FINAL SCIENTIFIC / TECHNICAL REPORT

Report Title:	Final Scientific / Technical Report for DOE Project DE-FC26-07NT43084 - Development of Biomimetic Membranes for Near Zero PC Power Plant Emissions
Report Type:	Final Scientific / Technical Report
Reporting Period Start Date:	March 28, 2007
Reporting Period End Date:	July 31, 2009
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Date Report was Issued:	March 13, 2011
DOE Award Number:	DE-FC26-07NT43084
Name and Address of Submitting Organization:	Carbozyme, Inc. 19 Laurel Wood Dr. Lawrenceville, NJ 08648

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Final Scientific / Technical Report for DOE Project DE-FC26-07NT43084 - Development of Biomimetic Membranes for Near Zero PC Power Plant Emissions

(For the period of March 28, 2007 through July 31, 2009)

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ABSTRACT

Project Objectives

The first objective of this project was to develop, evaluate and compare two different CO_2 separation (capture) systems. The second was to carry the preferred solution to pre-pilot development and testing. To achieve these objectives we undertook several infrastructure enabling elements – 1) development of a preferred catalyst coupled with its immobilization onto a microporous polymer membrane, 2) design and development of a microporous membrane-based, contained liquid membrane permeator and a membrane-based absorber/desorber apparatus, 3) development of a resin-wafer electrodialytic absorber/desorber apparatus, 4) development and demonstration of a pre-treatment process to condition the feed gas stream, 5) and development of computer modeling of the components and of the integrated system.

The first technology was an enzyme catalyzed, membrane supported, contained liquid membrane apparatus whose gas capture was pressure/vacuum and temperature driven. A first embodiment was as a permeator, *i.e.* a combined absorber/desorber in a single housing. The second embodiment was as discrete absorber and desorber units. The second technology was an enzyme catalyzed, ion exchange resin wafer electrodialytically-based separation. For each of these technologies the objective was to design, manufacture, test and demonstrate the apparatus, first in the laboratory and then at pre-pilot scale, and to run it for sufficient time at the pre-pilot scale to demonstrate stability even in the face of upset. Tests would include several ranks of coal, which had been appropriately pre-treated to remove NOx, SOx and particles, to a pre-determined acceptance level, as a basis for demonstrating efficient CO_2 capture. The pre-pilot tests would be run at the Energy and Environmental Research Center (EERC) in North Dakota. A larger scale test (400m^2 test unit) would later be run also at EERC.

An economic goal was to compare the cost of CO_2 capture by each of these methods with values obtained when using MEA (monoethanolamine) as a baseline case. Other metrics included capital and operating expense, parasitic loss and cost of electricity.

A final goal was to carry out an initial examination of market forces to understand what barriers to entry for installation of CO_2 capture equipment might exist and their relative importance.

Key Results

Working with our colleagues at the EERC we characterized the various boilers and flue gas mitigation apparati operative for about half the coal fired power plants in the US fleet. The data were grouped in terms of rank of coal burned. Analysis revealed a substantial range of NO_x and SO_x emissions. These values were the basis for evaluation of enzyme and carbonate carrier fluid sensitivity to acid-forming agents. The conclusion was that SO_x posed the most significant problem by virtue of its acidification of the carrier fluid. A second potential problem was ionized mercury, which might reduce enzyme activity. EERC developed a post-FGD polisher to manage the SO_x problem and reduce the flue gas concentration from 50-60ppmv to <10ppmv. EERC demonstrated the ability of this polisher to reduce even the most egregious SO_x emission level to a

value acceptable to our CO_2 capture system. This provided assurance that the enzyme/membrane system could operate with a variety of coals, provided that the flue gas stream had been conditioned.

