NETL report based on interviews with project developers/owners, financial organizations and law firms [20].

Exhibit 12 Global Economic Assumptions

Parameter	**Value**
TAXES	
Income Tax Rate	38% (Effective 34% Federal, 4% 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 internal rate of return on equity)	35 Years (capital expenditure period plus operational period)
TREATMENT OF CAPITAL COSTS	
Capital Cost Escalation During Capital Expenditure Period (nominal annual rate)	3.6%[a]
Distribution of Total Overnight Capital over the Capital Expenditure Period (before escalation)	5-Year Period: 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 if a substantial amount of TOC is actually non-depreciable)*
ESCALATION OF OPERATING REVENUES AND COSTS	
Escalation of COE (revenue), O&M Costs, and Fuel Costs (nominal annual rate)	3.0%[b]

Notes

a – A nominal average annual rate of 3.6 percent is assumed for escalation of capital costs during construction as per NETL report [1]. 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.

b – An average annual inflation rate of 3.0 percent is assumed. This rate is equivalent to the average annual escalation rate between 1947 and 2008 for the U.S. Department of Labor's Producer Price Index for Finished Goods [27], the so-called "headline" index of the various Producer Price Indices. (The Producer Price Index for the Electric Power Generation Industry may be more applicable, but that data does not provide a long-term historical perspective since it only dates back to December 2003.)

Exhibit 13 Financial Structure for Investor Owned Utility High and Low Risk Projects

Type of Security	% of Total	Current (Nominal) Dollar Cost	Weighted Current (Nominal) Cost	After Tax Weighted Cost of Capital
Low Risk				
Debt	50	4.5%	2.25%	
Equity	50	12%	6%	
Total			8.25%	7.39%
High Risk				
Debt	45	5.5%	2.475%	
Equity	55	12%	6.6%	
Total			9.075%	8.13%

Discounted Cash Flow Analysis and Cost of Electricity

The COE is the revenue received by the generator per net megawatt-hour during the power plant's first year of operation, assuming that the COE escalates thereafter at a nominal annual rate equal to the general inflation rate, i.e., that it remains constant in real terms over the operational period of the power plant. To calculate the COE, a "base-year" (2007) COE is determined that, when escalated at an assumed nominal annual general inflation rate of 3 percent, provided the stipulated internal rate of return on equity over the entire economic analysis period (capital expenditure period plus thirty years of operation).

Estimating COE with Capital Charge Factors

The global economic assumptions listed in Exhibit 12 were adhered to and one of the finance structures listed in Exhibit 13 was utilized in this study. This allowed for the following simplified equation to be used to estimate COE as a function of TOC, fixed O&M costs, variable O&M costs (including fuel), capacity factor and net output. For the cases in which PCC plant is included the equation requires the application of a CCF of 0.124 which represents a CCF for a high risk IOU finance structure with a capital expenditure period of five years. NETL Case 9 [1] utilizes a CCF of 0.1165 representing a CCF for a low risk IOU finance structure with a capital expenditure period of five years.

All factors in the COE equation are expressed in base-year dollars. The base year is the first year of capital expenditure, which for this study is assumed to be 2007. As shown in Exhibit 12, all factors (COE, O&M and fuel) are assumed to escalate at a nominal annual general inflation rate of 3.0 percent. Accordingly, all first-year costs (COE and O&M) are equivalent to base-year costs when expressed in base-year (2007) dollars where:

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

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

COE = revenue received by the generator ($/MWh, equivalent to mills/kWh) during the power plant's first year of operation (*but expressed in base-year dollars*), assuming that the COE escalates thereafter at a nominal annual rate equal to the general inflation rate, i.e., that it remains constant in real terms over the operational period of the power plant.

CCF = capital charge factor taken as 0.124 that matches the applicable finance structure and capital expenditure period

TOC = total overnight capital, 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 annual operating costs, including fuel at 100 percent capacity factor, *expressed in base-year dollars*

CF = plant capacity factor, assumed to be constant over the operational period

MWH = annual net megawatt-hours of power generated at 100 percent capacity factor

Levelized Cost of Electricity

The LCOE is the revenue received by the generator per net megawatt-hour during the power plant's first year of operation, assuming that the COE escalates thereafter at a nominal annual rate of 0 percent, i.e., that it remains constant in nominal terms over the operational period of the power plant. This study reports LCOE on a current-dollar basis over thirty years. "Current dollar" refers to the fact that levelization is done on a nominal, rather than a real, basis. "Thirty-years" refers to the length of the operational period assumed for the economic analysis. To calculate the LCOE, the PSFM was used to calculate a base-year COE that, when escalated at a nominal annual rate of 0 percent, provided the stipulated return on equity over the entire economic analysis period.

The capital expenditure period is assumed to start in 2007 for all cases in this report. All capital costs included in this analysis, including project development and construction costs, are assumed to be incurred during the capital expenditure period of five years, this means that the analysis assumes that the plant begins operating in 2012. By following the economic assumptions described above LCOE is calculated by multiplying the COE by 1.268.

Cost of CO_2 Capture and CO_2 Avoided

The cost of CO_2 capture ($/tonne) was calculated as illustrated in the equation below as per NETL guidance [21]. The COE utilized in the calculation of cost of CO_2 captured includes compression, but does not include the increment of plant COE attributable to TS&M costs.

$$Cost\ of\ CO_2\ Captured = \frac{(COE_{\mathbf{With\ CC}} - COE_{\mathbf{Without\ CC}})}{CO_2\ Captured}$$

In addition to the cost of CO_2 captured the first year cost of CO_2 avoided was calculated using the equation from [1] as follows:

$$Avoided\ Cost = \frac{\{COE_{with\ removal} - COE_{reference}\}\ \$/MWh}{\{CO_2\ Emissions_{reference} - CO_2\ Emissions_{with\ removal}\}\ tons/MWh}$$

The avoided cost was calculated using an analogous non-capture case as a reference (NETL Case 9). The COE utilized in the calculation of avoided cost is the full plant COE, including the TS&M COE increment.

4 Case DB1 Evaluation

Case DB1 considers enzyme-activated reaction kinetics with a stripper pressure of 6 psia and LP steam (73.5 psia, 570°F) utilized for reboiler duty. The bulk stripper temperature is 70°C.

Case DB1 has been covered in detail because, although it does not give the best cost and performance in terms of COE, of all the cases considered, it is believed to be the best case in terms of practicality with current available technology presenting the minimum amount of performance risk.

For all other cases only the cost performance is detailed, since the equipment is broadly the same as for Case DB1; however for Case DB2 with a deeper vacuum, extra strengthening for fabrication of the vacuum stripper and related components has been considered, with sensitivities applied to steam conditions and kinetics.

4.1 Performance Results

A block flow diagram and stream tables for Case DB1 are shown in Exhibit 14 and Exhibit 15 respectively. In addition, Exhibit 1 shows a simplified process flow diagram of the PCC plant. The Case DB1 plant description and modeling assumptions were presented previously in Section 2.

The plant produces a net output of 550 MWe at a net plant efficiency of 30.2 percent (HHV basis). Overall plant performance is summarized in Exhibit 16, which includes auxiliary power requirements. The PCC plant, including CO_2 compression, accounts for 65 percent of the auxiliary plant load. The cooling water system accounts for over 12 percent of the auxiliary load, largely due to the high cooling water demand of the PCC plant.

Exhibit 14 Case DB1 Block Flow Diagram, Subcritical Unit with CO_2 Capture

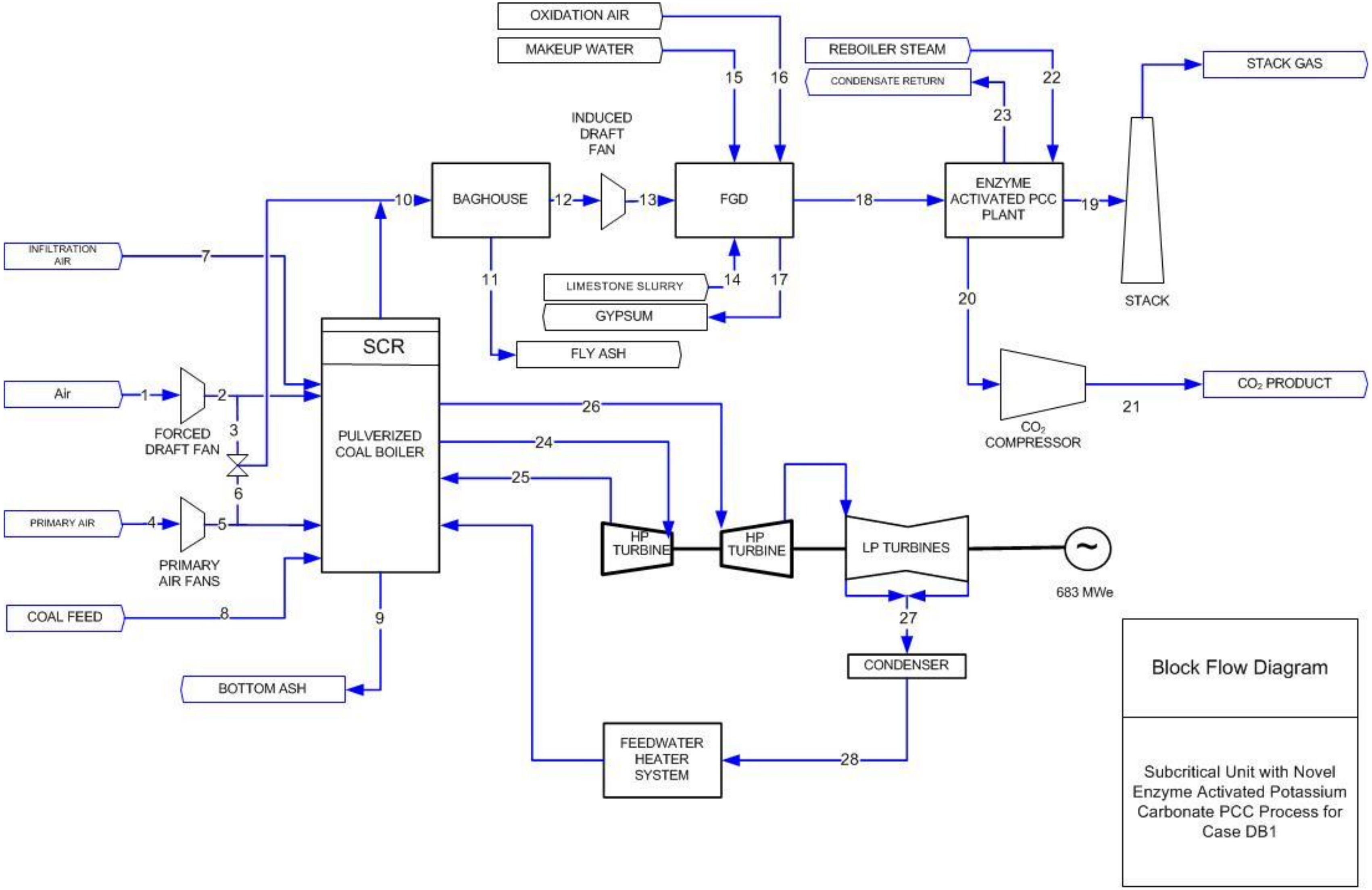


Exhibit 15 Case DB1 Stream Table, Subcritical Unit with CO_2 Capture

Stream Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14
V-L Mole Fraction														
Ar	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0092	0.0000	0.0000	0.0087	0.0000	0.0087	0.0087	0.0000
CO_2	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0000	0.0000	0.1450	0.0000	0.1450	0.1450	0.0000
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.0099	0.0099	0.0099	0.0099	0.0099	0.0099	0.0099	0.0000	0.0000	0.0870	0.0000	0.0870	0.0870	1.0000
N_2	0.7732	0.7732	0.7732	0.7732	0.7732	0.7732	0.7732	0.0000	0.0000	0.7324	0.0000	0.7324	0.7324	0.0000
O_2	0.2074	0.2074	0.2074	0.2074	0.2074	0.2074	0.2074	0.0000	0.0000	0.0247	0.0000	0.0247	0.0247	0.0000
SO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0021	0.0000	0.0021	0.0021	0.0000
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	0.0000	0.0000	1.0000	0.0000	1.0000	1.0000	1.0000
V-L Flowrate (kg_{mol}/hr)	62,871	62,871	1,877	19,313	19,313	2,658	1,453	0	0	88,494	0	88,494	88,494	3,169
V-L Flowrate (kg/hr)	1,814,254	1,814,254	54,167	557,320	557,320	76,715	41,932	0	0	2,632,092	0	2,632,092	2,632,092	57,099
Solids Flowrate(kg/hr)	0	0	0	0	0	0	0	242,093	4,706	18,825	18,825	0	0	24,709
Temperature (°C)	15.00	19.00	19.00	15.00	25.00	25.00	15.00	15.00	15.00	169.00	15.00	169.00	182.00	15.00
Pressure (MPa, abs)	0.10	0.11	0.11	0.10	0.11	0.11	0.10	0.10	0.10	0.10	0.10	0.10	0.11	10.00
Enthalpy (kJ/kg)^A	30.23	34.36	34.36	30.23	40.78	40.78	30.23	-	-	327.39	-	308.96	322.83	-
Density (kg/m^3)	1.20	1.20	1.20	1.20	1.30	1.30	1.20	-	-	0.80	-	0.80	0.80	-
V-L Molecular Weight	28.86	28.86	28.86	28.86	28.86	28.86	28.86	-	-	29.74	-	29.74	29.74	-
V-L Flowrate (lb_{mol}/hr)	138,606	138,606	4,138	42,578	42,578	5,860	3,203	0	0	195,095	0	195,095	195,095	6,987
V-L Flowrate (lb/hr)	3,999,741	3,999,741	119,418	1,228,679	1,228,679	169,127	92,444	0	0	5,802,763	0	5,802,763	5,802,763	125,881
Solids Flowrate(lb/hr)	0	0	0	0	0	0	0	533,723	10,376	41,503	41,503	0	0	54,473
Temperature (°F)	59.00	66.00	66.00	59.00	78.00	78.00	59.00	59.00	59.00	337.00	59.00	337.00	360.00	59.00
Pressure (psia)	14.70	15.30	15.30	14.70	16.10	16.10	14.70	14.70	14.70	14.40	14.70	14.20	15.40	15.00
Enthalpy (BTU/lb)^A	13.00	14.80	14.80	13.00	17.50	17.50	13.00	-	-	140.80	-	132.80	138.80	-
Density (lb/ft^3)	0.08	0.08	0.08	0.08	0.08	0.08	0.08	-	-	0.05	-	0.05	0.05	-

A - Reference conditions are 32.02°F & 0.089 psia

Exhibit 15 Case DB1 Stream Table, Subcritical Unit with CO_2 Capture (Continued)

Stream Number	15	16	17	18	19	20	21	22	23	24	25	26	27	28
V-L Mole Fraction														
Ar	0.0000	0.0128	0.0000	0.0081	0.0105	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO_2	0.0000	0.0005	0.0004	0.1350	0.0175	0.9650	0.9985	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	1.0000	0.0062	0.9996	0.1537	0.0640	0.0347	0.0015	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
N_2	0.0000	0.7506	0.0000	0.6794	0.8773	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O_2	0.0000	0.2300	0.0000	0.0238	0.0307	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
V-L Flowrate (kg_{mol}/hr)	13,259	913	234	96,640	74,214	12,176	11,767	34,013	34,013	129,590	120,519	120,519	108,362	108,988
V-L Flowrate (kg/hr)	238,854	26,499	4,215	2,785,915	2,090,733	534,656	517,411	612,742	612,742	2,334,606	2,171,183	2,171,183	1,952,160	1,963,460
Solids Flowrate(kg/hr)	0	0	38,108	0	0	0	0	0	0	0	0	0	0	0
Temperature (°C)	15.00	181.00	58.00	57.22	40.22	32.22	35.00	298.92	151.82	565.56	365.87	565.56	38.73	37.42
Pressure (MPa, abs)	0.10	0.31	0.10	0.10	0.10	0.14	15.27	0.51	0.51	16.65	4.28	3.93	0.01	1.14
Enthalpy (kJ/kg)	-46.80[A]	191.62[A]	-	58.42[B]	40.97[B]	32.74[B]	211.71[A]	3,061.01[B]	640.04[B]	3,474.84[B]	3,124.78[B]	3,595.00[B]	2,409.82[B]	157.54[B]
Density (kg/m^3)	1,003.10	2.40	-	1.10	1.11	2.42	795.90	1.94	915.36	47.66	15.66	10.39	0.05	993.63
V-L Molecular Weight	18.01	29.04	-	28.83	28.17	43.91	43.97	18.02	18.02	18.02	18.02	18.02	18.02	18.02
V-L Flowrate (lb_{mol}/hr)	29,231	2,012	516	213,054	163,613	26,844	25,943	74,985	74,985	285,697	265,700	265,700	238,896	240,278
V-L Flowrate (lb/hr)	526,582	58,420	9,292	6,141,885	4,609,272	1,178,713	1,140,695	1,350,862	1,350,862	5,146,918	4,786,634	4,786,634	4,303,772	4,328,684
Solids Flowrate(lb/hr)	0	0	84,014	0	0	0	0	0	0	0	0	0	0	0
Temperature (°F)	59.00	357.00	136.00	135.00	104.39	90.00	95.00	570.05	305.27	1,050.00	690.57	1,050.00	101.71	99.35
Pressure (psia)	14.70	45.00	14.90	15.20	15.00	20.50	2,214.50	73.50	73.50	2,414.70	620.70	570.70	1.00	165.00
Enthalpy (BTU/lb)	-20.10[A]	82.40[A]	-	25.11[B]	17.61[B]	14.08[B]	91.00[A]	1,316.00[B]	275.17[B]	1,493.92[B]	1,343.41[B]	1,545.57[B]	1,036.04[B]	67.73[B]
Density (lb/ft^3)	62.62	0.15	-	0.07	0.07	0.15	49.68	0.12	57.14	2.98	0.98	0.65	0.00	62.03

A - Reference conditions are 32.02°F & 0.089 psia

B - Reference conditions as per stream operating conditions

Exhibit 16 Case DB1 Plant Performance Summary

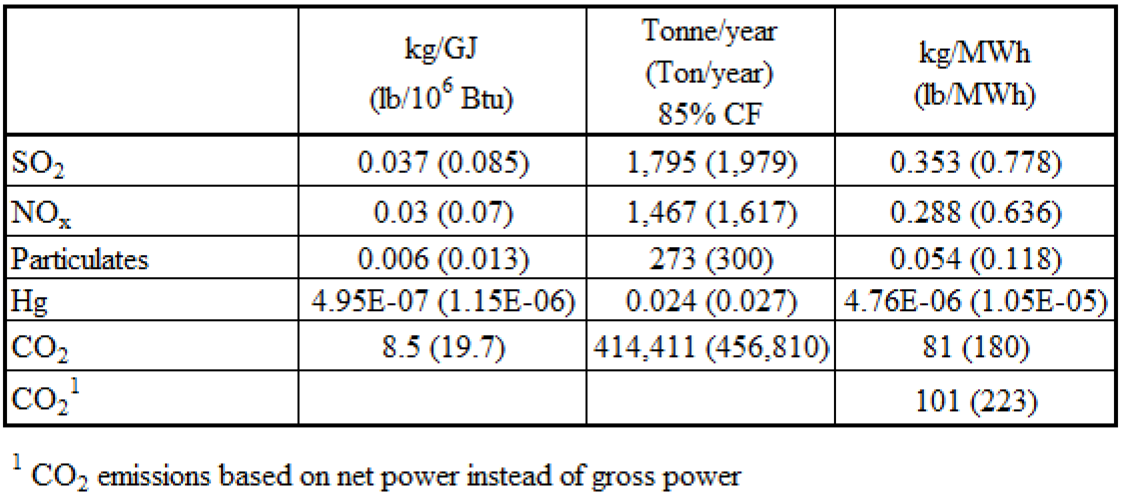
POWER SUMMARY (Gross Power at Generator Terminals, kWe)	
Steam Turbine Power	682,814
TOTAL (STEAM TURBINE) POWER, kWe	682,814
AUXILIARY LOAD SUMMARY, kWe	
Coal Handling and Conveying	471
Pulverizers	3,642
Sorbent Handling & Reagent Preparation	1,194
Ash Handling	697
Primary Air Fans	1,708
Forced Draft Fans	2,178
Induced Draft Fans	10,526
SCR	61
Baghouse	87
Wet FGD	3,895
Enzyme Activated PCC Plant Plus Auxiliaries	43,930
CO_2 Compression	42,512
Miscellaneous Balance of Plant[2,3]	1,867
Steam Turbine Auxiliaries	373
Condensate Pumps	653
Circulating Water Pumps	10,444
Ground Water Pumps	952
Cooling Tower Fans	5,432
Transformer Losses	2,193
TOTAL AUXILIARIES, kWe	**132,814**
NET POWER, kWe	**550,000**
Net Plant Efficiency (HHV)	30.2%
Net Plant Heat Rate, kJ/kWh (Btu/kWh)	11,934 (11,312)
CONDENSER COOLING DUTY 10^6 kJ/hr (10^6 Btu/hr)	2,475 (2,346)
CONSUMABLES	
As-Received Coal Feed, kg/hr (lb/hr)	242,093 (533,723)
Limestone Sorbent Feed, kg/hr (lb/hr)	24,709 (54,473)
Thermal Input, kWt[1]	1,823,296
Raw Water Withdrawal, m^3/min (gpm)	37 (9,783)
Raw Water Consumption, m^3/min (gpm)	28 (7,504)

1. HHV of As-Received Illinois No. 6 coal is 27,113 kJ/kg (11,666 Btu/lb)
2. Boiler feed pumps are turbine driven
3. Includes plant control systems, lighting, HVAC, and miscellaneous low voltage loads.

Environmental Performance

A summary of the plant air emissions for Case DB1 is presented in Exhibit 17.

Exhibit 17 Case DB1 Air Emissions



	kg/GJ (lb/10^6 Btu)	Tonne/year (Ton/year) 85% CF	kg/MWh (lb/MWh)
SO_2	0.037 (0.085)	1,795 (1,979)	0.353 (0.778)
NO_x	0.03 (0.07)	1,467 (1,617)	0.288 (0.636)
Particulates	0.006 (0.013)	273 (300)	0.054 (0.118)
Hg	4.95E-07 (1.15E-06)	0.024 (0.027)	4.76E-06 (1.05E-05)
CO_2	8.5 (19.7)	414,411 (456,810)	81 (180)
CO_2[1]			101 (223)

[1] CO_2 emissions based on net power instead of gross power

NO_x emissions are controlled to approximately 0.5 lb/10^6 Btu through the use of LNBs and OFA. An SCR unit then further reduces the NO_x concentration by 86 percent to 0.07 lb/10^6 Btu.

Particulate emissions are controlled using a pulse jet fabric filter, which operates at an efficiency of 99.8 percent.

SO_2 emissions are controlled using a wet limestone forced oxidation scrubber that achieves a removal efficiency of 98 percent. Unlike amine PCC the SO_2 does not have a degrading effect on the CA enzyme-activated K_2CO_3 solvent and as a result there is no requirement to further reduce emissions in the PCC plant. It is likely that much of the remaining SO_2 is removed in the PCC plant direct contact cooler and absorber vessel resulting in very low SO_2 air emissions but no credit has been taken for this.

Co-benefit mercury capture results in a 90 percent reduction of mercury emissions and 90 percent of the CO_2 in the flue gas is removed in the PCC Plant.

The carbon balance for the entire plant is shown in Exhibit 18. The carbon input to the plant consists of carbon in the coal in addition to carbon in the air and limestone for the FGD. Carbon in the air is not neglected here since the Aspen model accounts for air components throughout. Carbon leaves the plant as CO_2 in the stack gas, carbon in the FGD product, and the captured CO_2 product. The CO_2 capture efficiency is defined by the following fraction:

1-[(Stack Gas Carbon-Air Carbon)/(Total Carbon In-Air Carbon)]

or

[1-(34,753-674)/(346,450-674)*100] or 90.1 percent

Exhibit 18 Case DB1 Carbon Balance

Carbon In, kg/hr (lb/hr)		Carbon Out, kg/hr (lb/hr)	
Coal	154,334 (340,248)	**Stack Gas**	15,764 (34,753)
Air (CO_2)	306 (674)	**FGD Product**	264 (582)
FGD Reagent	2,507 (5,527)	**CO_2 Product**	141,119 (311,116)
Total	157,147 (346,450)	**Total**	157,147 (346,450)

Exhibit 19 shows the sulfur balance for the plant. Sulfur input comes solely from the sulfur content in the coal. Sulfur output includes the sulfur recovered in the FGD as gypsum and sulfur emitted in the stack gas.