We examined a variety of isozymes (provided by Sigma, Novozymes and Prof. J. G. Ferry of the Pennsylvania State University) to select a preferred variant for purposes of facilitating CO_2 uptake. CAM (the Ferry product) proved to be a preferred isozyme. CAM is a thermophilic form of carbonic anydrase that exhibits high activity at high temperature and is thus positioned to accept flue gas at its exit temperature (~50°C). To guarantee heterogeneous catalysis we developed a surface activation method for the polymer membranes coupled with a proprietary immobilization method to hold the enzyme catalyst at the gas-liquid interface. The immobilization process was designed such that the enzyme could be removed and replaced on demand. This was demonstrated for five cycles.

We generated several novel module designs to allow full countercurrent CO_2 extraction. CO_2 was extracted by conjoint use of vacuum and a thermal drive. This resulted in a modest vacuum and modest heating with the heat derived from the compression step.

Hollow fiber permeators were constructed to a final size of $0.5m^2$. These could be rearranged to form a $1m^2$ absorber and a $1m^2$ desorber. Such devices were capable of capturing 1.6 moles of CO_2 per day from a 15% CO_2 ersatz flue gas stream. In addition, initial testing was begun using an $11m^2$ scaled up hollow fiber apparatus designed and constructed by Membrana-Charlotte. The latter was run only under control conditions. However, Membrana did design and model the next larger size apparatus.

In parallel, working with our collaborators at Argonne National Laboratories (ANL) we designed, constructed and tested several electrodialytic designs each using the ANL patented resin wafer technology for electrochemically driven CO_2 capture and release. These early data indicated that this is a viable method for CO_2 capture and would benefit from further development.

A baseline economic and performance model was developed by our colleagues at Siemens Power Generation. They provided a model based on MEA as a CO_2 capture chemistry using DOE Cases 10 and 11 as the format basis. The data showed that the model was applicable to power plants ranging from 200-800MW in size. The model was designed to serve as a comparison basis for evaluating operation of the various Carbozyme designs.

With regard to future commercialization, the most important observation (generated by Visage Energy) was that unless and until a cap-and-trade system is in place there is no significant political driver to promote installation of CO_2 capture equipment. The second observation was that, because of cost transfer, it would be easier to carry out tests and later installations in PUC regulated states than in unregulated states.

This project was terminated early by mutual agreement between Carbozyme and the DOE NETL. Consequently other tasks will not be described.

ACKNOWLEDGEMENTS

This report is an account of research sponsored by the U.S. Department of Energy's National Energy Technology Center (DOE/NETL) under Project No. D6-FC26-07NT43084.

Special thanks are due to each and every one of the team members:

Carbozyme Team

Technical Team: Robert M. Cowan, David A. Smith, Xiaoqiu Wu, Liping Wang, Haibin Chen, Randal L. Reali, and Yla Angso.

Management Staff - Ira L. Sider, John Marsizewski, Alexander Vucelic, Judith N. Trachtenberg, Kelly Uckun, Arthur Cram, and Liza Sobhani.

Sub-contractors

Energy & Environmental Research Center: Melanie Jensen, Jason Laumb, and Robert R. Jensen.

Siemens Power Generation: Dennis Horazak, Andy Palisewski, and Robert Shannon.

Novozymes North America: Sonja Salmon, and Paria Saunders.

Argonne National Laboratory: Seth Snyder, Yupo Lin, Michael Henry, and Datta Surav.

Visage Energy: Will Johnson, and Daryl-Lynn Roberts.

Membrana-Charlotte: Gareth Taylor, Patrick McMurray, Allen Pittman, and Amit Gupta.

SRI International: Kevin O'Brien.

ElectroSep: Paul Parisi.

Kansas State University: Peter Pfromm.

Pennsylvania State University: J. Greg Ferry, and Sabrina Zimmerman.

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Finally, we would like to express sincere appreciation for the very excellent support and guidance of our DOE/NETL COR, Jose D. Figueroa as well as other DOE/NETL personnel including Sean Plasynski, Jared Ciferno and Lynn Brickett.

Responsibility for the content of this report, however, remains solely with the authors of this report.

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1. EXECUTIVE SUMMARY

This project was targeted at developing, testing, comparing and contrasting two different methods for CO_2 capture with the idea that the preferred method would go through to scale up and large-scale pre-pilot testing using three ranks of coal. An economic and engineering analysis would be forthcoming as would an analysis of the barriers to market entry.

Towards these goals the project was divided into nine tasks and involved 8 subcontractors. On July 31, 2009, Carbozyme and DOE agreed mutually to end the program. At that time seven of the tasks were completed in whole or part. The remaining tasks were cancelled.

Along with our sub-contractors, consultants and collaborators we accomplished the following:

1. An analysis of the flue gas streams from US power plants on the basis of rank of coal, boiler structure and cleanup equipment. This provided a range of flue gas chemical composition and revealed that SO_x, ionized mercury and particulates might provide some issues for the Carbozyme capture system. To manage this, our collaborators at EERC designed, built and tested a SO_x scrubber. They demonstrated its ability to reduce to under 5ppmv independent of the amount of SO_x in the flue gas stream, tested to a maximum of 3300ppmv in the pre-FGD outlet stream. In parallel, Carbozyme measured the sensitivity of the system to NO_x, SO_x and various acids in typical flue gas streams. We determined that SO_x and possibly mercury might pose some difficulties impacting on permeator performance. The EERC work provided a method to control SO_x to acceptable levels. The wet scrubber also removed particles.
2. Enzyme selection focused first on development of an enzyme that exhibited high activity while operating at high temperature. A second consideration was that the enzyme be inexpensive to make in a purified form. Unpurified material had a tendency to wet the polypropylene membrane. A preferred enzyme, CAM, was identified and used for experiments. Enzyme was also immobilized by a proprietary surface activation method by creation of an ultrathin polyamino acid (PAA) layer. The PAA was constructed to allow ready remove-and-replace capabilities. Using this process we demonstrated very high retained activity for a minimum of 90 days.
3. Membrana-Charlotte was selected as preferred membrane and module supplier. They cooperated in design of a novel multi-tubesheet module that could be used as a permeator, an absorber or a stripper.
4. In cooperation with Argonne National Laboratory (ANL) we designed, developed and tested an electrodialytic CO_2 absorber and stripper using the ANL resin wafer technology. The design relied on a pH shift as a means of capture and of release of CO_2. Enzyme facilitation was used. The data obtained demonstrated the viability of the approach. However, at that time the cost was on the order of \$65/tonne of CO_2 captured. The approach would benefit from further development.

5. We demonstrated very effective permeator performance with both bulk and immobilized enzyme. In addition, we were able to construct and test hollow fiber arrays to operate in absorber and desorber modes. Using an enzyme coated, surface activated polypropylene hollow fiber array running at 23°C we demonstrated very effective CO_2 capture capability and were run for periods up to 10 days. The permeance was 18.9 GPU with a CO_2/N_2 selectivity of 693 based on the expected absorptive capacity of the MTF at expected conditions of a pressure swing of 77.34 to 18.17cmHg and Temperature swing 52 to 65°C based on OLI calculations and engineering analysis. This selectivity is just a ratio of total moles transferred and not the typical ratio of permeance. If it were typical a typical permeance ratio, it would be much greater, because the Partial Pressure of N_2 is much greater than CO_2 Preliminary engineering analysis indicated a parasitic load of <20%.
6. Our colleagues at Siemens Power Generation performed an economic and engineering evaluation of CO_2 capture systems using MEA as the baseline as applied to the DOE cases 10 and 11 for power plants with and without CO_2 capture. The analysis method provided linear data from 200-800MW sized plants. The analytical method was to be the basis for comparison of the Carbozyme technology to MEA.
7. Our colleagues at Visage Energy initiated evaluation of the characteristics of the utility market with respect to introduction of new technologies, in particular carbon capture technologies. They recognized a variety large number of technical, economic, political and cultural factors as needing to be in place as enabling elements. They further recognized that testing would be easier in PUC regulated states than in deregulated states.
8. Cancelled.
9. Cancelled.
10. Management was carried out for all of the tasks noted.