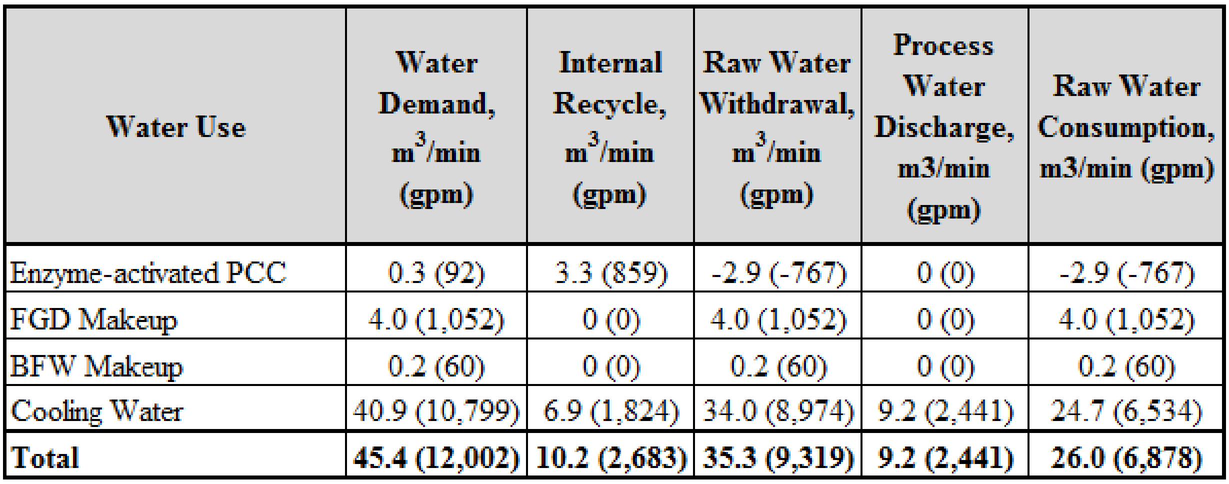
Exhibit 19 Case DB1 Sulfur Balance

Sulfur In, kg/hr (lb/hr)		Sulfur Out, kg/hr (lb/hr)	
Coal	6,077 (13,396)	**FGD Product**	5,955 (13,129)
		Stack Gas	122 (268)
Total	6,077 (13,396)	**Total**	6,077 (13,396)

Exhibit 20 shows the water balance for Case DB1. Water demand represents the total amount of water required for a particular process. The difference between demand and recycle is raw water withdrawal. Raw water withdrawal is defined as the water removed from the ground or diverted from a surface-water source for use in the plant and was assumed to be provided 50 percent by a plant operated treatment works and 50 percent from groundwater. Raw water withdrawal can be represented by the water metered from a raw water source and used in the plant processes for any and all purposes, such as FGD makeup, boiler feed water makeup, and cooling tower makeup. The difference between water withdrawal and process water discharge (water leaving the plant) is defined as water consumption and can be represented by the portion of the raw water withdrawn that is evaporated, transpired, incorporated into products or otherwise not returned to the water source from which it was withdrawn. Water consumption represents the net impact of the plant process on the water source.

As can be seen the CA enzyme-activated PCC plant is a net producer of water, that is, the water recovered through cooling the incoming flue gas is greater than the water requirements of the PCC plant and can be utilized to reduce PC boiler makeup requirements.

Exhibit 20 Case DB1 Water Balance



Water Use	Water Demand, m^3/min (gpm)	Internal Recycle, m^3/min (gpm)	Raw Water Withdrawal, m^3/min (gpm)	Process Water Discharge, m3/min (gpm)	Raw Water Consumption, m3/min (gpm)
Enzyme-activated PCC	0.3 (92)	3.3 (859)	-2.9 (-767)	0 (0)	-2.9 (-767)
FGD Makeup	4.0 (1,052)	0 (0)	4.0 (1,052)	0 (0)	4.0 (1,052)
BFW Makeup	0.2 (60)	0 (0)	0.2 (60)	0 (0)	0.2 (60)
Cooling Water	40.9 (10,799)	6.9 (1,824)	34.0 (8,974)	9.2 (2,441)	24.7 (6,534)
Total	**45.4 (12,002)**	**10.2 (2,683)**	**35.3 (9,319)**	**9.2 (2,441)**	**26.0 (6,878)**

Heat and Mass Balance Diagrams

A heat and mass balance diagram is shown for the Case DB1 PC Boiler, FGD, PCC Plant and steam cycle in Exhibit 21 and Exhibit 22 respectively. An overall plant energy balance is provided in Exhibit 23.

Exhibit 21 Case DB1 Heat and Mass Balance, Subcritical PC Boiler with Enzyme-activated CO_2 Capture

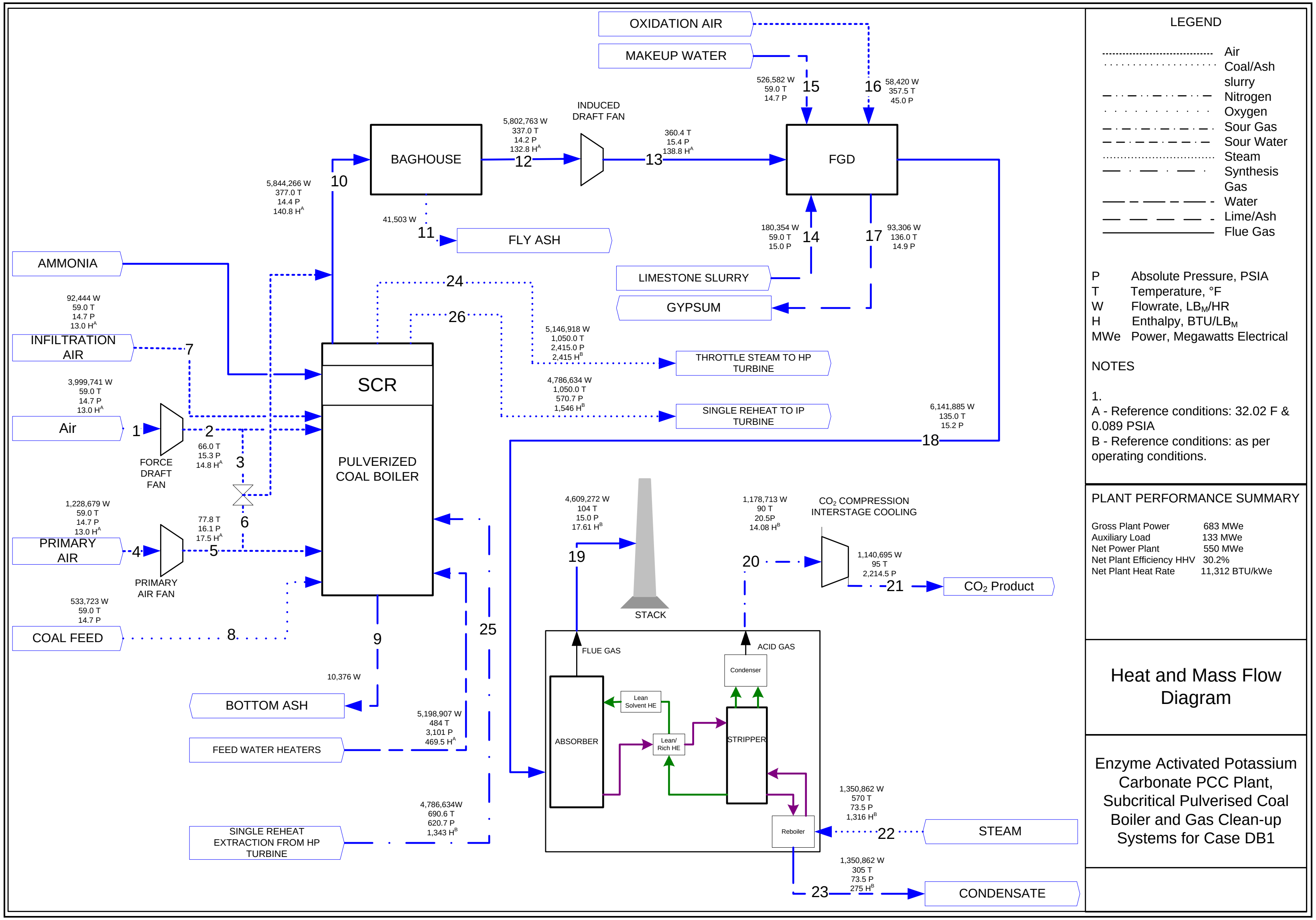


Exhibit 22 Case DB1 Heat and Mass Balance, Subcritical PC Boiler Steam Cycle

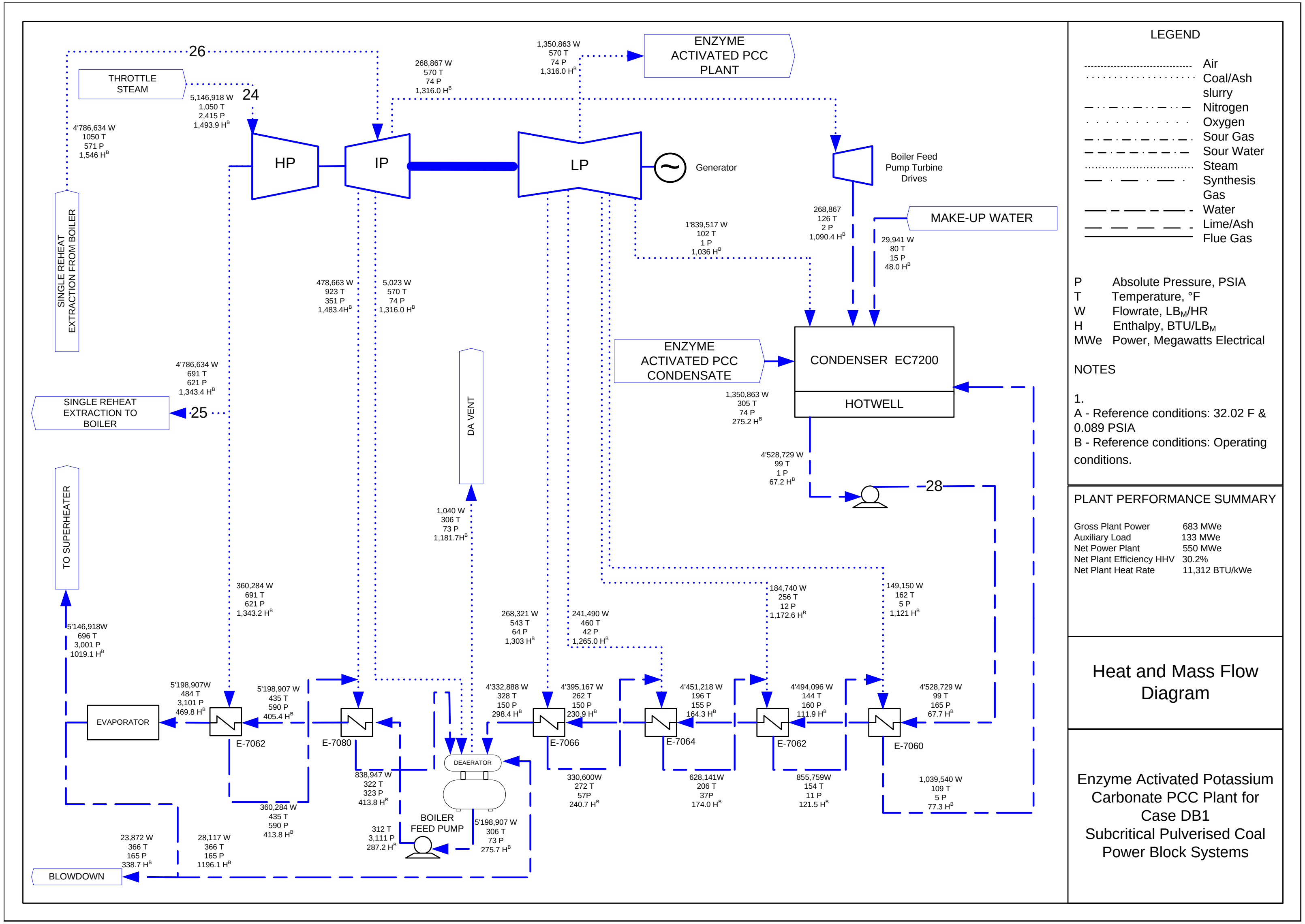


Exhibit 23 Case DB1 Overall Energy Balance (0°C [32°F] Reference)

	HHV	Sensible + Latent	Power	Total
Heat In GJ/hr (MMBtu/hr)				
Coal	6,564 (6,221)	5.7 (5.4)		6570 (6,227)
Air		61.1 (57.9)		61.1 (57.9)
Raw Water Makeup		153.7 (145.7)		153.7 (145.7)
Limestone		0.28 (0.26)		0.28 (0.26)
Auxiliary Power			478 (453)	478 (453)
Totals	**6,564 (6,221)**	**220.9 (209.4)**	**478 (453)**	**7263 (6,884)**
Heat Out GJ/hr (MMBtu/hr)				
Bottom Ash		0.6 (0.6)		0.6 (0.6)
Fly Ash + FGD Ash		2.3 (2.1)		2.3 (2.1)
Flue Gas		188 (178)		188 (178)
Condenser		2,475 (2,346)		2,475 (2,346)
CO_2		-109 (-104)		-109 (-104)
Cooling Tower Blowdown		63 (60)		63 (60)
Enzyme-Promoted Losses		2,142 (2,031)		2,142 (2,031)
Process Losses		43 (41)		43 (41)
Power			2,458 (2,330)	2,458 (2,330)
Totals	**0 (0)**	**4,805 (4,554)**	**2,458 (2,330)**	**7,263 (6,884)**

* Process losses are estimated to match the heat input to the plant. Process losses include losses from: turbines, gas cooling, etc.

4.2 Major Equipment List

Major equipment items for the subcritical PC plant with enzyme-activated K_2CO_3 solvent CO_2 capture are shown in the following tables. The accounts used in the equipment list correspond to the account numbers used in the cost estimates in Section 4.3. In general, the design conditions include a contingency for flows, heat duties and heads on pumps and fans.

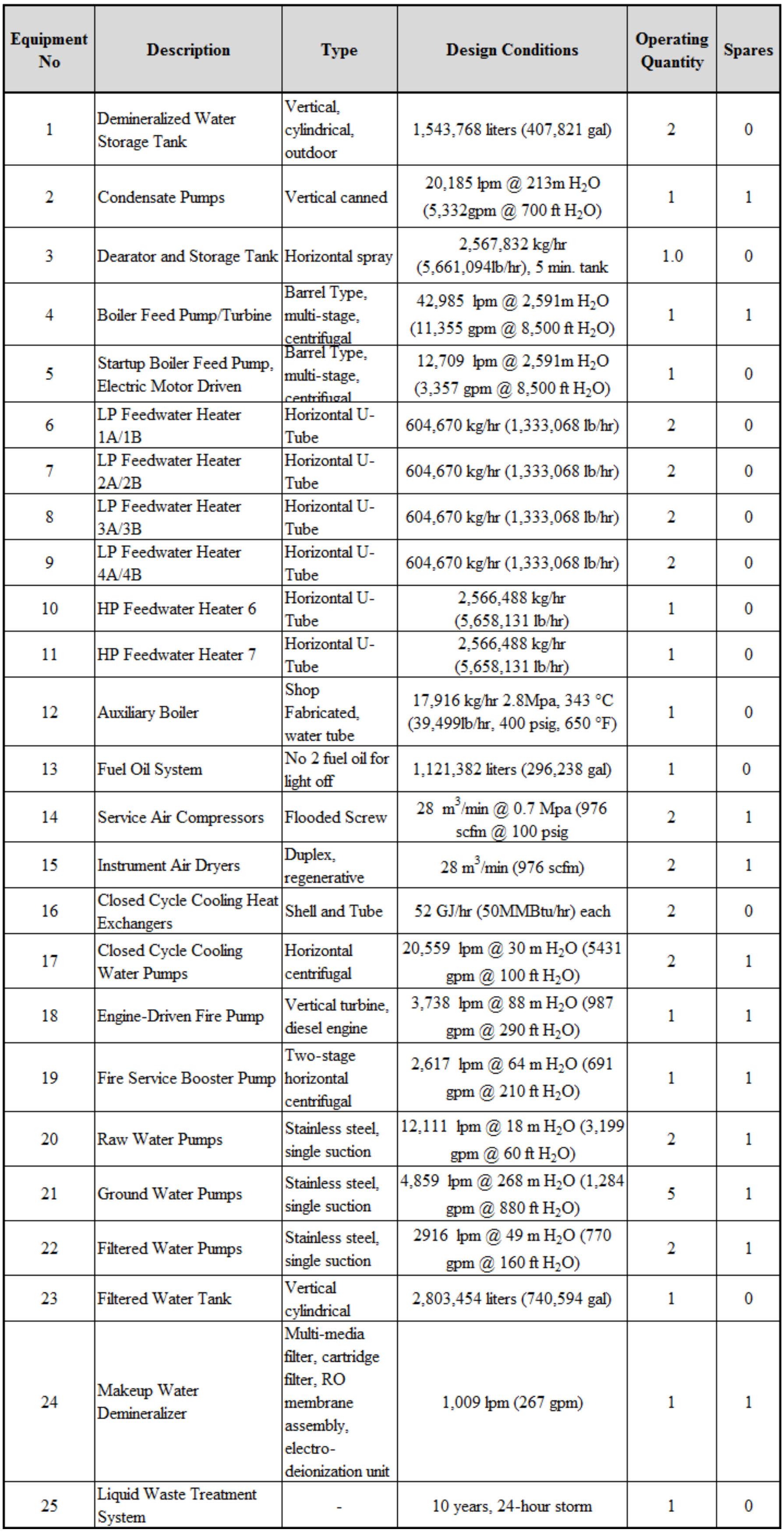
ACCOUNT 1 FUEL AND SORBENT HANDLING

Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Bottom Trestle Dumper and Receiving Hoppers	N/A	157 tonne (173ton)	2	0
2	Feeder	Belt	496 tonne/hr (547tph)	2	0
3	Conveyor No 1	Belt	984 tonne/hr (1085tph)	1	0
4	Transfer Tower No 1	Enclosed	N/A	1	0
5	Conveyor No 2	Belt	984 tonne/hr (1085tph)	1	0
6	As-Received Coal Sampling System	Two-stage	N/A	1	0
7	Stacker/Reclaimer	Traveling, linear	984 tonne/hr (1085tph)	1	0
8	Reclaim Hopper	N/A	47 tonne (52ton)	2	1
9	Feeder	Vibratory	197 tonne/hr (217tph)	2	1
10	Conveyor No 3	Belt w/tripper	402 tonne/hr (443tph)	1	0
11	Crusher Tower	N/A	N/A	1	0
12	Coal Surge Bin w/ Vent Filter	Dual outlet	197 tonne (217ton)	2	0
13	Crusher	Impactor Reduction	8 cm x 0 (3 in x 0) - 3 cm x0 (1-1/4 in x0)	2	0
14	As-Fired Coal Sampling System	Swing hammer	N/A	1	1
15	Conveyor No 4	Belt w/tripper	402 tonne/hr (443tph)	1	0
16	Transfer Tower No 2	Enclosed	N/A	1	0
17	Conveyor No 4	Belt w/tripper	402 tonne/hr (443tph)	1	0
18	Coal Silo w/ Vent Filter and Slide Gates	Field Erected	866 tonne/hr (955tph)	3	0
19	Limestone Truck Unloading Hopper	N/A	31 tonne/hr (34tph)	1	0
20	Limestone Feeder	Belt	102 tonne/hr (113tph)	1	0
21	Limestone Conveyor No L1	Belt	102 tonne/hr (113tph)	1	0
22	Limestone Reclaim Hopper	N/A	23 tonne/hr (26tph)	1	0
23	Limestone Reclaim Feeder	Belt	79 tonne/hr (87tph)	1	0
24	Limestone Conveyor No L2	Belt	79 tonne/hr (87tph)	1	0
25	Limestone Day Bin	w/ actuator	323 tonne/hr (356tph)	2	0

ACCOUNT 2 COAL AND SORBENT PREPARATION AND FEED

Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Coal Feeder	Gravimetric	47 tonne (52ton)	6	0
2	Coal Pulverizer	Ball Type or equivalent	47 tonne (52ton)	6	0
3	Limestone Weigh Feeder	Gravimetric	27 tonne/hr (30tph)	1	1
4	Limestone Ball Mill	Rotary	27 tonne/hr (30tph)	1	1
5	Limestone Mill Slurry Tank with Agitator	N/A	105,126 liters (27,771gal)	1	1
6	Limestone Mill Recycle Pumps	Horizontal centrifugal	1,741 lpm @ 12m H_2O (460gpm @ 40 ft H_2O)	1	1
7	Hydroclone Classifier	4 active cyclones in a 5 cyclone bank	427 lpm (113gpm) per cyclone	1	1
8	Distribution Box	2-way	N/A	1	1
9	Limestone Slurry Storage Tank with Agitator	Field Erected	584,762 liters (154,478gal)	1	1
10	Limestone Slurry Feed Pumps	Horizontal centrifugal	1,216 lpm @ 9m H_2O (321gpm @ 30 ft H_2O)	1	1