2. INTRODUCTION

Carbon dioxide (CO_2) capture and storage (CCS) is considered central to the idea of retaining the US coal-based electricity generation fleet by capturing most of the produced CO_2 and disposing of it underground, largely in saline reservoirs, to minimize the impact of this greenhouse gas on global climate. The DOE has set forth performance expectances for CO_2 capture methods. In specific it has set a target parasitic load of less than 20% and an increased cost of electricity of less than 35%. These requirements include capture of 90% of the CO_2 from a coal fired flue gas stream and qualifying the stream for insertion into a pipeline at a pressure of at least 12.4MPa (1800 psi).

Traditional absorption methods use a primary amine to form a carbamate, via a homogeneous reactant process, which takes place in a tower-type contactor. Desorption occurs in a second tower contactor. The desorption process occurs at elevated temperature (~120°C) that is realized by means of high value steam. Use of this steam reduces the steam available for power generation contributing substantially to the parasitic load.

Our approaches to carbon capture differ significantly from those currently in place, viz. a tower with trays, or a packing, unstructured or structured, with gas indirect contact with a reactive carrier fluid. In one of our designs, the permeator or absorber/desorber, the gas was separated from a carrier fluid by a microporous membrane; a CO_2 catalyst was immobilized onto the liquid side of the microporous membrane. Gas-liquid contact occurred by diffusion at a catalyzed interface. The principal design apparatus was structured as a permeator, a device where both the absorption and desorption occur in a single vessel. The permeator was constructed of microporous, hydrophobic, woven hollow fiber membranes arranged like a jelly-roll of alternating layers for absorption and desorption separated by a liquid film. The liquid film (contained liquid membrane – CLM) operated as the permeation barrier. Enzyme was immobilized at each the absorption and desorption liquid surfaces to derive the catalytic benefit for each operation. A mass transfer fluid (MTF) replaced the CLM in the absorber/desorber format. The MTF flowed between the absorber body and the desorber body. Desorption occurred by means of a vacuum, a water vapor sweep and modest temperature swing (50-65°C).

In the second design enzyme was to be immobilized onto or in the near vicinity of a mixture of cationic and anionic resin wafer beads where the beads were placed between ion exchange membranes or bipolar membranes. The objective was to replace, in whole or in part, the vacuum with a pH shift.

In either case the immobilized enzyme operates as a heterogeneous catalyst. Its location at the gas-liquid interface maximizes contact of CO_2 and the catalyst converting CO_2 to bicarbonate ions. The ionized bicarbonate dissolves immediately in the bicarbonate carrier fluid. The catalyst is the enzyme carbonic anhydrase, the fastest CO_2 catalyst known. The driver for absorption is the partial pressure of CO_2 in the feed gas into an alkaline solution. Desorption occurs by reversal of this process where the very low partial pressure of CO_2 in the sweep gas extracts CO_2 from the bicarbonate laden fluid.

Inasmuch as the lifetime of the enzyme and the membranes are different, with the enzyme being the shorter, it was necessary to develop methods to allow the enzyme to be removed and replaced, *in situ*, thereby avoiding disassembly of the apparatus.

This project was very ambitious. Successful demonstration of this system depended on considerable infrastructure as evidenced in terms of materials production, assembly and operation. This project was targeted at realizing both the infrastructure and primary product and process goals, integrating them and progressing in scale-up from small laboratory size to a pre-pilot demonstration using real coal flue gas, and comparing operation for three different ranks of coal.

The first three goals focused heavily on infrastructure development. The first goal was to identify and qualify an enzyme and an enzyme production process to provide a catalyst that could operate at high rate and at high temperature and whose delivery form would not wet the polymer membrane. Wetting of the membrane is taken to mean that the membrane pores normally filled with gas become water filled thereby greatly decreasing diffusion and adding a barrier that diminishes capture performance. Related to this was the ability to produce large quantities of enzyme readily and at low cost. Included was identification of an enzyme supplier. Part of this requirement also was development of a method for immobilization of the enzyme onto the membrane surface with the ability to remove and replace the enzyme *in situ*.

Another goal, carried out in parallel, was to identify a membrane, a membrane design and a membrane / module supplier that would manufacture the design. The membrane properties were identified as high hydrophobicity, resistant to wetting, high porosity, long lifetime, and ease of manufacture into a module with preferred properties. The module design had to provide sufficient access points to allow ready delivery and extraction of all requisite fluids.

Inasmuch as the physical and chemical properties and composition of flue gas is unique to each power plant a first issue was to determine boundary conditions, *i.e.* the range of composition to understand the range of scenarios that need be managed. Inasmuch as the enzyme or the carrier fluid might be susceptible to some of the chemicals in the flue gas it was necessary to determine their sensitivity and then to devise means of either decreasing sensitivity or of reducing the concentration of such a component before it was presented to the enzyme or to the carrier fluid, *i.e.* conditioning the feed. Similar considerations were applicable to the membrane and its interaction with particulates in the feed.

System design and testing

With a preferred enzyme, membrane and module in hand the next step was to integrate these into a performing test bed, a hollow fiber contained liquid membrane (HFCLM) permeator, that would effectively extract CO_2 from an ersatz flue gas mixture targeting performance sufficient to achieve the DOE goals noted above. This element was designed as a two-step program. Step one was laboratory performance. Step two was pre-pilot testing (at EERC). This HFCLM approach would be assessed on the basis of its economic and engineering performance.

As noted, the HFCLM design in the permeator module uses a vacuum to extract CO_2. An alternative approach is to extract CO_2 by means of a pH swing inasmuch as carbonic anhydrase is relatively pH sensitive in contrast to amine absorbents. To this end,

working with personnel from Argonne National Laboratory we designed an electrodialytic (EDI) apparatus that would generate a surfeit of hydroxyl ions at one site and an excess of protons at the other. Used in conjunction with their resin wafer design and carbonic anydrase we anticipated significant improvement in CO_2 capture capability. This element was also designed as a two-step program with step one being laboratory performance and step two being pre-pilot testing.

A critical step to qualifying these designs was to compare them on the basis of energy expended and CO_2 avoided with MEA and with each other as a means of down selecting among possible capture methods. An evaluation process needed to be constructed to achieve this end, *i.e.* economic and engineering analyses.

In anticipation of installation of CCS and commercialization of this technology we undertook an assessment of the state and evolution of the marketplace to provide guidance on methods of facilitating pilot scale testing in functioning power plants.

3. TASK 1 - FLUE GAS PRE-TREATMENT SYSTEM SPECIFICATION

Goal

Task 1 – Flue Gas Pre-Treatment System Specification, carried out on conjunction with EERC, addressed the interaction of the feed stream composition and the performance sensitivity and stability of the Carbozyme HFCLM System. A first step was to detail the physicochemical properties of likely flue gas streams in order to determine which components might be problematic for operation of the enzyme, immobilization of the enzyme, or performance of the liquid membrane. The next step was to determine the manner in which any these flue gas materials or properties would affect the immediate performance and long-term system stability of the Carbozyme HFCLM System. The last step was to develop strategies, equipment and processes, *i.e.* pretreatment regimens, to control or minimize any adverse effects due to feed gas stream properties.