ACCOUNT 3 FEEDWATER AND MISCELLANEOUS SYSTEMS AND EQUIPMENT

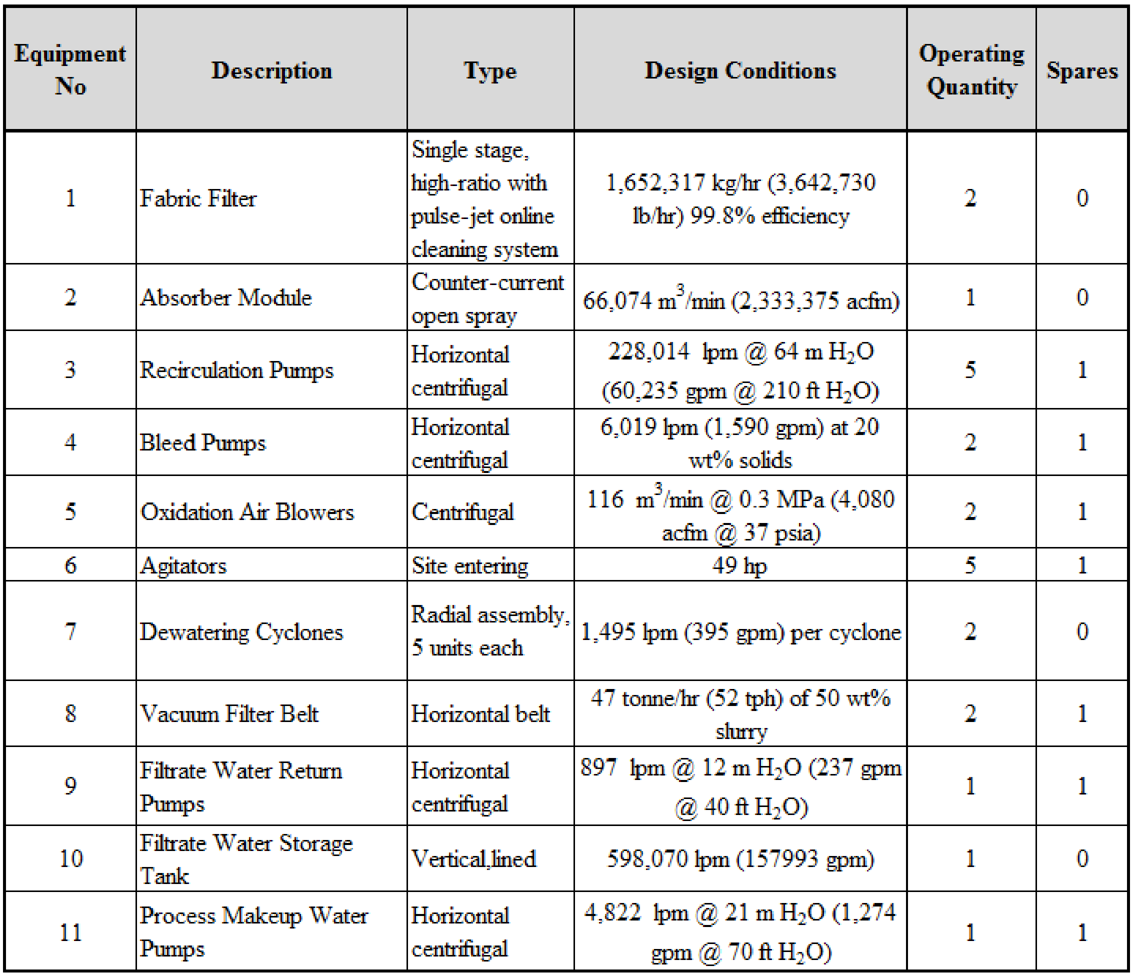


Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Demineralized Water Storage Tank	Vertical, cylindrical, outdoor	1,543,768 liters (407,821 gal)	2	0
2	Condensate Pumps	Vertical canned	20,185 lpm @ 213m H_2O (5,332gpm @ 700 ft H_2O)	1	1
3	Dearator and Storage Tank	Horizontal spray	2,567,832 kg/hr (5,661,094lb/hr), 5 min. tank	1.0	0
4	Boiler Feed Pump/Turbine	Barrel Type, multi-stage, centrifugal	42,985 lpm @ 2,591m H_2O (11,355 gpm @ 8,500 ft H_2O)	1	1
5	Startup Boiler Feed Pump, Electric Motor Driven	Barrel Type, multi-stage, centrifugal	12,709 lpm @ 2,591m H_2O (3,357 gpm @ 8,500 ft H_2O)	1	0
6	LP Feedwater Heater 1A/1B	Horizontal U-Tube	604,670 kg/hr (1,333,068 lb/hr)	2	0
7	LP Feedwater Heater 2A/2B	Horizontal U-Tube	604,670 kg/hr (1,333,068 lb/hr)	2	0
8	LP Feedwater Heater 3A/3B	Horizontal U-Tube	604,670 kg/hr (1,333,068 lb/hr)	2	0
9	LP Feedwater Heater 4A/4B	Horizontal U-Tube	604,670 kg/hr (1,333,068 lb/hr)	2	0
10	HP Feedwater Heater 6	Horizontal U-Tube	2,566,488 kg/hr (5,658,131 lb/hr)	1	0
11	HP Feedwater Heater 7	Horizontal U-Tube	2,566,488 kg/hr (5,658,131 lb/hr)	1	0
12	Auxiliary Boiler	Shop Fabricated, water tube	17,916 kg/hr 2.8Mpa, 343 °C (39,499lb/hr, 400 psig, 650 °F)	1	0
13	Fuel Oil System	No 2 fuel oil for light off	1,121,382 liters (296,238 gal)	1	0
14	Service Air Compressors	Flooded Screw	28 m^3/min @ 0.7 Mpa (976 scfm @ 100 psig	2	1
15	Instrument Air Dryers	Duplex, regenerative	28 m^3/min (976 scfm)	2	1
16	Closed Cycle Cooling Heat Exchangers	Shell and Tube	52 GJ/hr (50MMBtu/hr) each	2	0
17	Closed Cycle Cooling Water Pumps	Horizontal centrifugal	20,559 lpm @ 30 m H_2O (5431 gpm @ 100 ft H_2O)	2	1
18	Engine-Driven Fire Pump	Vertical turbine, diesel engine	3,738 lpm @ 88 m H_2O (987 gpm @ 290 ft H_2O)	1	1
19	Fire Service Booster Pump	Two-stage horizontal centrifugal	2,617 lpm @ 64 m H_2O (691 gpm @ 210 ft H_2O)	1	1
20	Raw Water Pumps	Stainless steel, single suction	12,111 lpm @ 18 m H_2O (3,199 gpm @ 60 ft H_2O)	2	1
21	Ground Water Pumps	Stainless steel, single suction	4,859 lpm @ 268 m H_2O (1,284 gpm @ 880 ft H_2O)	5	1
22	Filtered Water Pumps	Stainless steel, single suction	2916 lpm @ 49 m H_2O (770 gpm @ 160 ft H_2O)	2	1
23	Filtered Water Tank	Vertical cylindrical	2,803,454 liters (740,594 gal)	1	0
24	Makeup Water Demineralizer	Multi-media filter, cartridge filter, RO membrane assembly, electro-deionization unit	1,009 lpm (267 gpm)	1	1
25	Liquid Waste Treatment System	-	10 years, 24-hour storm	1	0

ACCOUNT 4 BOILER AND ACCESSORIES

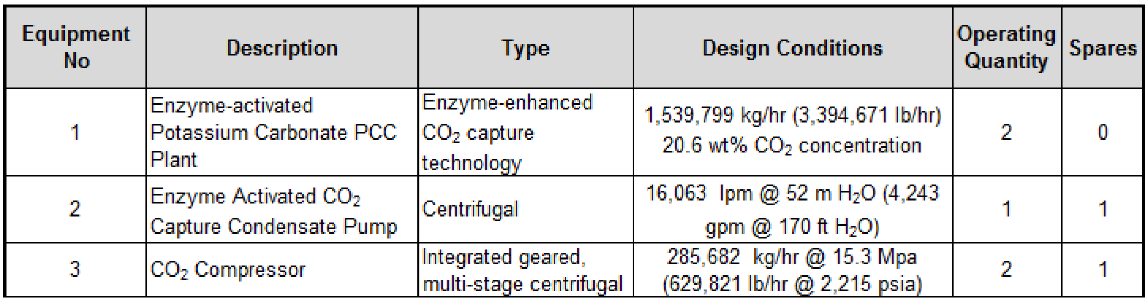
Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Boiler	Subcritical, drum wall-fired, low Nox burners, overfire air	2,566,519 kg/hr steam @17.9 Mpa/ 574 °C/574°C (5,658,199lb/hr steam @2,600 psig / 1,065 °F/1,065 °F)	1	0
2	Primary Air Fan	Centrifugal	349,856 kg/hr, 4,776 m^3/min @ 123 cm WG (771,300 lb/hr, 168,675 acfm @ 48 in. WG)	2	0
3	Forced Draft Fan	Centrifugal	1,139,019 kg/hr, 15,547 m^3/min @ 47 cm WG (2,511,104 lb/hr, 549,021 acfm @ 19 in. WG)	2	0
4	Induced Draft Fan	Centrifugal	1,652,317 kg/hr, 34,870 m^3/min @ 104 cm WG (3,642,730 lb/hr, 1,231,427 acfm @ 41 in. WG)	2	0
5	SCR Reactor Vessel	Space for spare layer	3,305,530 kg/hr (7,287,437 lb/hr)	2	0
6	SCR Catalyst	--	N/A	3	0
7	Dilution Air Blower	Centrifugal	197 m^3/min @ 108 cm WG (6,940 acfm @ 42 in. WG)	2	1
8	Ammonia Storage	Horizontal Tank	216,801 liter (57,273gal)	5	0
9	Ammonia Feed Pump	Centrifugal	41 lpm @ 91 m H_2O (11 gpm @ 300 ft H_2O)	1	1

ACCOUNT 5 FLUE GAS CLEAN UP



Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Fabric Filter	Single stage, high-ratio with pulse-jet online cleaning system	1,652,317 kg/hr (3,642,730 lb/hr) 99.8% efficiency	2	0
2	Absorber Module	Counter-current open spray	66,074 m^3/min (2,333,375 acfm)	1	0
3	Recirculation Pumps	Horizontal centrifugal	228,014 lpm @ 64 m H_2O (60,235 gpm @ 210 ft H_2O)	5	1
4	Bleed Pumps	Horizontal centrifugal	6,019 lpm (1,590 gpm) at 20 wt% solids	2	1
5	Oxidation Air Blowers	Centrifugal	116 m^3/min @ 0.3 MPa (4,080 acfm @ 37 psia)	2	1
6	Agitators	Site entering	49 hp	5	1
7	Dewatering Cyclones	Radial assembly, 5 units each	1,495 lpm (395 gpm) per cyclone	2	0
8	Vacuum Filter Belt	Horizontal belt	47 tonne/hr (52 tph) of 50 wt% slurry	2	1
9	Filtrate Water Return Pumps	Horizontal centrifugal	897 lpm @ 12 m H_2O (237 gpm @ 40 ft H_2O)	1	1
10	Filtrate Water Storage Tank	Vertical,lined	598,070 lpm (157993 gpm)	1	0
11	Process Makeup Water Pumps	Horizontal centrifugal	4,822 lpm @ 21 m H_2O (1,274 gpm @ 70 ft H_2O)	1	1

ACCOUNT 5B CARBON DIOXIDE RECOVERY



Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Enzyme-activated Potassium Carbonate PCC Plant	Enzyme-enhanced CO_2 capture technology	1,539,799 kg/hr (3,394,671 lb/hr) 20.6 wt% CO_2 concentration	2	0
2	Enzyme Activated CO_2 Capture Condensate Pump	Centrifugal	16,063 lpm @ 52 m H_2O (4,243 gpm @ 170 ft H_2O)	1	1
3	CO_2 Compressor	Integrated geared, multi-stage centrifugal	285,682 kg/hr @ 15.3 Mpa (629,821 lb/hr @ 2,215 psia)	2	1

ACCOUNT 6 COMBUSTION TURBINE/ACCESSORIES

N/A

ACCOUNT 7 HRSG, DUCTING & STACK

Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Stack	Reinforced concrete with FRP liner	150 m (492 ft) high x 5.7 m (19ft) diameter	1	0

ACCOUNT 8 STEAM TURBINE GENERATOR AND AUXILIARIES

Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Steam Turbine	Commercially available advanced steam turbine	699 MW 16.5 MPa/566°C/566 °C (2,400.3 psig/1050 °F/1050 °F	1	0
2	Steam Turbine Generator	Hydrogen cooled, static excitation	780 MVA @0.9 p.f., 24 kV, 60 Hz, 3-phase	1	0
3	Surface Condenser	Single pass, divided waterbox including vacuum pumps	2210 GJ/hr (2095 MMBtu/hr), inlet water temperature 16 °C (60°F), Water temperature rise 11°C (20°F)	1	0

ACCOUNT 9 COOLING WATER SYSTEM

Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Circulating Water Pumps	Vertical, wet pit	1,113,893 lpm @ 30 m H_2O (294,260 gpm @ 100 ft H_2O)	2	1
2	Cooling Tower	Evaporative, mechanical draft, multi cell	11°C (51.5 °F) wet bulb/16 °C (60 °F) CWT/27°C (80 °F) HWT /6,220GJ/hr (5,895 MMBtu/hr) heat duty	1	0

ACCOUNT 10 ASH/SPENT SORBENT RECOVERY AND HANDLING

Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	Economizer Hopper (part of boiler scope of supply	--	--	4	0
2	Bottom Ash Hopper (part of boiler scope of supply	--	--	2	0
3	Clinker Grinder	--	6 tonne/hr (7 tph)	1	1
4	Pyrites Hopper (part of pulverizer scope of supply included with boiler)	--	--	6	0
5	Hydroejectors	--	--	12	0
6	Economizer/ Pyrites Transfer Tank	--	--	1	0
7	Ash Sluice Pump	Vertical, wet pit	217 lpm @ 17 m H_2O (57 gpm @ 56 ft H_2O)	1	1
8	Ash Seal Water Pumps	Vertical, wet pit	7,228 lpm @ 9 m H_2O (1,909 gpm @ 28 ft H_2O)	1	1
9	Hydrobins	--	217 lpm (57 gpm)	1	1
10	Baghouse Hopper (part of baghouse scope of supply)	--	--	24	0
11	Air Heater Hopper (part of boiler scope of supply)	--	--	10	0
12	Air Blower	--	21 m^3/min @ 0.2 Mpa (742 scfm @ 24 psig	1	1
13	Fly Ash Silo	Reinforced concrete	1,270 tonne (1,400 ton)	2	0
14	Slide Gate Valves	--	--	2	0
15	Unloader	--	--	1	0
16	Telescoping Unloading Chute	--	130 tonne (143 ton)	1	0

ACCOUNT 11 ACCESSORY ELECTRIC PLANT

Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	STG Transformer	Oil-filled	24 kV/345 kV, 650 MVA, 3-ph, 60 Hz	1	0
2	Auxiliary Transformer	Oil-filled	24 kV/4.16 kV, 134 MVA, 3-ph, 60 Hz	1	1
3	Low Voltage Transformer	Dry ventilated	4.16 kV/ 480 V, 20 MVA, 3-ph, 60 Hz	1	1
4	STG Isolated Phase Bus Duct and Tap Bus	Aluminum, self-cooled	24 kV, 3-ph, 60 Hz	1	0
5	Medium Voltage Switchgear	Metal clad	4.16 kV, 3-ph, 60 Hz	1	1
6	Low Voltage Switchgeat	Metal enclosed	480V, 3-ph, 60 Hz	1	1
7	Emergency Diesel Generator	Sized for emergency shutdown	750 kW, 480 V, 3-ph, 60 Hz	1	0

ACCOUNT 12 INSTRUMENTATION AND CONTROL

Equipment No	Description	Type	Design Conditions	Operating Quantity	Spares
1	DCS - Main Control	Monitor keyboard; Operator printer (laser color); Engineering printer (laser B&W)	Operator stations/printers and engineering stations/printers	1	0
2	DCS - Processor	Microprocessor with redundant input/output	N/A	1	0
3	DCS - Data Highway	Fiber optic	Fully redundant, 25% spare	1	0

4.3 Case DB1 Cost Estimation

The cost estimating methodology has been described previously in Section 3.3. Exhibit 24 shows the total plant capital cost summary organized by cost account and Exhibit 25 shows a more detailed breakdown of the capital costs along with owner's costs, TOC, and TASC. Exhibit 26 shows the initial and annual O&M costs.

The estimated TOC of the subcritical PC boiler with Case DB1 CO_2 capture is $3,658/kW. Process contingency represents 3.3 percent of the TOC and project contingency represents 10.2 percent. The COE, including CO_2 TS&M costs of 5.9 mills/kWh, is 119.6 mills/kWh.

Exhibit 24 Case DB1 Total Plant Cost Summary (Cost base is 2007$ x 1000)

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
1	COAL & SORBENT HANDLING	$19,403	$5,210	$11,596	$0	$0	$36,209	$3,247	$0	$5,919	$45,375	$83
2	COAL & SORBENT PREP & FEED	$13,189	$771	$3,352	$0	$0	$17,312	$1,517	$0	$2,824	$21,653	$39
3	FEEDWATER & MISC. BOP SYSTEMS	$50,983	$0	$24,622	$0	$0	$75,605	$6,942	$0	$13,571	$96,118	$175
4	PC BOILER											
4.1	PC Boiler & Accessories	$170,716	$0	$109,786	$0	$0	$280,501	$27,327	$0	$30,782	$338,611	$616
4.2	SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4-4.9	Boiler BoP (w/ ID Fans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 4	**$170,716**	**$0**	**$109,786**	**$0**	**$0**	**$280,501**	**$27,327**	**$0**	**$30,782**	**$338,611**	**$616**
5	FLUE GAS CLEANUP	$92,617	$0	$31,909	$0	$0	$124,526	$11,920	$0	$13,644	$150,090	$273
5B	CO2 REMOVAL & COMPRESSION	$286,175	$0	$74,666	$0	$0	$360,840	$34,302	$65,189	$89,133	$549,464	$999
6	COMBUSTION TURBINE/ACCESSORIES											
6.1	Combustion Turbine Generator	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6.2-6.9	Combustion Turbine Other	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 6	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**
7	HRSG, DUCTING & STACK											
7.1	Heat Recovery Steam Generator N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7.2-7.9	HRSG Accessories, Ductwork and Stack	$19,036	$1,062	$12,906	$0	$0	$33,003	$3,026	$0	$4,724	$40,753	$74
	SUBTOTAL 7	**$19,036**	**$1,062**	**$12,906**	**$0**	**$0**	**$33,003**	**$3,026**	**$0**	**$4,724**	**$40,753**	**$74**
8	STEAM TURBINE GENERATOR											
8.1	Steam TG & Accessories	$55,754	$0	$6,973	$0	$0	$62,727	$6,010	$0	$6,873	$75,610	$137
8.2-8.9	Turbine Plant Auxiliaries and Steam Piping	$27,064	$1,225	$15,418	$0	$0	$43,707	$3,831	$0	$6,739	$54,278	$99
	SUBTOTAL 8	**$82,818**	**$1,225**	**$22,391**	**$0**	**$0**	**$106,434**	**$9,841**	**$0**	**$13,612**	**$129,887**	**$236**
9	COOLING WATER SYSTEM	$18,118	$8,900	$16,419	$0	$0	$43,437	$4,087	$0	$6,427	$53,952	$98
10	ASH/SPENT SORBENT HANDLING SYS	$5,115	$163	$6,839	$0	$0	$12,116	$1,165	$0	$1,366	$14,647	$27
11	ACCESSORY ELECTRIC PLANT	$26,353	$11,429	$32,325	$0	$0	$70,106	$6,206	$0	$9,603	$85,915	$156
12	INSTRUMENTATION & CONTROL	$10,044	$0	$10,186	$0	$0	$20,230	$1,834	$1,012	$2,835	$25,911	$47
13	IMPROVEMENTS TO SITE	$3,322	$1,910	$6,696	$0	$0	$11,928	$1,177	$0	$2,621	$15,727	$29
14	BUILDINGS & STRUCTURES	$0	$25,522	$24,189	$0	$0	$49,711	$4,485	$0	$8,130	$62,327	$113
	TOTAL COST	**$797,888**	**$56,191**	**$387,882**	**$0**	**$0**	**$1,241,960**	**$117,077**	**$66,201**	**$205,193**	**$1,630,431**	**$2,964**

Exhibit 25 Case DB1 Total Plant Cost Details

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
1	**COAL & SORBENT HANDLING**											
1.1	Coal Receive & Unload	$3,968	$0	$1,813	$0	$0	$5,781	$517	$0	$944	$7,242	$13
1.2	Coal Stackout & Reclaim	$5,129	$0	$1,162	$0	$0	$6,291	$550	$0	$1,026	$7,867	$14
1.3	Coal Conveyors	$4,769	$0	$1,149	$0	$0	$5,918	$518	$0	$965	$7,402	$13
1.4	Other Coal Handling	$1,247	$0	$266	$0	$0	$1,513	$132	$0	$247	$1,892	$3
1.5	Sorbent Receive & Unload	$163	$0	$49	$0	$0	$212	$18	$0	$35	$265	$0
1.6	Sorbent Stackout & Reclaim	$2,624	$0	$481	$0	$0	$3,105	$271	$0	$507	$3,883	$7
1.7	Sorbent Conveyors	$937	$202	$230	$0	$0	$1,368	$118	$0	$223	$1,710	$3
1.8	Other Sorbent Handling	$565	$133	$296	$0	$0	$994	$88	$0	$163	$1,245	$2
1.9	Coal & Sorbent Hnd.Foundations	$0	$4,875	$6,150	$0	$0	$11,025	$1,035	$0	$1,809	$13,869	$25
	SUBTOTAL 1.	**$19,403**	**$5,210**	**$11,596**	**$0**	**$0**	**$36,209**	**$3,247**	**$0**	**$5,919**	**$45,375**	**$83**
2	**COAL & SORBENT PREP & FEED**											
2.1	Coal Crushing & Drying	$2,298	$0	$448	$0	$0	$2,746	$240	$0	$448	$3,433	$6
2.2	Coal Conveyor to Storage	$5,882	$0	$1,284	$0	$0	$7,166	$627	$0	$1,168	$8,961	$16
2.3	Coal Injection System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.4	Misc.Coal Prep & Feed	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.5	Sorbent Prep Equipment	$4,470	$193	$928	$0	$0	$5,591	$487	$0	$912	$6,989	$13
2.6	Sorbent Storage & Feed	$539	$0	$206	$0	$0	$745	$66	$0	$121	$933	$2
2.7	Sorbent Injection System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.8	Booster Air Supply System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.9	Coal & Sorbent Feed Foundation	$0	$578	$485	$0	$0	$1,063	$99	$0	$174	$1,336	$2
	SUBTOTAL 2.	**$13,189**	**$771**	**$3,352**	**$0**	**$0**	**$17,312**	**$1,517**	**$0**	**$2,824**	**$21,653**	**$39**
3	**FEEDWATER & MISC. BOP SYSTEMS**											
3.1	FeedwaterSystem	$20,589	$0	$7,107	$0	$0	$27,696	$2,426	$0	$4,518	$34,641	$63
3.2	Water Makeup & Pretreating	$6,365	$0	$2,049	$0	$0	$8,413	$796	$0	$1,842	$11,051	$20
3.3	Other Feedwater Subsystems	$6,736	$0	$2,846	$0	$0	$9,582	$859	$0	$1,566	$12,007	$22
3.4	Service Water Systems	$1,248	$0	$679	$0	$0	$1,926	$182	$0	$422	$2,530	$5
3.5	Other Boiler Plant Systems	$8,066	$0	$7,964	$0	$0	$16,030	$1,523	$0	$2,633	$20,187	$37
3.6	FO Supply Sys & Nat Gas	$268	$0	$336	$0	$0	$604	$57	$0	$99	$761	$1
3.7	Waste Treatment Equipment	$4,859	$0	$2,770	$0	$0	$7,629	$742	$0	$1,674	$10,045	$18
3.8	Misc. Equip.(cranes,AirComp.,Comm.)	$2,852	$0	$872	$0	$0	$3,724	$358	$0	$817	$4,898	$9
	SUBTOTAL 3.	**$50,983**	**$0**	**$24,622**	**$0**	**$0**	**$75,605**	**$6,942**	**$0**	**$13,571**	**$96,118**	**$175**
4	**PC BOILER**											
4.1	PC Boiler & Accessories	$170,716	$0	$109,786	$0	$0	$280,501	$27,327	$0	$30,782	$338,611	$616
4.2	SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4	Boiler BoP (w/ ID Fans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.5	Primary Air System w/4.1	w/4.1	$0	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.6	Secondary Air System w/4.1	w/4.1	$0	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.8	Major Component Rigging	$0	w/4.1	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.9	Boiler Foundations	$0	w/14.1	w/14.1	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 4.	**$170,716**	**$0**	**$109,786**	**$0**	**$0**	**$280,501**	**$27,327**	**$0**	**$30,782**	**$338,611**	**$616**

Exhibit 25 Case DB1 Total Plant Cost Details (Continued)

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
5	**FLUE GAS CLEANUP**											
5.1	Absorber Vessels & Accessories	$63,311	$0	$13,629	$0	$0	$76,941	$7,335	$0	$8,427	$92,703	$169
5.2	Other FGD	$3,304	$0	$3,744	$0	$0	$7,048	$684	$0	$773	$8,504	$15
5.3	Bag House & Accessories	$19,248	$0	$12,216	$0	$0	$31,464	$3,032	$0	$3,450	$37,946	$69
5.4	Other Particulate Removal Materials	$1,303	$0	$1,394	$0	$0	$2,697	$261	$0	$296	$3,254	$6
5.5	Gypsum Dewatering System	$5,451	$0	$926	$0	$0	$6,377	$607	$0	$698	$7,682	$14
5.6	Mercury Removal System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
5.9	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 5.	**$92,617**	**$0**	**$31,909**	**$0**	**$0**	**$124,526**	**$11,920**	**$0**	**$13,644**	**$150,090**	**$273**
5B	**CO2 REMOVAL & COMPRESSION**											
5B.1	CO2 Removal System	$259,611	$0	$66,332	$0	$0	$325,943	$30,965	$65,189	$81,486	$503,583	$916
5B.2	CO2 Compression & Drying	$26,563	$0	$8,334	$0	$0	$34,897	$3,337	$0	$7,647	$45,881	$83
	SUBTOTAL 5B.	**$286,175**	**$0**	**$74,666**	**$0**	**$0**	**$360,840**	**$34,302**	**$65,189**	**$89,133**	**$549,464**	**$999**
6	**COMBUSTION TURBINE/ACCESSORIES**											
6.1	Combustion Turbine Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
6.2	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
6.3	Compressed Air Piping	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
6.9	Combustion Turbine Foundations	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 6.	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**
7	**HRSG, DUCTING & STACK**											
7.1	Heat Recovery Steam Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
7.2	HRSG Accessories	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
7.3	Ductwork	$9,783	$0	$6,285	$0	$0	$16,068	$1,401	$0	$2,620	$20,089	$37
7.4	Stack	$9,253	$0	$5,414	$0	$0	$14,668	$1,412	$0	$1,608	$17,689	$32
7.9	Duct & Stack Foundations	$0	$1,062	$1,206	$0	$0	$2,268	$213	$0	$496	$2,976	$5
	SUBTOTAL 7.	**$19,036**	**$1,062**	**$12,906**	**$0**	**$0**	**$33,003**	**$3,026**	**$0**	**$4,724**	**$40,753**	**$74**
8	**STEAM TURBINE GENERATOR**											
8.1	Steam TG & Accessories	$55,754	$0	$6,973	$0	$0	$62,727	$6,010	$0	$6,873	$75,610	$137
8.2	Turbine Plant Auxiliaries	$391	$0	$836	$0	$0	$1,227	$120	$0	$134	$1,481	$3
8.3	Condenser & Auxiliaries	$6,408	$0	$2,654	$0	$0	$9,062	$869	$0	$993	$10,925	$20
8.4	Steam Piping	$20,265	$0	$9,992	$0	$0	$30,257	$2,543	$0	$4,919	$37,719	$69
8.9	TG Foundations	$0	$1,225	$1,936	$0	$0	$3,161	$299	$0	$692	$4,152	$8
	SUBTOTAL 8.	**$82,818**	**$1,225**	**$22,391**	**$0**	**$0**	**$106,434**	**$9,841**	**$0**	**$13,612**	**$129,887**	**$236**
9	**COOLING WATER SYSTEM**											
9.1	Cooling Towers	$13,461	$0	$4,192	$0	$0	$17,653	$1,689	$0	$1,934	$21,275	$39
9.2	Circulating Water Pumps	$2,814	$0	$211	$0	$0	$3,025	$256	$0	$328	$3,609	$7
9.3	Circ.Water System Auxiliaries	$701	$0	$94	$0	$0	$794	$75	$0	$87	$956	$2
9.4	Circ.Water Piping	$0	$5,557	$5,386	$0	$0	$10,943	$1,024	$0	$1,795	$13,762	$25
9.5	Make-up Water System	$586	$0	$784	$0	$0	$1,370	$131	$0	$225	$1,726	$3
9.6	Component Cooling Water Sys	$555	$0	$442	$0	$0	$997	$94	$0	$164	$1,255	$2
9.9	Circ.Water System Foundations& Structures	$0	$3,343	$5,312	$0	$0	$8,655	$818	$0	$1,895	$11,368	$21
	SUBTOTAL 9.	**$18,118**	**$8,900**	**$16,419**	**$0**	**$0**	**$43,437**	**$4,087**	**$0**	**$6,427**	**$53,952**	**$98**