Approach

Flue Gas Specification

EERC approached selection of the most appropriate pretreatment system for the Carbozyme HFCLM System by identifying the range of combustion flue gas constituents that would be encountered most often. The steps to acquisition and analysis of this information were:

- Identify the most commonly used coals and perform proximate and ultimate analyses.
- Determine the most common plant configurations (*i.e.* boiler type and attendant APC devices) for the U.S. power production fleet.
- Estimate the composition of the flue gases produced by the most commonly mined coals when fired in the most common plant configurations as based on data from the Carnegie Mellon University Integrated Environmental Control Model (IECM).
- Examine the estimated flue gases to identify the expected range for each flue gas component.
- Compare the expected component ranges with the Carbozyme permeator acceptance criteria (based on the Direct Measurement predictions and testing) to determine the cleanup requirements of the pretreatment technology.

Table 3-1 lists the coals burned most commonly in the United States. These data are based on the majority of coal that is mined and used for this purpose. It does not indicate that such coals are used exclusively in those power plants. The names used for lignite and subbituminous coals commonly are the same as their mine name; bituminous coals are usually referred to by their seam name.

Table 3-1. Largest-Production Bituminous Coal, Subbituminous Coal, and Lignite Mines in the United States in 2005 (Energy Information Administration, 2007)

Mine Company	State	Production, short tons (US)
Powder River Basin (PRB) Subbituminous Coal		
Black Thunder/Thunder Basin Coal Company LLC	Wyoming	87,586,375
North Antelope Rochelle Complex/Powder River Coal Company	Wyoming	82,688,918
Cordero Mine/Cordero Mining Company	Wyoming	37,836,811
Jacobs Ranch Mine/Jacobs Ranch Coal Company	Wyoming	37,277,820
Caballo Mine/Caballo Coal Company	Wyoming	30,532,313
Antelope Coal Mine/Antelope Coal Company	Wyoming	29,953,375
Eagle Butte Mine/Rag Coal West, Inc.	Wyoming	24,133,324
Buckskin Mine/Triton Coal Company	Wyoming	19,568,058
Belle Ayr Mine/Foundation Coal West Incorporation	Wyoming	19,326,943
Bituminous Coal		
Bailey Mine/Consol Pennsylvania Coal Company	Pennsylvania	11,076,662
McElroy Mine/McElroy Coal Company	West Virginia	10,419,128
Enlow Fork Mine/Consol Pennsylvania Coal Company	Pennsylvania	9,773,883
Foidel Creek Mine/Twentymile Coal Company	Colorado	9,369,969
Sufco/Canyon Fuel Company LLC	Utah	7,568,934
Cumberland Mine/Cumberland Coal Resources, LP	Pennsylvania	7,090,672
Century Mine/American Energy Corporation	Ohio	6,630,590
Elk Creek Mine/Oxbow Mining, LLC	Colorado	6,545,485
Loveridge No. 22/Consolidation Coal Company	West Virginia	6,359,281
Emerald Mine No. 1/Emerald Coal Resources, LP	Pennsylvania	6,343,553
Lignite		
Freedom Mine/Coteau Properties Company	North Dakota	15,007,352
Falkirk Mine/The Falkirk Mining Company	North Dakota	7,743,341
Jewett Mine/Texas Westmoreland Coal Co.	Texas	6,916,386
Oak Hill Strip/TXU Mining Company LP	Texas	5,983,205
Beckville Strip/TXU Mining Company LP	Texas	5,524,859
South Hallsville No. 1 Mine/Sabine Mining Company	Texas	4,602,752
Big Brown Strip/TXU Mining Company LP	Texas	4,438,449
Center Mine/BNI Coal Ltd.	North Dakota	4,367,952

* The bituminous coal from Pennsylvania and West Virginia is a Pittsburgh No. 8 coal.

The most common power plant configurations were determined using EERC's U.S. Environmental Protection Agency (EPA) mercury information collection request (ICR) database (Laumb et al., 2000). In addition to coal analyses and mercury emissions, data contained in the database for each power plant include rank of coal fired, plant size, and

installed pollution control devices. The various configurations that were evaluated are shown in Table 3-2.