Exhibit 25 Case DB1 Total Plant Cost Details (Continued)

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
10	**SH/SPENT SORBENT HANDLING SYS**											
10.1	Ash Coolers	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.2	Cyclone Ash Letdown	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.3	HGCU Ash Letdown	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.4	High Temperature Ash Piping	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.5	Other Ash Recovery Equipment	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.6	Ash Storage Silos	$684	$0	$2,109	$0	$0	$2,793	$274	$0	$306	$3,373	$6
10.7	Ash Transport & Feed Equipment	$4,431	$0	$4,538	$0	$0	$8,969	$857	$0	$982	$10,808	$20
10.8	Misc. Ash Handling Equipment	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
10.9	Ash/Spent Sorbent Foundation	$0	$163	$192	$0	$0	$355	$33	$0	$78	$466	$1
	SUBTOTAL 10.	**$5,115**	**$163**	**$6,839**	**$0**	**$0**	**$12,116**	**$1,165**	**$0**	**$1,366**	**$14,647**	**$27**
11	**ACCESSORY ELECTRIC PLANT**											
11.1	Generator Equipment	$1,756	$0	$285	$0	$0	$2,041	$190	$0	$167	$2,398	$4
11.2	Station Service Equipment	$5,326	$0	$1,749	$0	$0	$7,075	$661	$0	$580	$8,316	$15
11.3	Switchgear & Motor Control	$6,122	$0	$1,041	$0	$0	$7,163	$664	$0	$783	$8,610	$16
11.4	Conduit & Cable Tray	$0	$3,838	$13,273	$0	$0	$17,111	$1,656	$0	$2,815	$21,582	$39
11.5	Wire & Cable	$0	$7,243	$13,982	$0	$0	$21,225	$1,789	$0	$3,452	$26,466	$48
11.6	Protective Equipment	$270	$0	$918	$0	$0	$1,188	$116	$0	$130	$1,434	$3
11.7	Standby Equipment	$1,379	$0	$31	$0	$0	$1,410	$129	$0	$154	$1,693	$3
11.8	Main Power Transformers	$11,500	$0	$191	$0	$0	$11,691	$886	$0	$1,258	$13,835	$25
11.9	Electrical Foundations	$0	$348	$854	$0	$0	$1,203	$115	$0	$264	$1,581	$3
	SUBTOTAL 11.	**$26,353**	**$11,429**	**$32,325**	**$0**	**$0**	**$70,106**	**$6,206**	**$0**	**$9,603**	**$85,915**	**$156**
12	**INSTRUMENTATION & CONTROL**											
12.1	PC Control Equipment	w/12.7	$0	w/12.7	$0	$0	$0	$0	$0	$0	$0	$0
12.2	Combustion Turbine Control	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
12.3	Steam Turbine Control	w/8.1	$0	w/8.1	$0	$0	$0	$0	$0	$0	$0	$0
12.4	Other Major Component Control	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
12.5	Signal Processing Equipment	W/12.7	$0	w/12.7	$0	$0	$0	$0	$0	$0	$0	$0
12.6	Control Boards,Panels & Racks	$517	$0	$310	$0	$0	$827	$78	$41	$142	$1,089	$2
12.7	Distributed Control System Equipment	$5,221	$0	$912	$0	$0	$6,134	$569	$307	$701	$7,711	$14
12.8	Instrument Wiring & Tubing	$2,831	$0	$5,615	$0	$0	$8,446	$719	$422	$1,438	$11,025	$20
12.9	Other I & C Equipment	$1,475	$0	$3,348	$0	$0	$4,823	$468	$241	$554	$6,086	$11
	SUBTOTAL 12.	**$10,044**	**$0**	**$10,186**	**$0**	**$0**	**$20,230**	**$1,834**	**$1,012**	**$2,835**	**$25,911**	**$47**

Exhibit 25 Case DB1 Total Plant Cost Details (Continued)

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
13	**IMPROVEMENTS TO SITE**											
13.1	Site Preparation	$0	$56	$1,117	$0	$0	$1,172	$116	$0	$258	$1,547	$3
13.2	Site Improvements	$0	$1,854	$2,303	$0	$0	$4,157	$410	$0	$913	$5,480	$10
13.3	Site Facilities	$3,322	$0	$3,277	$0	$0	$6,599	$651	$0	$1,450	$8,699	$16
	SUBTOTAL 13.	**$3,322**	**$1,910**	**$6,696**	**$0**	**$0**	**$11,928**	**$1,177**	**$0**	**$2,621**	**$15,727**	**$29**
14	**BUILDINGS & STRUCTURES**											
14.1	Boiler Building	$0	$9,131	$8,031	$0	$0	$17,162	$1,542	$0	$2,806	$21,510	$39
14.2	Turbine Building	$0	$13,368	$12,458	$0	$0	$25,826	$2,328	$0	$4,224	$32,378	$59
14.3	Administration Building	$0	$644	$682	$0	$0	$1,326	$121	$0	$217	$1,664	$3
14.4	Circulation Water Pumphouse	$0	$148	$118	$0	$0	$266	$24	$0	$44	$334	$1
14.5	Water Treatment Buildings	$0	$819	$747	$0	$0	$1,566	$141	$0	$255	$1,962	$4
14.6	Machine Shop	$0	$431	$289	$0	$0	$720	$64	$0	$118	$901	$2
14.7	Warehouse	$0	$292	$293	$0	$0	$585	$53	$0	$96	$734	$1
14.8	Other Buildings & Structures	$0	$238	$203	$0	$0	$442	$40	$0	$72	$553	$1
14.9	Waste Treating Building & Str.	$0	$451	$1,369	$0	$0	$1,819	$173	$0	$299	$2,292	$4
	SUBTOTAL 14.	**$0**	**$25,522**	**$24,189**	**$0**	**$0**	**$49,711**	**$4,485**	**$0**	**$8,130**	**$62,327**	**$113**
	TOTAL COST	**$797,888**	**$56,191**	**$387,882**	**$0**	**$0**	**$1,241,960**	**$117,077**	**$66,201**	**$205,193**	**$1,630,431**	**$2,964**

		$	$/kW
Owner's Costs			
Pre production costs			
6 months all labor		$10,547	$19
1 Month Maintenance Materials		$1,534	$3
1 Month Non fuel consumables		$1,789	$3
1 Month Waste disposal		$308	$1
25% of 1 months Fuels Cost at 100% CF		$1,861	$3
2% of TPC		$32,609	$59
Total		**$48,647**	**$88**
Inventory Capital			
60 days supply of fuel and consumables at 100% CF		$27,679	$50
0.5% of TPC (Spare Parts)		$8,152	$15
Total		**$35,831**	**$65**
Initial Fill Catalyst and Chemical cost		$7,306	$13
Land		$900	$2
Other Owner's costs		$244,565	$445
Financing costs		$44,022	$80
Total Overnight Costs (TOC)		**$2,011,701**	**$3,658**
TASC Multiplier	(High Risk, IOU Five years)	1.14	
Total as spent Cost (TASC)		**$2,293,339**	**$4,170**

Exhibit 26 Case DB1 Initial and Annual Operating and Maintenance Costs

OPERATING & MAINTENANCE LABOR						
Operating Labor						
Operating Labor Rate(base):	34.65 $/hour					
Operating Labor Burden:	30 % of base					
Labor O-H Charge Rate:	25 % of labor					
Total						
Skilled Operator 2.0 2.0	2	2				
Operator	11.3	11.3				
Foreman	1	1				
Lab Tech's, etc.	2	2				
TOTAL-O.J.'s	16.3	16.3				
					Annual Cost $	Annual Unit Cost $/kW-net
Annual Operating Labor Cost					$6,444,907	$11.718
Maintenance Labor Cost					$10,429,543	$18.963
Administrative & Support Labor					$4,218,612	$7.670
Property Taxes and Insurance					$32,608,619	$59.288
TOTAL FIXED OPERATING COSTS					**$53,701,681**	**$97.639**
VARIABLE OPERATING COSTS						
						$/kWh-net
Maintenance Material Cost					**$16,222,788**	**$0.00396**
Consumables	Consumption Initial	 /Day	Unit Cost	Initial Cost		
Water(/1000 gallons)	0	9845	1.08	$0	**$3,301,169**	**$0.00081**
Chemicals						
MU & WT Chem.(lb)	0	47660	0.17	$0	$2,515,449	$0.00061
Limestone (ton)	0	654	21.63	$0	$4,389,629	$0.00107
Carbon (Mercury Removal) (lb)	0	0	1.05	$0	$0	$0.00000
Solvent and antifoam (/1000 gallons)	1070	0	6648.20	$7,112,890	$0	$0.00000
Solvent make-up (kg)	0	2725.43	60.00	$0	$50,768,718	$0.01239
NaOH (tons)	69	6.87	433.68	$29,852	$925,624	$0.00023
H2SO4 (tons)	65	6.56	138.78	$9,069	$282,690	$0.00007
Corrosion Inhibitor	0	0	0.00	$154,511	$0	$0.00000
Activated Carbon(lb)	0	1649	1.05	$0	$537,401	$0.00013
Ammonia (28% NH3) ton	0	96	129.80	$0	$3,862,386	$0.00094
Subtotal Chemicals				**$7,306,322**	**$63,281,898**	**$0.01544**
Other						
Supplemental Fuel(MBtu)	0	0	0.00	$0	$0	$0.00000
SCR Catalyst(m3)	w/equip	0.40	5775.94	$0	$718,735	$0.00018
Emission Penalties	0	0	0.00	$0	$0	$0.00000
Subtotal Other				**$0**	**$718,735**	**$0.00018**
Waste Disposal						
Flyash (ton)	0	495	16.23	$0	$2,494,118	$0.00061
Bottom Ash(ton)	0	124	16.23	$0	$623,596	$0.00015
Subtotal-Waste Disposal				**$0**	**$3,117,714**	$0.00076
By-products & Emissions						
Gypsum (tons)	0	1120	0.00	$0	$0	$0.00000
Enzyme Waste (tons)	0	44	0.00	$0	$0	$0.00000
Subtotal By-Products				**$0**	**$0**	$0.00000
TOTAL VARIABLE OPERATING COSTS				**$7,306,322**	**$86,642,304**	$0.02114
Fuel(ton)	0	6405	38.18	**$0**	**$75,917,553**	**$0.02477**

Notes

1. Cost base is 2007 ($ x 1000)
2. Plant Net Output is 550 MWe
3. Plant Capacity Factor is 85%

4.4 Case DB1 Cost and Performance Summary

COE and LCOE

As described in section 3 the COE was calculated as follows:

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

$$COE = [(0.124)(2.01175x10^{9}) + 5.3702x10^{7} + (0.85)(1.9125x10^{8})] / [(0.85)(4.8180x10^{6})]$$

COE = 113.7 mills/kWh (excluding TS&M costs)

COE = 113.7 + 5.9 (including TS&M costs)

COE = 119.6 mills/kWh

LCOE = 151.7 mills/kWh

CO_2 Captured and CO_2 Avoided cost

As described in section 3 the cost of CO_2 captured was calculated as follows:

$$Cost\ of\ CO_2\ Captured = \frac{(COE_{With\ cc} - COE_{Without\ cc})}{CO_2\ Captured}$$

Cost of CO_2 captured = (113.7$/MWh – 59.4$/MWh) / (0.94 tonne/MWh x 0.85)

Cost of CO_2 captured = 68.0 $/tonne

As described in section 3 the cost of CO_2 avoided was calculated as follows:

$$Avoided\ Cost = \frac{\{COE_{with\ removal} - COE_{reference}\}\ \$/MWh}{\{CO_2\ Emissions_{reference} - CO_2\ Emissions_{with\ removal}\}\ tons/MWh}$$

Cost of CO_2 avoided = (119.6– 59.4) / (856.6 – 103.9)

Cost of CO_2 avoided = 80.0 $/ton

5 Case DB2 Evaluation

Case DB2 considers enzyme-activated reaction kinetics with a stripper pressure of 3 psia and LP steam (73.5 psia, 570°F) utilized for reboiler duty. The bulk stripper temperature is 53°C

5.1 Case DB2 Cost Estimation

The cost estimating methodology has been described previously in Section 3.3. Exhibit 27 shows the total plant capital cost summary organized by cost account and Exhibit 28 shows a more detailed breakdown of the capital costs along with owner's costs, TOC, and TASC. Exhibit 29 shows the initial and annual O&M costs.

The estimated TOC of the subcritical PC boiler with Case DB2 CO_2 capture is \$3,863/kW. Process contingency represents 3.4 percent of the TOC and project contingency represents 10.3 percent. The COE, including CO_2 TS&M costs of 5.9 mills/kWh, is 119.0 mills/kWh.

Exhibit 27 Case DB2 Total Plant Cost Summary (Cost base is 2007$ x 1000)

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
1	COAL & SORBENT HANDLING	$20,020	$5,714	$12,391	$0	$0	$38,125	$3,422	$0	$6,233	$47,780	$87
2	COAL & SORBENT PREP & FEED	$13,632	$796	$3,464	$0	$0	$17,892	$1,568	$0	$2,919	$22,379	$41
3	FEEDWATER & MISC. BOP SYSTEMS	$52,849	$0	$25,432	$0	$0	$78,281	$7,188	$0	$14,074	$99,544	$181
4	PC BOILER											
4.1	PC Boiler & Accessories	$175,448	$0	$112,829	$0	$0	$288,277	$28,085	$0	$31,636	$347,998	$633
4.2	SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4-4.9	Boiler BoP (w/ ID Fans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 4	**$175,448**	**$0**	**$112,829**	**$0**	**$0**	**$288,277**	**$28,085**	**$0**	**$31,636**	**$347,998**	**$633**
5	FLUE GAS CLEANUP	$100,840	$0	$34,418	$0	$0	$135,258	$12,946	$0	$14,820	$163,023	$296
5B	CO2 REMOVAL & COMPRESSION	$318,477	$0	$74,946	$0	$0	$393,423	$37,398	$71,470	$97,242	$599,534	$1,090
6	COMBUSTION TURBINE/ACCESSORIES											
6.1	Combustion Turbine Generator	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6.2-6.9	Combustion Turbine Other	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 6	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**
7	HRSG, DUCTING & STACK											
7.1	Heat Recovery Steam Generator N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7.2-7.9	HRSG Accessories, Ductwork and Stack	$19,192	$1,063	$13,007	$0	$0	$33,262	$3,049	$0	$4,765	$41,076	$75
	SUBTOTAL 7	**$19,192**	**$1,063**	**$13,007**	**$0**	**$0**	**$33,262**	**$3,049**	**$0**	**$4,765**	**$41,076**	**$75**
8	STEAM TURBINE GENERATOR											
8.1	Steam TG & Accessories	$57,482	$0	$7,189	$0	$0	$64,671	$6,196	$0	$7,086	$77,953	$142
8.2-8.9	Turbine Plant Auxiliaries and Steam Piping	$27,828	$1,264	$15,862	$0	$0	$44,953	$3,941	$0	$6,932	$55,825	$102
	SUBTOTAL 8	**$85,310**	**$1,264**	**$23,051**	**$0**	**$0**	**$109,624**	**$10,137**	**$0**	**$14,018**	**$133,779**	**$243**
9	COOLING WATER SYSTEM	$19,063	$9,616	$17,577	$0	$0	$46,255	$4,351	$0	$6,870	$57,475	$105
10	ASH/SPENT SORBENT HANDLING SYS	$5,259	$168	$7,032	$0	$0	$12,459	$1,198	$0	$1,405	$15,062	$27
11	ACCESSORY ELECTRIC PLANT	$27,853	$12,822	$36,106	$0	$0	$76,781	$6,811	$0	$10,571	$94,163	$171
12	INSTRUMENTATION & CONTROL	$10,408	$0	$10,554	$0	$0	$20,962	$1,900	$1,049	$2,937	$26,849	$49
13	IMPROVEMENTS TO SITE	$3,344	$1,922	$6,740	$0	$0	$12,006	$1,185	$0	$2,638	$15,829	$29
14	BUILDINGS & STRUCTURES	$0	$25,712	$24,373	$0	$0	$50,085	$4,519	$0	$8,191	$62,795	$114
	TOTAL COST	**$851,695**	**$59,076**	**$401,920**	**$0**	**$0**	**$1,312,690**	**$123,757**	**$72,519**	**$218,318**	**$1,727,285**	**$3,141**

Exhibit 28 Case DB2 Total Plant Cost Details

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
1	**COAL & SORBENT HANDLING**											
1.1	Coal Receive & Unload	$4,093	$0	$1,869	$0	$0	$5,962	$533	$0	$974	$7,469	$14
1.2	Coal Stackout & Reclaim	$5,290	$0	$1,199	$0	$0	$6,488	$568	$0	$1,058	$8,114	$15
1.3	Coal Conveyors	$4,918	$0	$1,185	$0	$0	$6,104	$535	$0	$996	$7,634	$14
1.4	Other Coal Handling	$1,287	$0	$274	$0	$0	$1,560	$136	$0	$255	$1,952	$4
1.5	Sorbent Receive & Unload	$168	$0	$51	$0	$0	$219	$19	$0	$36	$274	$0
1.6	Sorbent Stackout & Reclaim	$2,712	$0	$497	$0	$0	$3,209	$280	$0	$524	$4,013	$7
1.7	Sorbent Conveyors	$968	$209	$237	$0	$0	$1,414	$122	$0	$231	$1,767	$3
1.8	Other Sorbent Handling	$584	$137	$306	$0	$0	$1,027	$91	$0	$168	$1,286	$2
1.9	Coal & Sorbent Hnd.Foundations	$0	$5,368	$6,772	$0	$0	$12,140	$1,140	$0	$1,992	$15,271	$28
	SUBTOTAL 1.	**$20,020**	**$5,714**	**$12,391**	**$0**	**$0**	**$38,125**	**$3,422**	**$0**	**$6,233**	**$47,780**	**$87**
2	**COAL & SORBENT PREP & FEED**											
2.1	Coal Crushing & Drying	$2,374	$0	$463	$0	$0	$2,837	$248	$0	$463	$3,548	$6
2.2	Coal Conveyor to Storage	$6,079	$0	$1,327	$0	$0	$7,406	$647	$0	$1,207	$9,261	$17
2.3	Coal Injection System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.4	Misc.Coal Prep & Feed	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.5	Sorbent Prep Equipment	$4,622	$199	$960	$0	$0	$5,781	$503	$0	$943	$7,227	$13
2.6	Sorbent Storage & Feed	$557	$0	$213	$0	$0	$771	$68	$0	$126	$964	$2
2.7	Sorbent Injection System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.8	Booster Air Supply System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.9	Coal & Sorbent Feed Foundation	$0	$597	$501	$0	$0	$1,098	$102	$0	$180	$1,380	$3
	SUBTOTAL 2.	**$13,632**	**$796**	**$3,464**	**$0**	**$0**	**$17,892**	**$1,568**	**$0**	**$2,919**	**$22,379**	**$41**
3	**FEEDWATER & MISC. BOP SYSTEMS**											
3.1	FeedwaterSystem	$21,152	$0	$7,301	$0	$0	$28,453	$2,492	$0	$4,642	$35,587	$65
3.2	Water Makeup & Pretreating	$7,131	$0	$2,295	$0	$0	$9,427	$892	$0	$2,064	$12,382	$23
3.3	Other Feedwater Subsystems	$6,920	$0	$2,924	$0	$0	$9,844	$882	$0	$1,609	$12,335	$22
3.4	Service Water Systems	$1,398	$0	$760	$0	$0	$2,159	$203	$0	$472	$2,834	$5
3.5	Other Boiler Plant Systems	$8,309	$0	$8,204	$0	$0	$16,514	$1,569	$0	$2,713	$20,796	$38
3.6	FO Supply Sys & Nat Gas	$272	$0	$340	$0	$0	$612	$58	$0	$101	$770	$1
3.7	Waste Treatment Equipment	$4,779	$0	$2,724	$0	$0	$7,503	$730	$0	$1,647	$9,880	$18
3.8	Misc. Equip.(cranes,AirComp.,Comm.)	$2,888	$0	$882	$0	$0	$3,770	$363	$0	$827	$4,960	$9
	SUBTOTAL 3.	**$52,849**	**$0**	**$25,432**	**$0**	**$0**	**$78,281**	**$7,188**	**$0**	**$14,074**	**$99,544**	**$181**
4	**PC BOILER**											
4.1	PC Boiler & Accessories	$175,448	$0	$112,829	$0	$0	$288,277	$28,085	$0	$31,636	$347,998	$633
4.2	SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4	Boiler BoP (w/ ID Fans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.5	Primary Air System w/4.1	w/4.1	$0	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.6	Secondary Air System w/4.1	w/4.1	$0	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.8	Major Component Rigging	$0	w/4.1	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.9	Boiler Foundations	$0	w/14.1	w/14.1	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 4.	**$175,448**	**$0**	**$112,829**	**$0**	**$0**	**$288,277**	**$28,085**	**$0**	**$31,636**	**$347,998**	**$633**

Exhibit 28 Case DB2 Total Plant Cost Details (Continued)

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
5	**FLUE GAS CLEANUP**											
5.1	Absorber Vessels & Accessories	$70,066	$0	$15,084	$0	$0	$85,150	$8,118	$0	$9,326	$102,594	$187
5.2	Other FGD	$3,657	$0	$4,143	$0	$0	$7,800	$757	$0	$855	$9,412	$17
5.3	Bag House & Accessories	$20,133	$0	$12,778	$0	$0	$32,911	$3,172	$0	$3,608	$39,691	$72
5.4	Other Particulate Removal Materials	$1,363	$0	$1,458	$0	$0	$2,821	$273	$0	$310	$3,404	$6
5.5	Gypsum Dewatering System	$5,621	$0	$955	$0	$0	$6,577	$626	$0	$720	$7,923	$14
5.6	Mercury Removal System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
5.9	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 5.	**$100,840**	**$0**	**$34,418**	**$0**	**$0**	**$135,258**	**$12,946**	**$0**	**$14,820**	**$163,023**	**$296**
5B	**CO2 REMOVAL & COMPRESSION**											
5B.1	CO2 Removal System	$291,020	$0	$66,332	$0	$0	$357,352	$33,948	$71,470	$89,338	$552,108	$1,004
5B.2	CO2 Compression & Drying	$27,457	$0	$8,614	$0	$0	$36,072	$3,450	$0	$7,904	$47,426	$86
	SUBTOTAL 5.	**$318,477**	**$0**	**$74,946**	**$0**	**$0**	**$393,423**	**$37,398**	**$71,470**	**$97,242**	**$599,534**	**$1,090**
6	**COMBUSTION TURBINE/ACCESSORIES**											
6.1	Combustion Turbine Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
6.2	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
6.3	Compressed Air Piping	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
6.9	Combustion Turbine Foundations	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 6.	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**
7	**HRSG, DUCTING & STACK**											
7.1	Heat Recovery Steam Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
7.2	HRSG Accessories	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
7.3	Ductwork	$9,925	$0	$6,377	$0	$0	$16,301	$1,422	$0	$2,658	$20,381	$37
7.4	Stack	$9,267	$0	$5,422	$0	$0	$14,689	$1,415	$0	$1,610	$17,714	$32
7.9	Duct & Stack Foundations	$0	$1,063	$1,208	$0	$0	$2,271	$213	$0	$496	$2,980	$5
	SUBTOTAL 7.	**$19,192**	**$1,063**	**$13,007**	**$0**	**$0**	**$33,262**	**$3,049**	**$0**	**$4,765**	**$41,076**	**$75**
8	**STEAM TURBINE GENERATOR**											
8.1	Steam TG & Accessories	$57,482	$0	$7,189	$0	$0	$64,671	$6,196	$0	$7,086	$77,953	$142
8.2	Turbine Plant Auxiliaries	$403	$0	$862	$0	$0	$1,265	$124	$0	$138	$1,527	$3
8.3	Condenser & Auxiliaries	$6,590	$0	$2,730	$0	$0	$9,320	$894	$0	$1,022	$11,236	$20
8.4	Steam Piping	$20,835	$0	$10,273	$0	$0	$31,108	$2,614	$0	$5,058	$38,780	$71
8.9	TG Foundations	$0	$1,264	$1,997	$0	$0	$3,261	$308	$0	$714	$4,283	$8
	SUBTOTAL 8.	**$85,310**	**$1,264**	**$23,051**	**$0**	**$0**	**$109,624**	**$10,137**	**$0**	**$14,018**	**$133,779**	**$243**
9	**COOLING WATER SYSTEM**											
9.1	Cooling Towers	$13,966	$0	$4,349	$0	$0	$18,315	$1,752	$0	$2,007	$22,074	$40
9.2	Circulating Water Pumps	$3,086	$0	$231	$0	$0	$3,318	$280	$0	$360	$3,958	$7
9.3	Circ.Water System Auxiliaries	$759	$0	$101	$0	$0	$860	$81	$0	$94	$1,036	$2
9.4	Circ.Water Piping	$0	$6,018	$5,832	$0	$0	$11,850	$1,109	$0	$1,944	$14,903	$27
9.5	Make-up Water System	$650	$0	$868	$0	$0	$1,518	$145	$0	$249	$1,912	$3
9.6	Component Cooling Water Sys	$602	$0	$478	$0	$0	$1,080	$102	$0	$177	$1,360	$2
9.9	Circ.Water System Foundations& Structures	$0	$3,598	$5,716	$0	$0	$9,314	$881	$0	$2,039	$12,233	$22
	SUBTOTAL 9.	**$19,063**	**$9,616**	**$17,577**	**$0**	**$0**	**$46,255**	**$4,351**	**$0**	**$6,870**	**$57,475**	**$105**

Exhibit 28 Case DB2 Total Plant Cost Details (Continued)

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
10	**SH/SPENT SORBENT HANDLING SYS**											
10.1	Ash Coolers	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.2	Cyclone Ash Letdown	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.3	HGCU Ash Letdown	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.4	High Temperature Ash Piping	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.5	Other Ash Recovery Equipment	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.6	Ash Storage Silos	$703	$0	$2,169	$0	$0	$2,872	$282	$0	$315	$3,469	$6
10.7	Ash Transport & Feed Equipment	$4,556	$0	$4,666	$0	$0	$9,222	$881	$0	$1,010	$11,114	$20
10.8	Misc. Ash Handling Equipment	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
10.9	Ash/Spent Sorbent Foundation	$0	$168	$197	$0	$0	$365	$34	$0	$80	$479	$1
	SUBTOTAL 10.	**$5,259**	**$168**	**$7,032**	**$0**	**$0**	**$12,459**	**$1,198**	**$0**	**$1,405**	**$15,062**	**$27**
11	**ACCESSORY ELECTRIC PLANT**											
11.1	Generator Equipment	$1,800	$0	$292	$0	$0	$2,093	$194	$0	$172	$2,458	$4
11.2	Station Service Equipment	$5,990	$0	$1,968	$0	$0	$7,957	$744	$0	$653	$9,354	$17
11.3	Switchgear & Motor Control	$6,886	$0	$1,171	$0	$0	$8,056	$747	$0	$881	$9,684	$18
11.4	Conduit & Cable Tray	$0	$4,317	$14,928	$0	$0	$19,245	$1,863	$0	$3,166	$24,274	$44
11.5	Wire & Cable	$0	$8,146	$15,726	$0	$0	$23,872	$2,012	$0	$3,883	$29,767	$54
11.6	Protective Equipment	$270	$0	$918	$0	$0	$1,188	$116	$0	$130	$1,434	$3
11.7	Standby Equipment	$1,407	$0	$32	$0	$0	$1,439	$131	$0	$157	$1,727	$3
11.8	Main Power Transformers	$11,500	$0	$191	$0	$0	$11,691	$886	$0	$1,258	$13,835	$25
11.9	Electrical Foundations	$0	$359	$880	$0	$0	$1,239	$119	$0	$272	$1,630	$3
	SUBTOTAL 11.	**$27,853**	**$12,822**	**$36,106**	**$0**	**$0**	**$76,781**	**$6,811**	**$0**	**$10,571**	**$94,163**	**$171**
12	**INSTRUMENTATION & CONTROL**											
12.1	PC Control Equipment	w/12.7	$0	w/12.7	$0	$0	$0	$0	$0	$0	$0	$0
12.2	Combustion Turbine Control	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
12.3	Steam Turbine Control	w/8.1	$0	w/8.1	$0	$0	$0	$0	$0	$0	$0	$0
12.4	Other Major Component Control	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
12.5	Signal Processing Equipment	W/12.7	$0	w/12.7	$0	$0	$0	$0	$0	$0	$0	$0
12.6	Control Boards,Panels & Racks	$536	$0	$321	$0	$0	$857	$81	$43	$148	$1,129	$2
12.7	Distributed Control System Equipment	$5,410	$0	$945	$0	$0	$6,355	$589	$318	$727	$7,990	$15
12.8	Instrument Wiring & Tubing	$2,933	$0	$5,818	$0	$0	$8,752	$745	$438	$1,490	$11,424	$21
12.9	Other I & C Equipment	$1,528	$0	$3,469	$0	$0	$4,998	$485	$250	$574	$6,306	$11
	SUBTOTAL 12.	**$10,408**	**$0**	**$10,554**	**$0**	**$0**	**$20,962**	**$1,900**	**$1,049**	**$2,937**	**$26,849**	**$49**

Exhibit 28 Case DB2 Total Plant Cost Details (Continued)

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
13	**IMPROVEMENTS TO SITE**											
13.1	Site Preparation	$0	$56	$1,124	$0	$0	$1,180	$117	$0	$260	$1,557	$3
13.2	Site Improvements	$0	$1,866	$2,318	$0	$0	$4,184	$413	$0	$919	$5,516	$10
13.3	Site Facilities	$3,344	$0	$3,298	$0	$0	$6,642	$655	$0	$1,459	$8,756	$16
	SUBTOTAL 13.	**$3,344**	**$1,922**	**$6,740**	**$0**	**$0**	**$12,006**	**$1,185**	**$0**	**$2,638**	**$15,829**	**$29**
14	**BUILDINGS & STRUCTURES**											
14.1	Boiler Building	$0	$9,158	$8,054	$0	$0	$17,212	$1,547	$0	$2,814	$21,573	$39
14.2	Turbine Building	$0	$13,420	$12,507	$0	$0	$25,927	$2,337	$0	$4,240	$32,504	$59
14.3	Administration Building	$0	$646	$684	$0	$0	$1,330	$121	$0	$218	$1,669	$3
14.4	Circulation Water Pumphouse	$0	$160	$127	$0	$0	$287	$25	$0	$47	$360	$1
14.5	Water Treatment Buildings	$0	$909	$829	$0	$0	$1,737	$157	$0	$284	$2,177	$4
14.6	Machine Shop	$0	$432	$290	$0	$0	$722	$64	$0	$118	$904	$2
14.7	Warehouse	$0	$293	$294	$0	$0	$587	$53	$0	$96	$736	$1
14.8	Other Buildings & Structures	$0	$239	$204	$0	$0	$443	$40	$0	$72	$555	$1
14.9	Waste Treating Building & Str.	$0	$456	$1,384	$0	$0	$1,840	$175	$0	$302	$2,317	$4
	SUBTOTAL 14.	**$0**	**$25,712**	**$24,373**	**$0**	**$0**	**$50,085**	**$4,519**	**$0**	**$8,191**	**$62,795**	**$114**
	TOTAL COST	**$851,695**	**$59,076**	**$401,920**	**$0**	**$0**	**$1,312,690**	**$123,757**	**$72,519**	**$218,318**	**$1,727,285**	**$3,141**

Owner's Costs			
Pre production costs			
6 months all labor		$10,547	$19
1 Month Maintenance Materials		$1,534	$3
1 Month Non fuel consumables		$1,789	$3
1 Month Waste disposal		$323	$1
25% of 1 months Fuels Cost at 100% CF		$1,952	$4
2% of TPC		$34,546	$63
Total		**$50,691**	**$92**
Inventory Capital			
60 days supply of fuel and consumables at 100% CF		$23,877	$43
0.5% of TPC (Spare Parts)		$8,636	$16
Total		**$32,514**	**$59**
Initial Fill Catalyst and Chemical cost		$7,431	$14
Land		$900	$2
Other Owner's costs		$259,093	$471
Financing costs		$46,637	$85
Total Overnight Costs (TOC)		**$2,124,549**	**$3,863**
TASC Multiplier	(High Risk, IOU Five years)	1.14	
Total as spent Cost (TASC)		**$2,421,986**	**$4,404**

Exhibit 29 Case DB2 Initial and Annual Operating and Maintenance Costs

OPERATING & MAINTENANCE LABOR						
Operating Labor						
Operating Labor Rate(base):	34.65 $/hour					
Operating Labor Burden:	30 % of base					
Labor O-H Charge Rate:	25 % of labor					
Total						
Skilled Operator 2.0 2.0	2	2				
Operator	11.3	11.3				
Foreman	1	1				
Lab Tech's, etc.	2	2				
TOTAL-O.J.'s	16.3	16.3				
					Annual Cost	Annual Unit Cost
					$	$/kW-net
Annual Operating Labor Cost					$6,444,907	$11.718
Maintenance Labor Cost					$10,429,543	$18.963
Administrative & Support Labor					$4,218,612	$7.670
Property Taxes and Insurance					$34,545,693	$62.810
TOTAL FIXED OPERATING COSTS					**$55,638,755**	**$101.161**
VARIABLE OPERATING COSTS						
						$/kWh-net
Maintenance Material Cost					**$17,186,482**	**$0.00419**
	Consumption		Unit	Initial		
Consumables	Initial	/Day	Cost	Cost		
Water(/1000 gallons)	0	11556	1.08	$0	**$3,874,713**	**$0.00095**
Chemicals						
MU & WT Chem.(lb)	0	55941	0.17	$0	$2,952,483	$0.00072
Limestone (ton)	0	688	21.63	$0	$4,618,533	$0.00113
Carbon (Mercury Removal) (lb)	0	0	1.05	$0	$0	$0.00000
Solvent and antifoam (/1000 gallons)	1089	0.00	6648.20	$7,237,724	$0	$0.00000
Solvent make-up (kg)	0	1386.63	60.00	$0	$25,829,864	$0.00630
NaOH (tons)	69	7.23	433.68	$29,807	$972,868	$0.00024
H2SO4 (tons)	65	6.90	138.78	$9,055	$297,118	$0.00007
Corrosion Inhibitor	0	0	0.00	$154,511	$0	$0.00000
Activated Carbon(lb)	0	1733	1.05	$0	$564,830	$0.00014
Ammonia (28% NH3) ton	0	101	129.80	$0	$4,059,522	$0.00099
Subtotal Chemicals				**$7,431,097**	**$39,295,218**	**$0.00959**
Other						
Supplemental Fuel(MBtu)	0	0	0.00	$0	$0	$0.00000
SCR Catalyst(m3)	w/equip	0.42	5775.94	$0	$755,419	$0.00018
Emission Penalties	0	0	0.00	$0	$0	$0.00000
Subtotal Other				**$0**	**$755,419**	**$0.00018**
Waste Disposal						
Flyash (ton)	0	524	16.23	$0	$2,639,503	$0.00064
Bottom Ash(ton)	0	131	16.23	$0	$659,876	$0.00016
Subtotal-Waste Disposal				**$0**	**$3,299,378**	$0.00081
By-products & Emissions						
Gypsum (tons)	0	1095	0.00	$0	$0	$0.00000
Enzyme Waste (tons)	0	36	0.00	$0	$0	$0.00000
Subtotal By-Products				**$0**	**$0**	$0.00000
TOTAL VARIABLE OPERATING COSTS				**$7,431,097**	**$64,411,211**	$0.01572
Fuel(ton)	0	6717	38.18	**$0**	**$79,625,073**	**$0.02477**

Notes

1. Cost base is 2007 ($ x 1000)
2. Plant Net Output is 550 MWe
3. Plant Capacity Factor is 85%

5.2 Case DB2 Cost and Performance Summary

COE and LCOE

As described in section 3 the COE was calculated as follows:

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

COE = [(0.124)(2.1245x10^9) + 5.5639x10^7 + (0.85)(1.6945x10^8)] / [(0.85)(4.8180x10^6)]

COE = 113.1 mills/kWh (excluding TS&M costs)

COE = 113.1 + 5.9 (including TS&M costs)

COE = 119.0 mills/kWh

LCOE = 150.9 mills/kWh

CO_2 Captured and CO_2 Avoided cost

As described in section 3 the cost of CO_2 captured was calculated as follows:

$$Cost\ of\ CO_2\ Captured = \frac{(COE_{With\ cc} - COE_{Without\ cc})}{CO_2\ Captured}$$

Cost of CO_2 captured = (113.1$/MWh – 59.4$/MWh) / (0.995 tonne/MWh x 0.85)

Cost of CO_2 captured = 63.5 $/tonne

As described in section 3 the cost of CO_2 avoided was calculated as follows:

$$Avoided\ Cost = \frac{\{COE_{with\ removal} - COE_{reference}\}\ \$/MWh}{\{CO_2\ Emissions_{reference} - CO_2\ Emissions_{with\ removal}\}\ tons/MWh}$$

Cost of CO_2 avoided = (119.0 – 59.4) / (856.6 – 110.0)

Cost of CO_2 avoided = 79.8 $/ton

6 Case DB3 Evaluation

Case DB3 considers CA enzyme-activated reaction kinetics with a stripper pressure of 6 psia and VLP steam (8 psia, 208°F) utilized for reboiler duty. An additional turbine is included to generate electricity from production of VLP steam from the LP steam extracted from the turbine. The bulk stripper temperature is 70°C.

6.1 Case DB3 Cost Estimation

The cost estimating methodology has been described previously in Section 3.3. Exhibit 30 shows the total plant capital cost summary organized by cost account and Exhibit 31 shows a more detailed breakdown of the capital costs along with owner's costs, TOC, and TASC. Exhibit 32 shows the initial and annual O&M costs.

The estimated TOC of the subcritical PC boiler with Case DB3 CO_2 capture is $3,699/kW. Process contingency represents 3.8 percent of the TOC and project contingency represents 10.4 percent. The COE, including CO_2 TS&M costs of 5.9 mills/kWh, is 116.3 mills/kWh.

Exhibit 30 Case DB3 Total Plant Cost Summary (Cost base is 2007$ x 1000)

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
1	COAL & SORBENT HANDLING	$18,122	$5,175	$11,221	$0	$0	$34,519	$3,099	$0	$5,643	$43,261	$79
2	COAL & SORBENT PREP & FEED	$12,278	$719	$3,121	$0	$0	$16,118	$1,413	$0	$2,629	$20,159	$37
3	FEEDWATER & MISC. BOP SYSTEMS	$46,559	$0	$22,460	$0	$0	$69,019	$6,335	$0	$12,368	$87,721	$159
4	PC BOILER											
4.1	PC Boiler & Accessories	$157,168	$0	$101,073	$0	$0	$258,241	$25,159	$0	$28,340	$311,739	$567
4.2	SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4-4.9	Boiler BoP (w/ ID Fans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 4	**$157,168**	**$0**	**$101,073**	**$0**	**$0**	**$258,241**	**$25,159**	**$0**	**$28,340**	**$311,739**	**$567**
5	FLUE GAS CLEANUP	$89,682	$0	$30,533	$0	$0	$120,214	$11,506	$0	$13,171	$144,891	$263
5B	CO2 REMOVAL & COMPRESSION	$335,720	$0	$74,148	$0	$0	$409,868	$38,958	$75,428	$101,457	$625,711	$1,138
6	COMBUSTION TURBINE/ACCESSORIES											
6.1	Combustion Turbine Generator	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6.2-6.9	Combustion Turbine Other	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 6	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**
7	HRSG, DUCTING & STACK											
7.1	Heat Recovery Steam Generator N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7.2-7.9	HRSG Accessories, Ductwork and Stack	$18,655	$1,053	$12,655	$0	$0	$32,364	$2,969	$0	$4,625	$39,958	$73
	SUBTOTAL 7	**$18,655**	**$1,053**	**$12,655**	**$0**	**$0**	**$32,364**	**$2,969**	**$0**	**$4,625**	**$39,958**	**$73**
8	STEAM TURBINE GENERATOR											
8.1	Steam TG & Accessories	$59,875	$0	$7,489	$0	$0	$67,363	$6,454	$0	$7,381	$81,198	$148
8.2-8.9	Turbine Plant Auxiliaries and Steam Piping	$24,928	$1,317	$14,600	$0	$0	$40,846	$3,586	$0	$6,322	$50,754	$92
	SUBTOTAL 8	**$84,803**	**$1,317**	**$22,089**	**$0**	**$0**	**$108,209**	**$10,039**	**$0**	**$13,703**	**$131,952**	**$240**
9	COOLING WATER SYSTEM	$16,395	$7,724	$14,500	$0	$0	$38,620	$3,636	$0	$5,684	$47,940	$87
10	ASH/SPENT SORBENT HANDLING SYS	$4,810	$153	$6,431	$0	$0	$11,395	$1,095	$0	$1,285	$13,775	$25
11	ACCESSORY ELECTRIC PLANT	$25,985	$10,932	$30,991	$0	$0	$67,908	$6,007	$0	$9,281	$83,195	$151
12	INSTRUMENTATION & CONTROL	$9,899	$0	$10,038	$0	$0	$19,938	$1,807	$998	$2,794	$25,536	$46
13	IMPROVEMENTS TO SITE	$3,299	$1,896	$6,648	$0	$0	$11,843	$1,169	$0	$2,602	$15,614	$28
14	BUILDINGS & STRUCTURES	$0	$25,313	$23,989	$0	$0	$49,302	$4,448	$0	$8,063	$61,814	$112
	TOTAL COST	**$823,374**	**$54,283**	**$369,898**	**$0**	**$0**	**$1,247,555**	**$117,640**	**$76,426**	**$211,645**	**$1,653,267**	**$3,006**

Exhibit 31 Case DB3 Total Plant Cost Details

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
1	**COAL & SORBENT HANDLING**											
1.1	Coal Receive & Unload	$3,708	$0	$1,693	$0	$0	$5,401	$483	$0	$882	$6,766	$12
1.2	Coal Stackout & Reclaim	$4,792	$0	$1,086	$0	$0	$5,878	$514	$0	$958	$7,350	$13
1.3	Coal Conveyors	$4,455	$0	$1,074	$0	$0	$5,529	$484	$0	$902	$6,915	$13
1.4	Other Coal Handling	$1,165	$0	$248	$0	$0	$1,414	$123	$0	$231	$1,768	$3
1.5	Sorbent Receive & Unload	$152	$0	$46	$0	$0	$198	$17	$0	$32	$248	$0
1.6	Sorbent Stackout & Reclaim	$2,449	$0	$449	$0	$0	$2,898	$253	$0	$473	$3,623	$7
1.7	Sorbent Conveyors	$874	$189	$214	$0	$0	$1,277	$110	$0	$208	$1,595	$3
1.8	Other Sorbent Handling	$527	$124	$277	$0	$0	$928	$82	$0	$152	$1,162	$2
1.9	Coal & Sorbent Hnd.Foundations	$0	$4,862	$6,134	$0	$0	$10,997	$1,032	$0	$1,804	$13,834	$25
	SUBTOTAL 1.	**$18,122**	**$5,175**	**$11,221**	**$0**	**$0**	**$34,519**	**$3,099**	**$0**	**$5,643**	**$43,261**	**$79**
2	**COAL & SORBENT PREP & FEED**											
2.1	Coal Crushing & Drying	$2,137	$0	$417	$0	$0	$2,554	$223	$0	$417	$3,194	$6
2.2	Coal Conveyor to Storage	$5,471	$0	$1,194	$0	$0	$6,666	$583	$0	$1,087	$8,335	$15
2.3	Coal Injection System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.4	Misc.Coal Prep & Feed	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.5	Sorbent Prep Equipment	$4,167	$180	$865	$0	$0	$5,212	$454	$0	$850	$6,515	$12
2.6	Sorbent Storage & Feed	$502	$0	$192	$0	$0	$695	$61	$0	$113	$869	$2
2.7	Sorbent Injection System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.8	Booster Air Supply System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.9	Coal & Sorbent Feed Foundation	$0	$539	$452	$0	$0	$991	$92	$0	$163	$1,246	$2
	SUBTOTAL 2.	**$12,278**	**$719**	**$3,121**	**$0**	**$0**	**$16,118**	**$1,413**	**$0**	**$2,629**	**$20,159**	**$37**
3	**FEEDWATER & MISC. BOP SYSTEMS**											
3.1	FeedwaterSystem	$18,978	$0	$6,551	$0	$0	$25,529	$2,236	$0	$4,165	$31,930	$58
3.2	Water Makeup & Pretreating	$5,598	$0	$1,802	$0	$0	$7,400	$700	$0	$1,620	$9,720	$18
3.3	Other Feedwater Subsystems	$6,209	$0	$2,623	$0	$0	$8,832	$791	$0	$1,444	$11,067	$20
3.4	Service Water Systems	$1,098	$0	$597	$0	$0	$1,694	$160	$0	$371	$2,225	$4
3.5	Other Boiler Plant Systems	$7,373	$0	$7,280	$0	$0	$14,652	$1,392	$0	$2,407	$18,451	$34
3.6	FO Supply Sys & Nat Gas	$261	$0	$327	$0	$0	$588	$55	$0	$97	$740	$1
3.7	Waste Treatment Equipment	$4,267	$0	$2,433	$0	$0	$6,700	$652	$0	$1,471	$8,823	$16
3.8	Misc. Equip.(cranes,AirComp.,Comm.)	$2,775	$0	$848	$0	$0	$3,623	$348	$0	$794	$4,766	$9
	SUBTOTAL 3.	**$46,559**	**$0**	**$22,460**	**$0**	**$0**	**$69,019**	**$6,335**	**$0**	**$12,368**	**$87,721**	**$159**
4	**PC BOILER**											
4.1	PC Boiler & Accessories	$157,168	$0	$101,073	$0	$0	$258,241	$25,159	$0	$28,340	$311,739	$567
4.2	SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4	Boiler BoP (w/ ID Fans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.5	Primary Air System w/4.1	w/4.1	$0	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.6	Secondary Air System w/4.1	w/4.1	$0	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.8	Major Component Rigging	$0	w/4.1	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.9	Boiler Foundations	$0	w/14.1	w/14.1	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 4.	**$157,168**	**$0**	**$101,073**	**$0**	**$0**	**$258,241**	**$25,159**	**$0**	**$28,340**	**$311,739**	**$567**

Exhibit 31 Case DB3 Total Plant Cost Details (Continued)