Table 3-2. Most Common Existing U.S. Power Plant Configurations

Boiler Type and Pollution Control Devices	Number of Units	Percentage of Total U.S. Fleet
Bituminous Coal		
Wall-Fired, In-Furnace NO_x Control, Cold-Side ESP, No SO_x Scrubber	89	8.2
Wall-Fired, No NO_x Control, Cold-Side ESP, No SO_x Scrubber	63	5.8
Tangentially Fired, In-Furnace NO_x Control, Cold-Side ESP, No SO_x Scrubber	94	8.7
Tangentially Fired, No NO_x Control, Cold-Side ESP, No SO_x Scrubber	66	6.1
Wall-Fired, In-Furnace NO_x Control, Cold-Side ESP, Wet SO_x Scrubber	42	3.9
Wall-Fired, In-Furnace NO_x Control, Fabric Filter, No SO_x Scrubber	6	0.5
Tangentially Fired, In-Furnace NO_x Control, Fabric Filter, No SO_x Scrubber	4	0.4
Subbituminous Coal		
Wall-Fired, In-Furnace NO_x Control, Cold-Side ESP, No SO_x Scrubber	22	2.0
Wall-Fired, No NO_x Control, Cold-Side ESP, No SO_x Scrubber	14	1.3
Tangentially Fired, In-Furnace NO_x Control, Cold-Side ESP, No SO_x Scrubber	37	3.4
Tangentially Fired, No NO_x Control, Cold-Side ESP, No SO_x Scrubber	25	2.3
Tangentially Fired, In-Furnace NO_x Control, Cold-Side ESP, Wet SO_x Scrubber	6	0.5
Tangentially Fired, No NO_x Control, Cold-Side ESP, Wet SO_x Scrubber	5	0.5
Wall-Fired, In-Furnace NO_x Control, Fabric Filter, No SO_x Control	9	0.8
Tangentially Fired, In-Furnace NO_x Control, Fabric Filter, No SO_x Control	5	0.5
Lignite		
Wall-Fired, In-Furnace NO_x Control, Cold-Side ESP, No SO_x Scrubber	2	0.2
Tangentially Fired, In-Furnace NO_x Control, Cold-Side ESP, Wet SO_x Scrubber	4	0.4

Tangentially Fired, No NO_x Control, Cold-Side ESP, Wet SO_x Scrubber	4	0.4
Tangentially Fired, In-Furnace NO_x Control, Dry SO_x Scrubber, Fabric Filter	3	0.3
Total Plants, All Coals	500	46.1

*Assuming 1084 units in the United States (total from the EERC mercury ICR database).

The proximate, ultimate, and trace element analyses for the most commonly fired coals within each coal rank were obtained from the U.S. Geological Survey (USGS) database (U.S. Geological Survey, 2007). These are listed in Table 3-3, Table 3-4 and Table 3-5. Many of the coals contained in the database are stored by seam name. The *Keystone Coal Industry Manual* was used to access these coals by identifying the seams from which they were mined (Keystone Coal Industry Manual, 1992). The data obtained from the USGS Web site were averaged and the average values input into the Carnegie Mellon IECM to obtain an estimate of the flue gas composition that would be produced. (Carnegie Mellon University Department of Engineering and Public Policy, 2007).