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
5	**FLUE GAS CLEANUP**											
5.1	Absorber Vessels & Accessories	$62,367	$0	$13,426	$0	$0	$75,793	$7,226	$0	$8,302	$91,320	$166
5.2	Other FGD	$3,255	$0	$3,688	$0	$0	$6,943	$674	$0	$761	$8,378	$15
5.3	Bag House & Accessories	$17,750	$0	$11,265	$0	$0	$29,015	$2,796	$0	$3,181	$34,993	$64
5.4	Other Particulate Removal Materials	$1,202	$0	$1,285	$0	$0	$2,487	$241	$0	$273	$3,001	$5
5.5	Gypsum Dewatering System	$5,108	$0	$868	$0	$0	$5,977	$569	$0	$654	$7,200	$13
5.6	Mercury Removal System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
5.9	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 5.	**$89,682**	**$0**	**$30,533**	**$0**	**$0**	**$120,214**	**$11,506**	**$0**	**$13,171**	**$144,891**	**$263**
5B	**CO2 REMOVAL & COMPRESSION**											
5B.1	CO2 Removal System	$310,808	$0	$66,332	$0	$0	$377,140	$35,828	$75,428	$94,285	$582,681	$1,059
5B.2	CO2 Compression & Drying	$24,912	$0	$7,816	$0	$0	$32,728	$3,130	$0	$7,172	$43,030	$78
	SUBTOTAL 5.	**$335,720**	**$0**	**$74,148**	**$0**	**$0**	**$409,868**	**$38,958**	**$75,428**	**$101,457**	**$625,711**	**$1,138**
6	**COMBUSTION TURBINE/ACCESSORIES**											
6.1	Combustion Turbine Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
6.2	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
6.3	Compressed Air Piping	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
6.9	Combustion Turbine Foundations	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 6.	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**
7	**HRSG, DUCTING & STACK**											
7.1	Heat Recovery Steam Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
7.2	HRSG Accessories	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
7.3	Ductwork	$9,476	$0	$6,088	$0	$0	$15,565	$1,357	$0	$2,538	$19,460	$35
7.4	Stack	$9,179	$0	$5,371	$0	$0	$14,549	$1,401	$0	$1,595	$17,546	$32
7.9	Duct & Stack Foundations	$0	$1,053	$1,196	$0	$0	$2,249	$211	$0	$492	$2,952	$5
	SUBTOTAL 7.	**$18,655**	**$1,053**	**$12,655**	**$0**	**$0**	**$32,364**	**$2,969**	**$0**	**$4,625**	**$39,958**	**$73**
8	**STEAM TURBINE GENERATOR**											
8.1	Steam TG & Accessories	$59,875	$0	$7,489	$0	$0	$67,363	$6,454	$0	$7,381	$81,198	$148
8.2	Turbine Plant Auxiliaries	$420	$0	$898	$0	$0	$1,318	$129	$0	$144	$1,591	$3
8.3	Condenser & Auxiliaries	$5,874	$0	$2,433	$0	$0	$8,308	$797	$0	$911	$10,015	$18
8.4	Steam Piping	$18,634	$0	$9,188	$0	$0	$27,822	$2,338	$0	$4,524	$34,684	$63
8.9	TG Foundations	$0	$1,317	$2,081	$0	$0	$3,398	$321	$0	$744	$4,464	$8
	SUBTOTAL 8.	**$84,803**	**$1,317**	**$22,089**	**$0**	**$0**	**$108,209**	**$10,039**	**$0**	**$13,703**	**$131,952**	**$240**
9	**COOLING WATER SYSTEM**											
9.1	Cooling Towers	$12,412	$0	$3,865	$0	$0	$16,276	$1,557	$0	$1,783	$19,617	$36
9.2	Circulating Water Pumps	$2,376	$0	$178	$0	$0	$2,554	$216	$0	$277	$3,047	$6
9.3	Circ.Water System Auxiliaries	$606	$0	$81	$0	$0	$686	$65	$0	$75	$826	$2
9.4	Circ.Water Piping	$0	$4,802	$4,654	$0	$0	$9,455	$885	$0	$1,551	$11,891	$22
9.5	Make-up Water System	$522	$0	$698	$0	$0	$1,220	$117	$0	$200	$1,537	$3
9.6	Component Cooling Water Sys	$480	$0	$382	$0	$0	$862	$82	$0	$141	$1,085	$2
9.9	Circ.Water System Foundations& Structures	$0	$2,923	$4,643	$0	$0	$7,566	$715	$0	$1,656	$9,937	$18
	SUBTOTAL 9.	**$16,395**	**$7,724**	**$14,500**	**$0**	**$0**	**$38,620**	**$3,636**	**$0**	**$5,684**	**$47,940**	**$87**

Exhibit 31 Case DB3 Total Plant Cost Details (Continued)

Acct.	Item/Description	Equipment	Material	Labor		Sales	Bare Erected	Eng'g CM	Contingencies		Total Plant Cost	
No.		Cost	Cost	Direct	Indirect	Tax	Cost	H.O. & Fee	Process	Project	$	$/kW
10	**SH/SPENT SORBENT HANDLING SYS**											
10.1	Ash Coolers	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.2	Cyclone Ash Letdown	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.3	HGCU Ash Letdown	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.4	High Temperature Ash Piping	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.5	Other Ash Recovery Equipment	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.6	Ash Storage Silos	$643	$0	$1,983	$0	$0	$2,627	$258	$0	$288	$3,173	$6
10.7	Ash Transport & Feed Equipment	$4,167	$0	$4,268	$0	$0	$8,434	$806	$0	$924	$10,164	$18
10.8	Misc. Ash Handling Equipment	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
10.9	Ash/Spent Sorbent Foundation	$0	$153	$180	$0	$0	$333	$31	$0	$73	$438	$1
	SUBTOTAL 10.	**$4,810**	**$153**	**$6,431**	**$0**	**$0**	**$11,395**	**$1,095**	**$0**	**$1,285**	**$13,775**	**$25**
11	**ACCESSORY ELECTRIC PLANT**											
11.1	Generator Equipment	$1,861	$0	$302	$0	$0	$2,163	$201	$0	$177	$2,541	$5
11.2	Station Service Equipment	$5,075	$0	$1,667	$0	$0	$6,742	$630	$0	$553	$7,925	$14
11.3	Switchgear & Motor Control	$5,834	$0	$992	$0	$0	$6,826	$633	$0	$746	$8,205	$15
11.4	Conduit & Cable Tray	$0	$3,657	$12,648	$0	$0	$16,305	$1,578	$0	$2,682	$20,565	$37
11.5	Wire & Cable	$0	$6,901	$13,324	$0	$0	$20,225	$1,704	$0	$3,290	$25,219	$46
11.6	Protective Equipment	$270	$0	$918	$0	$0	$1,188	$116	$0	$130	$1,434	$3
11.7	Standby Equipment	$1,445	$0	$33	$0	$0	$1,478	$135	$0	$161	$1,774	$3
11.8	Main Power Transformers	$11,500	$0	$191	$0	$0	$11,691	$886	$0	$1,258	$13,835	$25
11.9	Electrical Foundations	$0	$374	$916	$0	$0	$1,290	$123	$0	$283	$1,696	$3
	SUBTOTAL 11.	**$25,985**	**$10,932**	**$30,991**	**$0**	**$0**	**$67,908**	**$6,007**	**$0**	**$9,281**	**$83,195**	**$151**
12	**INSTRUMENTATION & CONTROL**											
12.1	PC Control Equipment	w/12.7	$0	w/12.7	$0	$0	$0	$0	$0	$0	$0	$0
12.2	Combustion Turbine Control	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
12.3	Steam Turbine Control	w/8.1	$0	w/8.1	$0	$0	$0	$0	$0	$0	$0	$0
12.4	Other Major Component Control	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
12.5	Signal Processing Equipment	W/12.7	$0	w/12.7	$0	$0	$0	$0	$0	$0	$0	$0
12.6	Control Boards,Panels & Racks	$510	$0	$306	$0	$0	$815	$77	$41	$140	$1,073	$2
12.7	Distributed Control System Equipment	$5,146	$0	$899	$0	$0	$6,045	$561	$303	$691	$7,599	$14
12.8	Instrument Wiring & Tubing	$2,790	$0	$5,534	$0	$0	$8,324	$709	$416	$1,417	$10,866	$20
12.9	Other I & C Equipment	$1,454	$0	$3,300	$0	$0	$4,753	$461	$238	$546	$5,998	$11
	SUBTOTAL 12.	**$9,899**	**$0**	**$10,038**	**$0**	**$0**	**$19,938**	**$1,807**	**$998**	**$2,794**	**$25,536**	**$46**

Exhibit 31 Case DB3 Total Plant Cost Details (Continued)

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
13	**IMPROVEMENTS TO SITE**											
13.1	Site Preparation	$0	$55	$1,109	$0	$0	$1,164	$115	$0	$256	$1,536	$3
13.2	Site Improvements	$0	$1,841	$2,286	$0	$0	$4,127	$407	$0	$907	$5,441	$10
13.3	Site Facilities	$3,299	$0	$3,253	$0	$0	$6,552	$646	$0	$1,439	$8,637	$16
	SUBTOTAL 13.	**$3,299**	**$1,896**	**$6,648**	**$0**	**$0**	**$11,843**	**$1,169**	**$0**	**$2,602**	**$15,614**	**$28**
14	**BUILDINGS & STRUCTURES**											
14.1	Boiler Building	$0	$9,102	$8,005	$0	$0	$17,106	$1,538	$0	$2,797	$21,441	$39
14.2	Turbine Building	$0	$13,310	$12,405	$0	$0	$25,715	$2,318	$0	$4,205	$32,238	$59
14.3	Administration Building	$0	$642	$679	$0	$0	$1,321	$120	$0	$217	$1,658	$3
14.4	Circulation Water Pumphouse	$0	$129	$103	$0	$0	$232	$21	$0	$38	$290	$1
14.5	Water Treatment Buildings	$0	$728	$664	$0	$0	$1,392	$125	$0	$227	$1,745	$3
14.6	Machine Shop	$0	$429	$288	$0	$0	$717	$64	$0	$117	$898	$2
14.7	Warehouse	$0	$291	$292	$0	$0	$583	$53	$0	$95	$731	$1
14.8	Other Buildings & Structures	$0	$237	$203	$0	$0	$440	$40	$0	$72	$551	$1
14.9	Waste Treating Building & Str.	$0	$445	$1,351	$0	$0	$1,796	$171	$0	$295	$2,263	$4
	SUBTOTAL 14.	**$0**	**$25,313**	**$23,989**	**$0**	**$0**	**$49,302**	**$4,448**	**$0**	**$8,063**	**$61,814**	**$112**
	TOTAL COST	**$823,374**	**$54,283**	**$369,898**	**$0**	**$0**	**$1,247,555**	**$117,640**	**$76,426**	**$211,645**	**$1,653,267**	**$3,006**

Owner's Costs			
Pre production costs			
6 months all labor		$10,547	$19
1 Month Maintenance Materials		$1,534	$3
1 Month Non fuel consumables		$1,789	$3
1 Month Waste disposal		$276	$1
25% of 1 months Fuels Cost at 100% CF		$1,664	$3
2% of TPC		$33,065	$60
Total		**$48,875**	**$89**
Inventory Capital			
60 days supply of fuel and consumables at 100% CF		$24,427	$44
0.5% of TPC (Spare Parts)		$8,266	$15
Total		**$32,694**	**$59**
Initial Fill Catalyst and Chemical cost		$6,360	$12
Land		$900	$2
Other Owner's costs		$247,990	$451
Financing costs		$44,638	$81
Total Overnight Costs (TOC)		**$2,034,724**	**$3,699**
TASC Multiplier	(High Risk, IOU Five years)	1.14	
Total as spent Cost (TASC)		**$2,319,585**	**$4,217**

Exhibit 32 Case DB3 Initial and Annual Operating and Maintenance Costs

OPERATING & MAINTENANCE LABOR						
Operating Labor						
Operating Labor Rate(base):	34.65 $/hour					
Operating Labor Burden:	30 % of base					
Labor O-H Charge Rate:	25 % of labor					
Total						
Skilled Operator 2.0 2.0	2	2				
Operator	11.3	11.3				
Foreman	1	1				
Lab Tech's, etc.	2	2				
TOTAL-O.J.'s	16.3	16.3				
					Annual Cost	Annual Unit Cost
					$	$/kW-net
Annual Operating Labor Cost					$6,444,907	$11.718
Maintenance Labor Cost					$10,429,543	$18.963
Administrative & Support Labor					$4,218,612	$7.670
Property Taxes and Insurance					$33,065,333	$60.119
TOTAL FIXED OPERATING COSTS					**$54,158,395**	**$98.470**
VARIABLE OPERATING COSTS						
						$/kWh-net
Maintenance Material Cost					**$16,450,003**	**$0.00401**
	Consumption		Unit	Initial		
Consumables	Initial	/Day	Cost	Cost		
Water(/1000 gallons)	0	8217	1.08	$0	**$2,755,213**	**$0.00067**
Chemicals						
MU & WT Chem.(lb)	0	39778	0.17	$0	$2,099,438	$0.00051
Limestone (ton)	0	586	21.63	$0	$3,937,762	$0.00096
Carbon (Mercury Removal) (lb)	0	0	1.05	$0	$0	$0.00000
Solvent and antifoam (/1000 gallons)	928	0.00	6648.20	$6,170,885	$0	$0.00000
Solvent make-up (kg)	0	2364.49	60.00	$0	$44,045,094	$0.01075
NaOH (tons)	62	6.16	433.68	$26,751	$829,468	$0.00020
H2SO4 (tons)	59	5.88	138.78	$8,127	$253,323	$0.00006
Corrosion Inhibitor	0	0	0.00	$154,511	$0	$0.00000
Activated Carbon(lb)	0	1477	1.05	$0	$481,574	$0.00012
Ammonia (28% NH3) ton	0	86	129.80	$0	$3,461,150	$0.00084
Subtotal Chemicals				**$6,360,274**	**$55,107,809**	**$0.01345**
Other						
Supplemental Fuel(MBtu)	0	0	0.00	$0	$0	$0.00000
SCR Catalyst(m3)	w/equip	0.36	5775.94	$0	$644,071	$0.00016
Emission Penalties	0	0	0.00	$0	$0	$0.00000
Subtotal Other				**$0**	**$644,071**	**$0.00016**
Waste Disposal						
Flyash (ton)	0	447	16.23	$0	$2,250,441	$0.00055
Bottom Ash(ton)	0	112	16.23	$0	$562,610	$0.00014
Subtotal-Waste Disposal				**$0**	**$2,813,051**	$0.00069
By-products & Emissions						
Gypsum (tons)	0	934	0.00	$0	$0	$0.00000
Enzyme Waste (tons)	0	31	0.00	$0	$0	$0.00000
Subtotal By-Products				**$0**	**$0**	$0.00000
TOTAL VARIABLE OPERATING COSTS				**$6,360,274**	**$77,770,147**	$0.01898
Fuel(ton)	0	5727	38.18	**$0**	**$67,888,354**	**$0.02477**

Notes

1. Cost base is 2007 ($ x 1000)
2. Plant Net Output is 550 MWe
3. Plant Capacity Factor is 85%

6.2 Case DB3 Cost and Performance Summary

COE and LCOE

As described in section 3 the COE was calculated as follows:

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

COE = [(0.124)(2.0347x10^9) + 5.4158x10^7 + (0.85)(1.7136x10^8)] / [(0.85)(4.8180x10^6)]

COE = 110.4 mills/kWh (excluding TS&M costs)

COE = 110.4 + 5.9 (including TS&M costs)

COE = 116.3 mills/kWh

LCOE = 147.5 mills/kWh

CO_2 Captured and CO_2 Avoided cost

As described in section 3 the cost of CO_2 captured was calculated as follows:

$$Cost\ of\ CO_2\ Captured = \frac{(COE_{With\ cc} - COE_{Without\ cc})}{CO_2\ Captured}$$

Cost of CO_2 captured = (110.4$/MWh – 59.4$/MWh) / (0.85 tonne/MWh x 0.85)

Cost of CO_2 captured = 70.7 $/tonne

As described in section 3 the cost of CO_2 avoided was calculated as follows:

$$Avoided\ Cost = \frac{\{COE_{with\ removal} - COE_{reference}\}\ \$/MWh}{\{CO_2\ Emissions_{reference} - CO_2\ Emissions_{with\ removal}\}\ tons/MWh}$$

Cost of CO_2 avoided = (116.3 – 59.4) / (856.6 – 93.8)

Cost of CO_2 avoided = 74.6 $/ton

7 Case DB4 Evaluation

Case DB4 considers enzyme-activated reaction kinetics limited to the absorber, and excluded from the stripper, with a stripper pressure of 6 psia and VLP steam (8 psia, 208°F) utilized for reboiler duty. An additional turbine is included to generate electricity from production of VLP steam from the LP steam extracted from the turbine. The bulk stripper temperature is 70°C.

Even though Case DB4 limits enzyme to the absorber, the same dissolved CA enzyme-activated absorption kinetics were applied for evaluation of Case DB4 as were used for Cases DB1 to DB3. Initial fill and solvent make-up costs were left unchanged compared to DB3 as a way to account for the cost of limiting enzyme to the absorber and maintaining it in that configuration. This simplification of the case, and probable overestimation of related solvent make-up costs, was applied because consideration of a specific technology for maintaining enzyme in the absorber was outside the scope of this assessment.

7.1 Case DB4 Cost Estimation

The cost estimating methodology was described previously in Section 3.3. Exhibit 33 shows the total plant capital cost summary organized by cost account and Exhibit 34 shows a more detailed breakdown of the capital costs along with owner's costs, TOC, and TASC. Exhibit 35 shows the initial and annual O&M costs.

The estimated TOC of the subcritical PC boiler with Case DB4 CO_2 capture is \$3,699/kW. Process contingency represents 3.8 percent of the TOC and project contingency represents 10.4 percent. The COE, including CO_2 TS&M costs of 5.9 mills/kWh, is 116.2 mills/kWh.

Exhibit 33 Case DB4 Total Plant Cost Summary (Cost base is 2007$ x 1000)

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
1	COAL & SORBENT HANDLING	$18,081	$5,163	$11,196	$0	$0	$34,440	$3,092	$0	$5,631	$43,162	$78
2	COAL & SORBENT PREP & FEED	$12,248	$717	$3,113	$0	$0	$16,079	$1,409	$0	$2,623	$20,111	$37
3	FEEDWATER & MISC. BOP SYSTEMS	$46,444	$0	$22,404	$0	$0	$68,847	$6,319	$0	$12,337	$87,503	$159
4	PC BOILER											
4.1	PC Boiler & Accessories	$156,771	$0	$100,818	$0	$0	$257,589	$25,095	$0	$28,268	$310,952	$565
4.2	SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4-4.9	Boiler BoP (w/ ID Fans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 4	**$156,771**	**$0**	**$100,818**	**$0**	**$0**	**$257,589**	**$25,095**	**$0**	**$28,268**	**$310,952**	**$565**
5	FLUE GAS CLEANUP	$89,440	$0	$30,449	$0	$0	$119,889	$11,474	$0	$13,136	$144,499	$263
5B	CO2 REMOVAL & COMPRESSION	$337,198	$0	$74,130	$0	$0	$411,328	$39,097	$75,735	$101,824	$627,984	$1,142
6	COMBUSTION TURBINE/ACCESSORIES											
6.1	Combustion Turbine Generator	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
6.2-6.9	Combustion Turbine Other	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 6	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**
7	HRSG, DUCTING & STACK											
7.1	Heat Recovery Steam Generator N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7.2-7.9	HRSG Accessories, Ductwork and Stack	$18,643	$1,053	$12,647	$0	$0	$32,343	$2,967	$0	$4,622	$39,932	$73
	SUBTOTAL 7	**$18,643**	**$1,053**	**$12,647**	**$0**	**$0**	**$32,343**	**$2,967**	**$0**	**$4,622**	**$39,932**	**$73**
8	STEAM TURBINE GENERATOR											
8.1	Steam TG & Accessories	$59,980	$0	$7,502	$0	$0	$67,482	$6,465	$0	$7,394	$81,341	$148
8.2-8.9	Turbine Plant Auxiliaries and Steam Piping	$24,873	$1,319	$14,579	$0	$0	$40,771	$3,579	$0	$6,311	$50,661	$92
	SUBTOTAL 8	**$84,853**	**$1,319**	**$22,080**	**$0**	**$0**	**$108,253**	**$10,044**	**$0**	**$13,705**	**$132,002**	**$240**
9	COOLING WATER SYSTEM	$16,351	$7,707	$14,466	$0	$0	$38,524	$3,627	$0	$5,671	$47,822	$87
10	ASH/SPENT SORBENT HANDLING SYS	$4,800	$153	$6,418	$0	$0	$11,371	$1,093	$0	$1,282	$13,747	$25
11	ACCESSORY ELECTRIC PLANT	$25,892	$10,839	$30,738	$0	$0	$67,468	$5,967	$0	$9,217	$82,652	$150
12	INSTRUMENTATION & CONTROL	$9,872	$0	$10,011	$0	$0	$19,884	$1,802	$995	$2,786	$25,467	$46
13	IMPROVEMENTS TO SITE	$3,298	$1,895	$6,646	$0	$0	$11,839	$1,169	$0	$2,601	$15,609	$28
14	BUILDINGS & STRUCTURES	$0	$25,307	$23,983	$0	$0	$49,290	$4,447	$0	$8,061	$61,799	$112
	TOTAL COST	**$823,891**	**$54,154**	**$369,100**	**$0**	**$0**	**$1,247,145**	**$117,604**	**$76,730**	**$211,764**	**$1,653,242**	**$3,006**

Exhibit 34 Case DB4 Total Plant Cost Details

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
1	**COAL & SORBENT HANDLING**											
1.1	Coal Receive & Unload	$3,699	$0	$1,690	$0	$0	$5,389	$481	$0	$880	$6,750	$12
1.2	Coal Stackout & Reclaim	$4,781	$0	$1,083	$0	$0	$5,864	$513	$0	$956	$7,333	$13
1.3	Coal Conveyors	$4,445	$0	$1,071	$0	$0	$5,517	$483	$0	$900	$6,900	$13
1.4	Other Coal Handling	$1,163	$0	$248	$0	$0	$1,410	$123	$0	$231	$1,764	$3
1.5	Sorbent Receive & Unload	$152	$0	$46	$0	$0	$198	$17	$0	$32	$247	$0
1.6	Sorbent Stackout & Reclaim	$2,443	$0	$448	$0	$0	$2,891	$252	$0	$472	$3,615	$7
1.7	Sorbent Conveyors	$872	$188	$214	$0	$0	$1,274	$110	$0	$208	$1,592	$3
1.8	Other Sorbent Handling	$526	$123	$276	$0	$0	$926	$82	$0	$152	$1,159	$2
1.9	Coal & Sorbent Hnd.Foundations	$0	$4,851	$6,120	$0	$0	$10,972	$1,030	$0	$1,800	$13,802	$25
	SUBTOTAL 1.	**$18,081**	**$5,163**	**$11,196**	**$0**	**$0**	**$34,440**	**$3,092**	**$0**	**$5,631**	**$43,162**	**$78**
2	**COAL & SORBENT PREP & FEED**											
2.1	Coal Crushing & Drying	$2,132	$0	$416	$0	$0	$2,548	$222	$0	$416	$3,186	$6
2.2	Coal Conveyor to Storage	$5,458	$0	$1,192	$0	$0	$6,650	$581	$0	$1,084	$8,315	$15
2.3	Coal Injection System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.4	Misc.Coal Prep & Feed	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.5	Sorbent Prep Equipment	$4,157	$179	$863	$0	$0	$5,199	$453	$0	$848	$6,500	$12
2.6	Sorbent Storage & Feed	$501	$0	$192	$0	$0	$693	$61	$0	$113	$867	$2
2.7	Sorbent Injection System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.8	Booster Air Supply System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
2.9	Coal & Sorbent Feed Foundation	$0	$538	$451	$0	$0	$989	$92	$0	$162	$1,243	$2
	SUBTOTAL 2.	**$12,248**	**$717**	**$3,113**	**$0**	**$0**	**$16,079**	**$1,409**	**$0**	**$2,623**	**$20,111**	**$37**
3	**FEEDWATER & MISC. BOP SYSTEMS**											
3.1	FeedwaterSystem	$18,931	$0	$6,535	$0	$0	$25,465	$2,231	$0	$4,154	$31,850	$58
3.2	Water Makeup & Pretreating	$5,583	$0	$1,797	$0	$0	$7,380	$698	$0	$1,615	$9,693	$18
3.3	Other Feedwater Subsystems	$6,193	$0	$2,617	$0	$0	$8,810	$789	$0	$1,440	$11,040	$20
3.4	Service Water Systems	$1,095	$0	$595	$0	$0	$1,690	$159	$0	$370	$2,219	$4
3.5	Other Boiler Plant Systems	$7,352	$0	$7,260	$0	$0	$14,612	$1,388	$0	$2,400	$18,401	$33
3.6	FO Supply Sys & Nat Gas	$261	$0	$327	$0	$0	$587	$55	$0	$97	$739	$1
3.7	Waste Treatment Equipment	$4,256	$0	$2,426	$0	$0	$6,683	$650	$0	$1,467	$8,800	$16
3.8	Misc. Equip.(cranes,AirComp.,Comm.)	$2,772	$0	$847	$0	$0	$3,620	$348	$0	$794	$4,761	$9
	SUBTOTAL 3.	**$46,444**	**$0**	**$22,404**	**$0**	**$0**	**$68,847**	**$6,319**	**$0**	**$12,337**	**$87,503**	**$159**
4	**PC BOILER**											
4.1	PC Boiler & Accessories	$156,771	$0	$100,818	$0	$0	$257,589	$25,095	$0	$28,268	$310,952	$565
4.2	SCR (w/4.1)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.3	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.4	Boiler BoP (w/ ID Fans)	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
4.5	Primary Air System w/4.1	w/4.1	$0	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.6	Secondary Air System w/4.1	w/4.1	$0	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.8	Major Component Rigging	$0	w/4.1	w/4.1	$0	$0	$0	$0	$0	$0	$0	$0
4.9	Boiler Foundations	$0	w/14.1	w/14.1	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 4.	**$156,771**	**$0**	**$100,818**	**$0**	**$0**	**$257,589**	**$25,095**	**$0**	**$28,268**	**$310,952**	**$565**

Exhibit 34 Case DB4 Total Plant Cost Details (Continued)

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
5	**FLUE GAS CLEANUP**											
5.1	Absorber Vessels & Accessories	$62,200	$0	$13,390	$0	$0	$75,590	$7,206	$0	$8,279	$91,076	$166
5.2	Other FGD	$3,246	$0	$3,678	$0	$0	$6,924	$672	$0	$759	$8,355	$15
5.3	Bag House & Accessories	$17,699	$0	$11,233	$0	$0	$28,931	$2,788	$0	$3,172	$34,892	$63
5.4	Other Particulate Removal Materials	$1,198	$0	$1,282	$0	$0	$2,480	$240	$0	$272	$2,992	$5
5.5	Gypsum Dewatering System	$5,097	$0	$866	$0	$0	$5,963	$568	$0	$653	$7,184	$13
5.6	Mercury Removal System	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
5.9	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 5.	**$89,440**	**$0**	**$30,449**	**$0**	**$0**	**$119,889**	**$11,474**	**$0**	**$13,136**	**$144,499**	**$263**
5B	**CO2 REMOVAL & COMPRESSION**											
5B.1	CO2 Removal System	$312,341	$0	$66,332	$0	$0	$378,673	$35,974	$75,735	$94,668	$585,050	$1,064
5B.2	CO2 Compression & Drying	$24,857	$0	$7,798	$0	$0	$32,655	$3,123	$0	$7,156	$42,934	$78
	SUBTOTAL 5.	**$337,198**	**$0**	**$74,130**	**$0**	**$0**	**$411,328**	**$39,097**	**$75,735**	**$101,824**	**$627,984**	**$1,142**
6	**COMBUSTION TURBINE/ACCESSORIES**											
6.1	Combustion Turbine Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
6.2	Open	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
6.3	Compressed Air Piping	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
6.9	Combustion Turbine Foundations	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
	SUBTOTAL 6.	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**	**$0**
7	**HRSG, DUCTING & STACK**											
7.1	Heat Recovery Steam Generator	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
7.2	HRSG Accessories	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
7.3	Ductwork	$9,466	$0	$6,082	$0	$0	$15,548	$1,356	$0	$2,535	$19,439	$35
7.4	Stack	$9,177	$0	$5,369	$0	$0	$14,546	$1,401	$0	$1,595	$17,542	$32
7.9	Duct & Stack Foundations	$0	$1,053	$1,196	$0	$0	$2,249	$211	$0	$492	$2,951	$5
	SUBTOTAL 7.	**$18,643**	**$1,053**	**$12,647**	**$0**	**$0**	**$32,343**	**$2,967**	**$0**	**$4,622**	**$39,932**	**$73**
8	**STEAM TURBINE GENERATOR**											
8.1	Steam TG & Accessories	$59,980	$0	$7,502	$0	$0	$67,482	$6,465	$0	$7,394	$81,341	$148
8.2	Turbine Plant Auxiliaries	$420	$0	$900	$0	$0	$1,320	$129	$0	$144	$1,594	$3
8.3	Condenser & Auxiliaries	$5,866	$0	$2,430	$0	$0	$8,295	$796	$0	$909	$10,001	$18
8.4	Steam Piping	$18,587	$0	$9,164	$0	$0	$27,751	$2,332	$0	$4,512	$34,595	$63
8.9	TG Foundations	$0	$1,319	$2,085	$0	$0	$3,405	$322	$0	$745	$4,472	$8
	SUBTOTAL 8.	**$84,853**	**$1,319**	**$22,080**	**$0**	**$0**	**$108,253**	**$10,044**	**$0**	**$13,705**	**$132,002**	**$240**
9	**COOLING WATER SYSTEM**											
9.1	Cooling Towers	$12,378	$0	$3,854	$0	$0	$16,232	$1,553	$0	$1,779	$19,564	$36
9.2	Circulating Water Pumps	$2,370	$0	$178	$0	$0	$2,547	$215	$0	$276	$3,039	$6
9.3	Circ.Water System Auxiliaries	$604	$0	$81	$0	$0	$685	$65	$0	$75	$824	$1
9.4	Circ.Water Piping	$0	$4,791	$4,643	$0	$0	$9,433	$883	$0	$1,547	$11,864	$22
9.5	Make-up Water System	$521	$0	$696	$0	$0	$1,217	$116	$0	$200	$1,534	$3
9.6	Component Cooling Water Sys	$479	$0	$381	$0	$0	$860	$81	$0	$141	$1,082	$2
9.9	Circ.Water System Foundations& Structures	$0	$2,916	$4,633	$0	$0	$7,550	$714	$0	$1,653	$9,916	$18
	SUBTOTAL 9.	**$16,351**	**$7,707**	**$14,466**	**$0**	**$0**	**$38,524**	**$3,627**	**$0**	**$5,671**	**$47,822**	**$87**

Exhibit 34 Case DB4 Total Plant Cost Details (Continued)

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
10	**SH/SPENT SORBENT HANDLING SYS**											
10.1	Ash Coolers	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.2	Cyclone Ash Letdown	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.3	HGCU Ash Letdown	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.4	High Temperature Ash Piping	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.5	Other Ash Recovery Equipment	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
10.6	Ash Storage Silos	$642	$0	$1,979	$0	$0	$2,621	$257	$0	$288	$3,166	$6
10.7	Ash Transport & Feed Equipment	$4,158	$0	$4,259	$0	$0	$8,417	$805	$0	$922	$10,144	$18
10.8	Misc. Ash Handling Equipment	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
10.9	Ash/Spent Sorbent Foundation	$0	$153	$180	$0	$0	$333	$31	$0	$73	$437	$1
	SUBTOTAL 10.	**$4,800**	**$153**	**$6,418**	**$0**	**$0**	**$11,371**	**$1,093**	**$0**	**$1,282**	**$13,747**	**$25**
11	**ACCESSORY ELECTRIC PLANT**											
11.1	Generator Equipment	$1,864	$0	$303	$0	$0	$2,166	$201	$0	$178	$2,545	$5
11.2	Station Service Equipment	$5,030	$0	$1,652	$0	$0	$6,682	$624	$0	$548	$7,854	$14
11.3	Switchgear & Motor Control	$5,782	$0	$983	$0	$0	$6,765	$627	$0	$740	$8,132	$15
11.4	Conduit & Cable Tray	$0	$3,625	$12,535	$0	$0	$16,160	$1,564	$0	$2,658	$20,382	$37
11.5	Wire & Cable	$0	$6,840	$13,205	$0	$0	$20,045	$1,689	$0	$3,260	$24,995	$45
11.6	Protective Equipment	$270	$0	$918	$0	$0	$1,188	$116	$0	$130	$1,434	$3
11.7	Standby Equipment	$1,447	$0	$33	$0	$0	$1,479	$135	$0	$162	$1,776	$3
11.8	Main Power Transformers	$11,500	$0	$191	$0	$0	$11,691	$886	$0	$1,258	$13,835	$25
11.9	Electrical Foundations	$0	$374	$918	$0	$0	$1,292	$124	$0	$283	$1,699	$3
	SUBTOTAL 11.	**$25,892**	**$10,839**	**$30,738**	**$0**	**$0**	**$67,468**	**$5,967**	**$0**	**$9,217**	**$82,652**	**$150**
12	**INSTRUMENTATION & CONTROL**											
12.1	PC Control Equipment	w/12.7	$0	w/12.7	$0	$0	$0	$0	$0	$0	$0	$0
12.2	Combustion Turbine Control	N/A	$0	N/A	$0	$0	$0	$0	$0	$0	$0	$0
12.3	Steam Turbine Control	w/8.1	$0	w/8.1	$0	$0	$0	$0	$0	$0	$0	$0
12.4	Other Major Component Control	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0	$0
12.5	Signal Processing Equipment	W/12.7	$0	w/12.7	$0	$0	$0	$0	$0	$0	$0	$0
12.6	Control Boards,Panels & Racks	$508	$0	$305	$0	$0	$813	$76	$41	$140	$1,070	$2
12.7	Distributed Control System Equipment	$5,132	$0	$897	$0	$0	$6,028	$559	$302	$689	$7,578	$14
12.8	Instrument Wiring & Tubing	$2,782	$0	$5,519	$0	$0	$8,301	$707	$415	$1,413	$10,837	$20
12.9	Other I & C Equipment	$1,450	$0	$3,291	$0	$0	$4,741	$460	$237	$544	$5,982	$11
	SUBTOTAL 12.	**$9,872**	**$0**	**$10,011**	**$0**	**$0**	**$19,884**	**$1,802**	**$995**	**$2,786**	**$25,467**	**$46**

Exhibit 34 Case DB4 Total Plant Cost Details (Continued)

Acct. No.	Item/Description	Equipment Cost	Material Cost	Labor		Sales Tax	Bare Erected Cost	Eng'g CM H.O. & Fee	Contingencies		Total Plant Cost	
				Direct	Indirect				Process	Project	$	$/kW
13	**IMPROVEMENTS TO SITE**											
13.1	Site Preparation	$0	$55	$1,108	$0	$0	$1,164	$115	$0	$256	$1,535	$3
13.2	Site Improvements	$0	$1,840	$2,286	$0	$0	$4,126	$407	$0	$906	$5,439	$10
13.3	Site Facilities	$3,298	$0	$3,252	$0	$0	$6,550	$646	$0	$1,439	$8,634	$16
	SUBTOTAL 13.	**$3,298**	**$1,895**	**$6,646**	**$0**	**$0**	**$11,839**	**$1,169**	**$0**	**$2,601**	**$15,609**	**$28**
14	**BUILDINGS & STRUCTURES**											
14.1	Boiler Building	$0	$9,101	$8,003	$0	$0	$17,104	$1,537	$0	$2,796	$21,438	$39
14.2	Turbine Building	$0	$13,308	$12,402	$0	$0	$25,710	$2,317	$0	$4,205	$32,232	$59
14.3	Administration Building	$0	$641	$679	$0	$0	$1,321	$120	$0	$216	$1,657	$3
14.4	Circulation Water Pumphouse	$0	$129	$102	$0	$0	$231	$20	$0	$38	$290	$1
14.5	Water Treatment Buildings	$0	$726	$662	$0	$0	$1,388	$125	$0	$227	$1,740	$3
14.6	Machine Shop	$0	$429	$288	$0	$0	$717	$64	$0	$117	$898	$2
14.7	Warehouse	$0	$291	$292	$0	$0	$583	$53	$0	$95	$731	$1
14.8	Other Buildings & Structures	$0	$237	$203	$0	$0	$440	$40	$0	$71	$551	$1
14.9	Waste Treating Building & Str.	$0	$445	$1,351	$0	$0	$1,796	$171	$0	$295	$2,262	$4
	SUBTOTAL 14.	**$0**	**$25,307**	**$23,983**	**$0**	**$0**	**$49,290**	**$4,447**	**$0**	**$8,061**	**$61,799**	**$112**
	TOTAL COST	**$823,891**	**$54,154**	**$369,100**	**$0**	**$0**	**$1,247,145**	**$117,604**	**$76,730**	**$211,764**	**$1,653,242**	**$3,006**

Owner's Costs			
Pre production costs			
6 months all labor		$10,547	$19
1 Month Maintenance Materials		$1,534	$3
1 Month Non fuel consumables		$1,789	$3
1 Month Waste disposal		$275	$0
25% of 1 months Fuels Cost at 100% CF		$1,658	$3
2% of TPC		$33,065	$60
Total		**$48,867**	**$89**
Inventory Capital			
60 days supply of fuel and consumables at 100% CF		$24,338	$44
0.5% of TPC (Spare Parts)		$8,266	$15
Total		**$32,604**	**$59**
Initial Fill Catalyst and Chemical cost		$6,338	$12
Land		$900	$2
Other Owner's costs		$247,986	$451
Financing costs		$44,638	$81
Total Overnight Costs (TOC)		**$2,034,574**	**$3,699**
TASC Multiplier	(High Risk, IOU Five years)	1.14	
Total as spent Cost (TASC)		**$2,319,415**	**$4,217**

Exhibit 35 Case DB4 Initial and Annual Operating and Maintenance Costs

OPERATING & MAINTENANCE LABOR						
Operating Labor						
Operating Labor Rate(base):	34.65 $/hour					
Operating Labor Burden:	30 % of base					
Labor O-H Charge Rate:	25 % of labor					
Total						
Skilled Operator 2.0 2.0	2	2				
Operator	11.3	11.3				
Foreman	1	1				
Lab Tech's, etc.	2	2				
TOTAL-O.J.'s	16.3	16.3				
					Annual Cost	Annual Unit Cost
					$	$/kW-net
Annual Operating Labor Cost					$6,444,907	$11.718
Maintenance Labor Cost					$10,429,543	$18.963
Administrative & Support Labor					$4,218,612	$7.670
Property Taxes and Insurance					$33,064,834	$60.118
TOTAL FIXED OPERATING COSTS					**$54,157,896**	**$98.469**
VARIABLE OPERATING COSTS						
						$/kWh-net
Maintenance Material Cost					**$16,449,755**	**$0.00401**
	Consumption		Unit	Initial		
Consumables	Initial	/Day	Cost	Cost		
Water(/1000 gallons)	0	8186	1.08	$0	**$2,744,694**	**$0.00067**
Chemicals						
MU & WT Chem.(lb)	0	39626	0.17	$0	$2,091,422	$0.00051
Limestone (ton)	0	584	21.63	$0	$3,923,356	$0.00096
Carbon (Mercury Removal) (lb)	0	0	1.05	$0	$0	$0.00000
Solvent and antifoam (/1000 gallons)	925	0	6648.20	$6,148,309	$0	$0.00000
Solvent make-up (kg)	0	2355.84	60.00	$0	$43,883,962	$0.01071
NaOH (tons)	61	6.14	433.68	$26,653	$826,433	$0.00020
H2SO4 (tons)	58	5.86	138.78	$8,097	$252,396	$0.00006
Corrosion Inhibitor	0	0	0.00	$154,511	$0	$0.00000
Activated Carbon(lb)	0	1472	1.05	$0	$479,813	$0.00012
Ammonia (28% NH3) ton	0	86	129.80	$0	$3,448,488	$0.00084
Subtotal Chemicals				**$6,337,571**	**$54,905,871**	**$0.01340**
Other						
Supplemental Fuel(MBtu)	0	0	0.00	$0	$0	$0.00000
SCR Catalyst(m3)	w/equip	0.36	5775.94	$0	$641,714	$0.00016
Emission Penalties	0	0	0.00	$0	$0	$0.00000
Subtotal Other				**$0**	**$641,714**	**$0.00016**
Waste Disposal						
Flyash (ton)	0	445	16.23	$0	$2,242,208	$0.00055
Bottom Ash(ton)	0	111	16.23	$0	$560,552	$0.00014
Subtotal-Waste Disposal				**$0**	**$2,802,760**	$0.00068
By-products & Emissions						
Gypsum (tons)	0	930	0.00	$0	$0	$0.00000
Enzyme Waste (tons)	0	31	0.00	$0	$0	$0.00000
Subtotal By-Products				**$0**	**$0**	$0.00000
TOTAL VARIABLE OPERATING COSTS				**$6,337,571**	**$77,544,794**	$0.01892
Fuel(ton)	0	5706	38.18	**$0**	**$67,639,996**	**$0.02477**

Notes

1. Cost base is 2007 ($ x 1000)
2. Plant Net Output is 550 MWe
3. Plant Capacity Factor is 85%

7.2 Case DB4 Cost and Performance Summary

COE and LCOE

As described in section 3 the COE was calculated as follows:

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

COE = [(0.124)(2.0346x10^9) + 5.4158x10^7 + (0.85)(1.7081x10^8)] / [(0.85)(4.8180x10^6)]

COE = 110.3 mills/kWh (excluding TS&M costs)

COE = 110.3 + 5.9 (including TS&M costs)

COE = 116.2 mills/kWh

LCOE = 147.3 mills/kWh

CO_2 Captured and CO_2 Avoided cost

As described in section 3 the cost of CO_2 captured was calculated as follows:

$$Cost\ of\ CO_2\ Captured = \frac{(COE_{With\ cc} - COE_{Without\ cc})}{CO_2\ Captured}$$

Cost of CO_2 captured = (110.3$/MWh – 59.4$/MWh) / (0.85 tonne/MWh x 0.85)

Cost of CO_2 captured = 70.8 $/tonne

As described in section 3 the cost of CO_2 avoided was calculated as follows:

$$Avoided\ Cost = \frac{\{COE_{with\ removal} - COE_{reference}\}\ \$/MWh}{\{CO_2\ Emissions_{reference} - CO_2\ Emissions_{with\ removal}\}\ tons/MWh}$$

Cost of CO_2 avoided = (116.2 – 59.4) / (856.6 – 93.4)

Cost of CO_2 avoided = 74.4 $/ton

8 Case DB5 Evaluation

For Case DB5 the PCC plant was modelled using the default Aspen Plus® reaction kinetics for CO_2 absorption and desorption in a K_2CO_3 solvent. This was carried out to simulate using a non-enzyme-activated K_2CO_3 solvent to determine the benefit provided by the addition of enzyme.

Case DB5 was created using the same basic PCC plant system as Case DB3, in which an overall CO_2 capture of 90% was achieved, with a stripper pressure of 6 psia and VLP steam (8 psia, 208°F) utilized for reboiler duty. However, with non-enzyme-activated K_2CO_3 solvent kinetics a maximum capture rate of 17.7% was achieved.

Case DB5 was not considered further, since the predicted CO_2 capture performance does not meet the target value of 90%. The result does, however, demonstrate the significant beneficial effect that the CA enzyme has on the capture performance and hence viability of a PCC plant utilizing a CA enzyme-activated K_2CO_3 solvent.

9 Case Summary

The results for each case are summarized in Exhibit 36.

Exhibit 36 All Cases Performance and Cost Summary

Case	**Case 9[1]**	**Case 10[1]**	**Case DB1**	**Case DB2**	**Case DB3**	**Case DB4**	**Case DB5**
Performance							
CO_2 Capture	0%	90%	90%	90%	90%	90%	18%
Gross Power Output (kWe)	582,600	672,700	682,814	724,569	668,721	666,275	N/A
Auxiliary Power Requirement (kWe)	32,580	122,740	132,814	174,569	118,721	116,275	
Net Power Output (kWe)	550,020	549,960	550,000	550,000	550,000	550,000	
Coal Flowrate (lb/hr)	437,378	614,994	533,723	560,964	478,278	476,528	
HHV Thermal Input (kWth)	1,495,379	2,102,643	1,823,296	1,916,357	1,633,886	1,627,909	
Net Plant HHV Efficiency (%)	36.8%	26.2%	30.2%	28.7%	33.7%	33.8%	
Net Plant HHV Heat Rate (Btu/kWh)	9,277	13,046	11,312	11,889	10,136	10,099	
Raw Water Withdrawl (gpm/MW_{net})	10.7	20.4	16.9	19.2	15.2	13.4	N/A
Process Water Discharge (gpm/MW_{net})	2.2	4.7	4.4	5	4	3.5	
Raw Water Consumption (gpm/MW_{net})	8.5	15.7	12.5	14.2	11.2	9.9	
CO_2 Emissions (lb/MMBtu)	204	20	19.7	19.9	19.9	19.9	N/A
CO_2 Emissions (lb/MWh_{gross})	1,783	217	180	179	179	165	
CO_2 Emissions (lb/MWh_{net})	1,888	266	223	236	236	200	
SO_2 Emissions (lb/MMBtu)	0.0858	0.0017	0.085	0.067	0.067	0.067	
SO_2 Emissions (lb/MWh_{gross})	0.7515	0.0176	0.778	0.604	0.558	0.558	
NO_x Emissions (lb/MMBtu)	0.070	0.070	0.070	0.070	0.070	0.070	
NO_x Emissions (lb/MWh_{gross})	0.613	0.747	0.636	0.634	0.586	0.586	
PM Emissions (lb/MMBtu)	0.0130	0.0130	0.0130	0.0130	0.0130	0.0130	
PM Emissions (lb/MWh_{gross})	0.114	0.139	0.118	0.118	0.109	0.109	
Hg Emissions (lb/TBtu)	1.143	1.143	1.15	1.16	1.16	1.16	
Hg Emissions (lb/MWh_{gross})	1.00E-05	1.22E-05	1.05E-05	1.05E-05	9.67E-06	9.67E-06	
Cost							
Total Plant Cost (2007$/kW)	1,622	2,942	2,964	3,141	3,006	3,006	N/A
Total Overnight Cost (2007$/kW)	1,996	3,610	3,658	3,863	3,699	3,699	
- Bare Erected Cost	*1,317*	*2,255*	*2,258*	*2,387*	*2,268*	*2,268*	
- Home Office Expenses	*124*	*213*	*213*	*225*	*214*	*214*	
- Project Contingency	*182*	*369*	*373*	*397*	*385*	*385*	
- Process Contingency	*0*	*105*	*120*	*132*	*139*	*140*	
- Owner's Costs	*374*	*667*	*694*	*722*	*693*	*693*	
Total Overnight Cost (2007$ x 1000)	1,098,124	1,985,432	2,011,701	2,124,549	2,034,724	2,034,574	
Total As Spent Capital (2007$/kW)	2,264	4,115	4,170	4,404	4,217	4,217	
COE (mills/kWh, 2007$)	59.4	109.6	119.6	119.0	116.3	116.2	
- CO_2 TS&M Costs	*0*	*5.8*	*5.9*	*5.9*	*5.9*	*5.9*	
- Fuel Costs	*15.2*	*21.3*	*18.5*	*19.4*	*16.6*	*16.5*	
- Variable Costs	*5.1*	*9.2*	*21.2*	*15.7*	*19.0*	*18.9*	
- Fixed Costs	*7.8*	*13.1*	*13.1*	*13.6*	*13.2*	*13.2*	
- Capital Costs	*31.2*	*60.2*	*60.9*	*64.3*	*61.6*	*61.6*	
LCOE (mills/kWh, 2007$)	75.3	139.0	151.7	150.9	147.5	147.3	
Cost of CO_2 Captured ($2007/tonne)	N/A	48.1	68.0	63.5	70.7	70.8	
Cost of CO_2 Avoided ($2007/ton)	N/A	68.2	80.0	79.8	74.6	74.4	

Case DB4 gave the best performance with a COE of 116.2 mills/kWh (2007$), a 6.0% increase on the equivalent MEA PCC NETL Case 10 [1]. Case DB3 shows a similar result with a COE of 116.3 mills/kWh (2007$). Without enzyme present, Case DB5, the levels of CO_2 capture only reached 18%, far below the 90% capture target, and clearly illustrating why un-promoted K_2CO_3 solvent has not been considered viable for ambient pressure flue gas scrubbing applications. Case DB2 shows that the application of a deeper vacuum in the stripper has a small benefit with a slight reduction in COE when compared to Case DB1.

Despite Cases DB2, DB3 and DB4 showing the best COE results, Case DB1 is considered to be the most practical solution. The basis for Case DB1 is considered to have the lowest inherent technical risk with the highest confidence in physical system performance, utilizing commercially available equipment and related process technologies. Cases DB2, DB3 and DB4 each consider equipment requirements or operation at or beyond the limit of current available technology, and therefore carry a greater degree of uncertainty.

Case DB1 shows a COE of 119.6 mills/kWh (2007$) which represents a 9.1% increase on the equivalent MEA PCC NETL Case 10 [1].

Cases DB3 and DB4 show a relatively lower auxiliary power requirement compared to the other cases. This is due to the additional power output generated from the VLP turbine when producing VLP steam from the LP steam extracted from the power turbine. The additional power output means that a smaller PC plant, PCC plant and turbine are required to produce the net 550MWe output. However, this benefit is slightly offset by the corresponding additional capital costs of installing the VLP turbine, but overall still delivers the best economic performance in terms of COE.

Case DB2 shows the best performance in terms of cost of CO_2 captured for the enzyme-activated PCC cases with 63.5 2007$/tonne of CO_2 but this is significantly higher (28.5%) than the equivalent NETL MEA PCC Case 10 baseline [1] of 48.1 2007$/tonne of CO_2.

It should be noted that there are limitations in scaling up a process from bench scale data to a representative full scale plant using process models. Further process performance assessment and validation should be carried out on a larger scale demonstration, to validate and confirm kinetic parameters and hence predicted performance to reduce uncertainty.

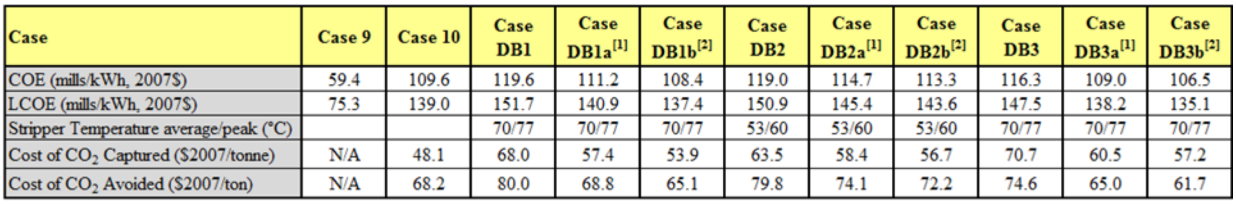
10 Sensitivity Study

The performance summary in Exhibit 36 shows that variable costs are the key differentiator in COE performance between the enzyme-activated cases and NETL Case 10. In Case DB1 the variable costs contribution to COE is more than double that of NETL Case 10. Exposure of the prototype CA enzyme to thermal stress, even at moderate temperatures such as 70°C, results in degradation of the enzyme and a loss in performance that requires removal and replacement of degraded enzyme. The high enzyme make-up rate required to maintain system performance results in a significant operating cost that is reflected in the increased variable costs and ultimately the COE.

Using Novozymes’ expertise it has been determined that the longevity of the CA enzyme could be improved from the current prototype in two stages of commercial development. The first stage could involve a combination of further enzyme-solvent dose optimization and selection among known CA variants with favorable longevity characteristics at the required process conditions compared to the prototype enzyme used in the present study. The second stage could involve a variety of different approaches, such as protein engineering, chemical modification and enzyme-immobilization, used alone or in combination to achieve further enzyme longevity improvements, resulting in reduced replenishment rates and corresponding cost reductions. As supported by findings published in the literature [25], the probability of success for both stage 1 and stage 2 enzyme developments are deemed by Novozymes to be high.

For the purposes of analyzing the sensitivities it is assumed that overall CO_2 capture process performance for each new stage of enzyme development is unchanged relative to the corresponding main case based on the prototype enzyme, and the key improvement is extension of enzyme longevity resulting in operational cost reductions. The application of these potential enzyme developments to Cases DB1, DB2 and DB3 are shown here:

Exhibit 37 Enzyme Development Sensitivity Study Summary



Case	Case 9	Case 10	Case DB1	Case DB1a[1]	Case DB1b[2]	Case DB2	Case DB2a[1]	Case DB2b[2]	Case DB3	Case DB3a[1]	Case DB3b[2]
COE (mills/kWh, 2007$)	59.4	109.6	119.6	111.2	108.4	119.0	114.7	113.3	116.3	109.0	106.5
LCOE (mills/kWh, 2007$)	75.3	139.0	151.7	140.9	137.4	150.9	145.4	143.6	147.5	138.2	135.1
Stripper Temperature average/peak (°C)			70/77	70/77	70/77	53/60	53/60	53/60	70/77	70/77	70/77
Cost of CO_2 Captured ($2007/tonne)	N/A	48.1	68.0	57.4	53.9	63.5	58.4	56.7	70.7	60.5	57.2
Cost of CO_2 Avoided ($2007/ton)	N/A	68.2	80.0	68.8	65.1	79.8	74.1	72.2	74.6	65.0	61.7

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

The result, when stage 1 development of enzyme is applied to Case DB1, is a reduction in COE from 119.6 mills/kWh (2007$) to 111.2 mills/kWh (2007$) representing a 1.5% (rather than 9.1%) increase when compared to NETL Case 10. The results of applying the stage 2 enzyme development are a further reduction in COE to 108.4 mills/kWh (2007$), a performance that represents an improvement of 1.1% when compared to NETL Case 10. Application of the stage 2 enzyme development to Case DB3 results in a COE of 106.5 mills/kWh (2007$), which represents an improvement of 2.8% on NETL Case 10. For all cases it should be noted that further enzyme-related improvements do not have as great an effect on the COE since other factors such as CAPEX become more dominant than OPEX.

Exhibit 36 shows that the biggest contribution to the increased COE is the variable operating costs. This is in part due to the reduced, compared to MEA, CA enzyme-activated K_2CO_3 solvent CO_2 loading capacity. The reduced CO_2 loading capacity requires a greater recirculation rate, hence inventory, to achieve the same amount of CO_2 capture. The solvent composition considered for the present assessment, comprising CA enzyme and K_2CO_3, is also more expensive than MEA and requires a high replenishment rate under the conditions of Case DB1 when prototype CA enzyme is used.

The capital cost element of the COE for Case DB1 increases by 1.2% compared to the equivalent MEA PCC NETL Case 10 [1] despite a 16% decrease in the amount of CO_2 captured to achieve 550MWe net output. This is because the reduced solvent loading capacity of the CA enzyme-activated K_2CO_3 solvent results in an increased size requirement for the equipment due to the greater solvent circulation flow rates required. This increase is somewhat mitigated by the model-predicted increase in performance of the enzyme-activated solvent. i.e. less steam is required in the stripper reboiler than in NETL Case 10 and is therefore utilized to produce power.

However, the main increase in capital cost is due to the additional equipment and component strengthening required for the vacuum creation and operation of the stripper and associated equipment. Utilizing vacuum regeneration results in an increase in performance (i.e. lower stripper reboiler heat duty) due to the ability to operate at a lower temperature as saturation temperature is reduced. The lower temperature in the stripper also extends enzyme life, hence reduces solvent make-up rate requirements and associated costs.

This means CAPEX reductions should be a parallel consideration in developing more cost effective CA enzyme-activated CO_2 capture processes.

11 Discussion

Case DB1 was identified as the best case, in terms of minimized technical risk and greatest readiness for deployment using existing equipment and process technologies based on bench scale test results and process model predictions. However, DB1 was found to have a poorer COE performance than the NETL Case 10. Sensitivity assessment on Case DB1 revealed that the COE performance could show a 1.1% improvement on NETL Case 10 through improvements in enzyme longevity (Exhibit 37). Also, a potential benefit of the enzyme-activated K_2CO_3 solvent over MEA is the fact that the solvent and solvent degradation products are benign and therefore pose no significant environmental, health or safety concerns and are compliant with Federal legislation [24].

Case DB5 was modelled with no enzyme present, utilizing default kinetic parameters for K_2CO_3. The model predicted results show that with a non-enzyme-activated K_2CO_3 solvent a maximum CO_2 capture rate of 17.7% was achieved. The presence of enzyme has a significant effect on the performance of the solvent, resulting in 90% CO_2 capture, and clearly illustrates why non-activated K_2CO_3 solvent has not been considered viable for ambient pressure flue gas scrubbing applications.

Comparisons between Case DB1 and Case DB2 show the effect of utilizing a deeper vacuum for regeneration. The lower pressure lowers the saturation temperature of the solvent and hence allows the stripper to operate at a lower temperature. This improves the model predicted system performance in terms of a reduced parasitic steam load of the reboiler and also improves the enzyme longevity, hence reduces enzyme make-up required and associated variable operating costs. However, there is an additional auxiliary power requirement to produce the deeper vacuum that results in a need for a bigger plant to deliver the 550MWe net power output and therefore increased capital costs. The capital costs of the stripper and associated equipment are further increased with the need for stronger physical components of suitable design to withstand the stress of the deeper vacuum. The current assessment showed that resultant additional capital costs are slightly offset by the model predicted increased reboiler performance and the reduced enzyme make up requirement.

There is potential merit in carrying out further work on Case DB2 as the reduced saturation temperature, hence reduced stripper operating temperature, may have potential operating benefits. Operating at a lower temperature means that it may be possible to directly inject low temperature exhaust steam into the stripper to reduce energy demand for vaporization of water [28]. Alternatively the reboiler heating source could be provided from outside the turbine cycle resulting in a reduction in the parasitic load and hence size requirements of the PC plant to achieve a net 550MWe output. The benefits would have to be offset against the additional costs, power consumption and technical considerations caused by employing a deeper vacuum and alternative source of heat. It also should be noted that steam taken from outside of the power cycle could potentially have a reduced efficiency in generation and therefore have a higher energy or cost impact. A detailed process optimization study and cost-benefit analysis, underpinned by larger-scale experimental and model validated data, would have to be undertaken to determine the optimum operating point and thermal integration scheme at which vacuum regeneration delivers improved process performance without having a significant impact on capital costs.

Cases DB3 and DB4 were found to have an almost identical economic performance in all aspects despite having differing reaction kinetics specified in the stripper and different predicted reboiler duties. The stripper simulation for Case DB3 utilizes enzyme-catalyzed reaction kinetics based on the validated bench scale models; whereas Case DB4 uses Aspen default reaction kinetics; meaning, Case DB4 simulates the stripper performance absent of any kinetic contribution by enzyme.

Case DB4 has a higher predicted reboiler thermal duty compared to DB3, this results in more power being created in the letdown turbine and hence a main steam flow increase smaller than would be expected in order to meet a net 550MWe output. The resulting change is relatively insignificant hence the comparable economic performance predicted. These cases suggest that the enzyme has a limited effect on the regeneration stage under the process conditions considered. The regeneration stage could potentially be equilibrium-limited with respect to CO_2 gas release from the liquid and therefore may not benefit from the effect of enzyme increasing the rate of bicarbonate conversion to dissolved CO_2. However, these results are based only on process models and should be tested on plant, both at bench scale and larger, to determine the process performance of the regeneration stage with no kinetic contribution from the enzyme. If the limited model predicted effect of the enzyme on the regeneration stage is observed in plant tests then further economic improvement could potentially be made by redesigning the process to localize the enzyme to the absorption stage. As the absorption stage operates at a lower temperature than the stripper, there would be a significant improvement in the enzyme longevity and an increased flexibility in the stripper stage to use the optimal combination of heat and pressure conditions without concern for enzyme degradation.

Enzyme Localization

Several potential configurations could achieve the enzyme segregation and localization in the absorber as follows:

- Membrane based separation that would allow low molecular weight CO_2 rich solvent to pass through the membrane and travel to the stripper while causing the higher molecular weight enzyme to be carried, via an absorber recirculation loop, back to the top of the absorber for mixing with lean solvent.
- An increase in the physical size of enzyme molecules by (bio-)chemical modification, crosslinking or combining enzyme in a solid matrix in the form of nanometer or micrometer sized particles that could circulate with the liquid. These larger particles could be separated from the CO_2 rich liquid using filters, centrifuges, cyclones or other solid-liquid separation techniques, before being carried, via an absorber recirculation loop, back to the top of the absorber for mixing with lean solvent.
- Immobilize the enzyme on a fixed surface inside the absorber column. This fixation could be done in several different ways using different chemistries or techniques to immobilize enzyme on the absorber column internals.

For all the potential configurations above the absorption kinetics for such particles or immobilization would need to be measured, and using dissolved enzyme kinetics would only be an approximation of the actual performance.

For the enzyme-liquid separation processes required for two of the localization methods outlined, the equipment and efficiency requirements would be important parameters to consider. The equipment for slurry handling and solid-liquid separation as part of a recirculation loop is well known from wet limestone FGD processes [23] and could potentially be applied to enzyme processes.

A system where enzyme is held in the absorber was demonstrated by Akermin, Inc. under project number DE-FE0004228 [22]. Akermin's field trial on a PC flue gas slipstream at the National Carbon Capture Center, utilized CA immobilized in a porous high surface area polymer-based coating applied to packing material in the absorber. The immobilized enzyme was used to accelerate CO_2 absorption into two different solvents, a K_2CO_3 based solvent and a proprietary solvent. Localizing enzyme in the absorber by immobilization on a fixed surface allowed use of thermal stripping without causing enzyme inactivation, and benefits from very close equipment similarity to conventional solvent-based absorber-stripper configurations, and hence could be considered a ‘drop-in’ approach. The trial ran for more than 2800 hours without loss of CO_2 capture performance in spite of intermittent start-up and shut down and without changing the enzyme-coated packing, demonstrating the robustness potential of enzyme restrained in the absorber. A drawback to the coated packing approach is that enzyme would eventually lose activity, and replacement of packing in absorbers scaled for full power plant flue gas clean-up would not be trivial.

Some consideration has been given in the literature to in situ rejuvenation of packing surfaces, typically involving a chemical or affinity linkage between the enzyme and the surface that could be broken to wash out spent enzyme and afterwards be re-established by adding fresh enzyme, and, if needed, refreshing of the corresponding binding or affinity chemistry, however such approaches have not been demonstrated for a CO_2 capture system beyond lab scale.

In a system with enzyme localized to the absorption stage, low temperature vacuum stripping would not necessarily be required. Elimination of vacuum operation would reduce capital costs, reduce auxiliary power consumption and hence require a smaller PC boiler and associated equipment to achieve 550MWe net output. These cost reductions would be offset to some extent by the cost of localizing the enzyme in the absorber, and the impact on process performance would have to be assessed. Given the results observed in Case DB4 it is certainly possible that such a solution could result in a COE a few percent lower than that of NETL Case 10, however the performance of the configuration where enzyme is localized to the absorption stage and the effect of vacuum regeneration and non-vacuum regeneration on such a case would have to be assessed through practical demonstration.

Nevertheless processes, such as described in the present assessment, where dissolved CA enzyme recirculates throughout the system and can be readily replenished as needed could still provide an important practical alternative to localized enzyme processes, provided that the enzyme can sufficiently withstand the stripper temperature and thereby avoid excessive biocatalyst replenishment costs.

12 Conclusions

Using information gathered from the bench scale unit, validated kinetic data, PCC plant predictive models and industrial experience of PCC plant design and cost estimation the process and cost performance of several cases were analyzed and compared to NETL baseline Case 9 and Case 10 to judge relative performance. It was concluded that:

- Case DB1 is considered to be the most practical solution. Case DB1 shows a COE of 119.6 mills/kWh (2007$) which represents a 9.1% increase on the equivalent MEA based NETL Case 10.
- Case DB5 was modelled with no enzyme present, utilizing default kinetic parameters for K_2CO_3. The model predicted results show that with a non-enzyme-activated K_2CO_3 solvent a maximum capture rate of 17.7% was achieved. The presence of enzyme has a significant effect on the performance of the solvent and clearly illustrates why non-activated K_2CO_3 solvent has not been considered viable for ambient pressure flue gas scrubbing applications.
- Case DB2 shows that the application of a deeper vacuum in the stripper has a small benefit with a slight reduction in COE when compared to Case DB1. The small

increase in predicted performance is considered insufficient when compared to the greater uncertainty and technical risks associated with employing a deeper vacuum.

- Case DB4 gave the best performance with a COE of 116.2 mills/kWh (2007$), a 6.0% increase on NETL Case 10 [1]. Case DB3 shows a similar result with a COE of 116.3 mills/kWh (2007$).
- Predicted variable costs are the key differentiator in COE performance between the enzyme-activated cases and NETL Case 10. Exposure of the enzyme to thermal stress, even at moderate temperatures such as 70°C, results in degradation of the enzyme and a loss in performance that requires removal and replacement of degraded enzyme. The high enzyme make-up rate required to maintain system performance results in a significant operating cost that is reflected in the increased variable costs and ultimately the COE.
- The longevity of the enzyme could be improved from the current prototype in two stages of commercial development.
- First stage enzyme development can be achieved through a combination of further enzyme-solvent dose optimization and selection among known CA variants with favorable longevity characteristics at the required process conditions. The result, when stage 1 development of enzyme is applied to Case DB1, is a reduction in COE from 119.6 mills/kWh (2007$) to 111.2 mills/kWh (2007$) representing a 1.5% (rather than 9.1%) increase when compared to NETL Case 10.
- Second stage enzyme development could involve a variety of different approaches, such as protein engineering, chemical modification and enzyme-immobilization, used alone or in combination to achieve further enzyme longevity improvements, resulting in reduced replenishment rates and corresponding cost reductions. The result of applying the stage 2 enzyme development to Case DB1 is a further reduction in COE to 108.4 mills/kWh (2007$), a performance that represents an improvement of 1.1% when compared to NETL Case 10.
- A notable and practical aspect of the bench scale to full scale feasibility assessment was establishment of a dissolved enzyme replenishment approach, including spent enzyme removal.
- The limitations of predicting full scale plant performance from such data has been noted. It is recommended that further work on a larger scale test unit be carried out to reduce the level of uncertainty by validating performance on a larger scale particularly with regards to vacuum performance, enzyme longevity and enzyme kinetics.
- The further enzyme and process developments outlined could result in economically favorable operating parameters for the enzyme-activated process that would provide an alternative process option to the MEA approach with potential environmental advantages.

13 Recommendations for Further Work

A number of potential process improvements have been identified from the results presented in this report and these should be investigated further to determine the best possible operating parameters for the enzyme-activated process. Further aspects and improvements to be investigated include:

- Process and cost performance with enzyme localized in the absorber stage and utilizing vacuum regeneration with low enthalpy K_2CO_3 based solvent.

- Process and cost performance with enzyme localized in the absorber stage and utilizing non-vacuum regeneration, to avoid the additional capital costs and auxiliary power consumption associated with the construction and operation of vacuum systems.
- Utilization of heat sources from outside the PC plant steam cycle to provide heating in the reboiler, such as process waste heat or low grade steam, and determine cost and process performance.
- Utilization of less costly materials of construction that could be compatible with K_2CO_3, or other bicarbonate based solvents.
- Utilization of alternative solvents or mixed solvents that could provide higher CO_2 loading capacity, resulting in reduced recirculation rates so reducing equipment sizing and minimizing pumping energy and reboiler duty.
- Development of enzymes with improved longevity, especially improved longevity at elevated temperature conditions. Such longevity improvements could also be possible by developing modified enzymes. The modification of enzymes could include utilizing enzymes in combination with physical matrices, such as particles, or through chemical modifications.
- Development of enzymes or modified enzymes with reduced dosage requirement to minimize initial fill and replenishment costs. Reduced dosage could, for example, be achieved by increasing the enzyme activity per unit amount or by localizing the enzyme to the gas-liquid interface.
- Further investigation of the cases presented herein or potential improvements to these should be validated on a larger scale PCC test plant utilizing enzyme-activated K_2CO_3 solvent to reduce uncertainties and confirm the predicted process and cost performance for implementation at full scale.

Revision History

Rev	Description	Date	Released by	Approved by
0	Initial submission to DOE/NETL			

References

[1] "Cost and Performance Baseline for Fossil Energy Plants – Volume 1: Bituminous Coal and Natural Gas to Electricity," DOE/NETL-2010/1397 Study, Final Report, Rev. 2a, (September 2013)

[2] W.G. Gorman, J.K. Reinker, Steam Turbines for Utility Applications, GER-3646C, GE Power Generation, 1994

[3] Coal Specifications for Quality Guidelines, Revision 0, May 31, 2005

[4] NETL Power Systems Financial Model Version 5.0, December 2008

User Guide available at: http://www.netl.doe.gov/business/solicitations/ssc2008/references/PSFM%20User%20Guide.pdf

[5] Gross Domestic Product: Chain-type Price Index, Seasonally Adjusted, http://research.stlouisfed.org/fred2/series/GDPCTPI

[6] "Quality Guidelines for Energy System Studies: Capital Cost Scaling Methodology," DOE/NETL-341/013113, January 2013, http://www.netl.doe.gov/File%20Library/research/energy%20analysis/publications/QGESS_CapitalCostScalingMethodology_Final_20130201.pdf

[7] "Cost Estimate Classification System – As Applied in Engineering, Procurement, and Construction for the Process Industries; TCM Framework 7.3 – Cost Estimating and Budgeting," AACE International Recommended Practice No. 18R-97, 2005

[8] "Conducting Technical and Economic Evaluations – As Applied for the Process and Utility Industries; TCM Framework: 3.2 – Asset Planning, 3.3 Investment Decision Making, AACE International Recommended Practice 16R-90, 2003

[9] Economic Evaluation of CO_2 Storage and Sink Enhancement Options, Tennessee Valley Authority, NETL and EPRI, December 2002

[10] Smith, Lawrence A., Gupta, Neeraj, Sass, Bruce M. and Bubenik, Thomas A., "Engineering and Economic Assessment of Carbon Dioxide Sequestration in Saline Formations," Battelle Memorial Institute, 2001

[11] Ciferno, Jared P. and McIlvried, Howard, "CO_2 Flow Modeling and Pipe Diameter Determination," February, 2003

[12] Economic Evaluation of CO_2 Storage and Sink Enhancement Options, Tennessee Valley Authority, NETL and EPRI, December 2002

[13] Parker, N., "Using Natural Gas Transmission Pipeline Costs to Estimate Hydrogen Pipeline Costs," Institute of Transportation Studies, University of California, Davis, CA, 2004.

[14] Gresham, R. L., Apt, J., et. al, "Implications of Compensating Property-Owners for Geologic Sequestration of CO_2," Department of Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, PA, 1999.

[15] Klass, A.B., Wilson, E.J., "Climate Change and Carbon Sequestration: Assessing a Liability Regime for Long-Term Storage of Carbon Dioxide," 58 Emory Law Journal 103, 2008

[16] Senate Bill No. 2095, 61st Legislative Assembly of North Dakota, January 6th, 2009

[17] House Bill No. 661, Louisiana House of Representatives Regular Session, 2009

[18] Enrolled Act No. 20 (Original House Bill No. 58), 60th Legislature of the State of Wyoming, General Session, 2009

[19] Overview of Monitoring Requirements for Geologic Storage Projects. IEA Greenhouse Gas R&D Programme, Report Number PH4/29, November 2004

[20] "Recommended Project Finance Structures for the Economic Analysis of Fossil-Based Energy Projects," DOE/NETL-401/090808, September 2008

[21] Matuszewski, M., "System Analysis Guidance for Assessment of Carbon Capture Technology: Targeting $40/tonne CO_2 Captured Costs," NETL CO_2 Capture Technology Meeting, July 2014 http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/M-Matuszewski-NETL-System-Analysis-Guidance.pdf

[22] Reardon, John, et al, "Advanced Low Energy Enzyme Catalyzed Solvent for CO_2 Capture: Final Scientific/Technical Report", DE-FE0004228, December, 2013

[23] U.S. Environmental Protection Agency. 1981. Sulfur Oxides Control Technology Series: Flue Gas Desulfurization – Lime/Limestone Processes. EPA Summary Report No. 625/8-81-006

[24] Slater, Jonathan, et al, "Preliminary Environmental, Health and Safety Risk Assessment on the Integration of a Process Utilizing Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration with a Subcritical PC Power Plant", DE-FE0007741 – Task 7.1, December 31st, 2014

[25] Salmon S. and A. House. 2015. Enzyme catalyzed solvents for CO_2 separation. *In* Shi, F. and B. Morreale (eds.) Novel Materials for Carbon Dioxide Mitigation Technology. pg. 23-86. Elsevier B.V. Available online: doi:10.1016/B978-0-444-63259-3.01001-6

[26] "Technical Assessment Guide (TAG®) – Power Generation and Storage Technology Options", EPRI, December 2009

[27] U.S. Department of Labor's Producer Price Index for Finished Goods, http://data.bls.gov/cgi-bin/surveymost?wp

[28] Lu, Yongqi, Ye, Xinhuai, Zhang, Zhaohui, Khodayari, Arezoo, and Djukadi, Tatiana, Development of a carbonate absorption-based process for post-combustion CO_2 capture: the role of biocatalyst to promote CO_2 absorption rate, Energy Procedia, 4 (2011) 1286-1293