The base plant was taken to be a 500MW, subcritical, PC-fired power plant operating at 75% capacity. The boiler is 89% efficient and has a steam cycle heat rate of 8.3MJ/kWh (7880 Btu/kWh). It operates with 20% excess air (stoichiometric). When in-furnace NO_x control is employed, it consists of low-NO_x burners and overfire air that have a maximum NO_x removal efficiency of 60% and an actual NO_x removal efficiency of 47%. Air leakage at the preheater is 19% (stoichiometric). Gas leaves the air preheater at 149°C (300°F) and the economizer at 371°C (700°F). Nominally, 80% of the ash enters the flue gas stream. With regard to sulfur entering the system, 2.5% is retained in the fly ash. SO_3 makes up 0.8% of the SO_x, while NO is 95% of the NO_x. The ESP removes 99.7% of the particulate. Its actual SO_3 removal efficiency is 25%. For configurations that use a fabric filter, a reverse-gas baghouse system was assumed. Its removal efficiency is 99.7%, with an actual SO_3 removal efficiency of 90%. Flue gas desulfurization, when employed, usually consisted of a wet limestone process with no bypass. The maximum SO_2 removal efficiency for this system is 98%; scrubber SO_2 removal efficiency is 89.7%, while 50% of the SO_3 is removed. The particulate removal efficiency is 50%, and 90% of the chloride is removed in the scrubber. For one lignite configuration, a dry desulfurization system with lime was used. The dry system removed 89.7% of the SO_2 and 90% of the SO_3. The maximum SO_2 removal efficiency is 98%. None of the particulate is removed in this system.

Table 3-3. Analysis of Bituminous Coals

Component	Pittsburgh No. 8 Seam	Sufco (Sevier County, UT)	Foidel Creek (Routt County, Wadge Bed, CO)	Century Mine (Belmont County, OH)
C, wt%	71.92	61.38	62.01	66.18
H, wt%	4.90	4.45	4.42	4.67

N, wt%	1.42	1.23	1.42	1.20
S, wt%	2.47	0.85	0.65	3.64
O, wt%	6.11	10.73	12.29	6.70
Cl, ppmw	353	74	242	747
Hg, ppmw	0.130	0.101	0.060	0.186
Ash, wt%	10.64	13.78	9.50	14.59
Moisture, wt%	2.52	7.59	9.71	3.01
Higher Heating Value, Btu/lb	12,910	10,801	10,906	12,000

Table 3-4. Analysis of PRB Subbituminous Coals

Component	Rosebud	Black Thunder	Buckskin/Belle Ayr/Antelope	North Antelope/ Eagle Butte	Caballo	Cordero
C, wt%	50.25	53.59	50.83	44.59	45.79	48.87
H, wt%	3.40	3.57	3.35	2.53	3.00	3.49
N, wt%	0.74	0.83	0.75	1.21	0.88	0.90
S, wt%	1.31	0.35	0.40	0.76	0.72	0.57
O, wt%	10.56	14.16	12.26	14.89	12.54	12.00
Cl, ppmw	70	123	76	140	103	76
Hg, ppmw	0.097	0.136	0.113	0.072	0.085	0.138
Ash, wt%	9.67	5.35	5.82	7.29	7.33	7.17
Moisture, wt%	24.04	22.15	26.61	28.72	29.71	27.04
Higher Heating Value, Btu/lb	8680	9164	8658	7105	7665	8474

Table 3-5. Analysis of Lignites

Component	Big Brown Strip	Freedom	Center	Falkirk
C, wt%	46.77	41.70	44.04	35.33
H, wt%	3.42	2.67	3.04	2.73
N, wt%	0.83	0.63	0.75	0.63
S, wt%	0.67	1.18	0.60	0.47
O, wt%	12.93	12.67	14.50	10.79

Cl, ppmw	70	100	ND[a]	70
Hg, ppmw	0.219	0.130	0.100	0.077
Ash, wt%	7.90	10.68	5.08	16.30
Moisture, wt%	27.47	30.44	31.99	33.90
Higher Heating Value, Btu/lb	7957	6903	7376	5965

[a] Data not available.

Estimated Flue Gas Composition

All 92 of the flue gas compositions that were estimated using the IECM are listed in Table 3-6. Note that these are the compositions of the flue gases following cleanup by the pollution control (APC) systems.

Table 3-6 Flue Gas Component Concentration Ranges as Estimated Using the IECM

	Bituminous Coals			PRB Subbituminous Coals			Lignites		
Flue Gas Component	**Min**	**Max**	**Med**	**Min**	**Max**	**Med**	**Min**	**Max**	**Med**
N_2, wt%	65.34	69.83	69.13	62.91	67.69	67.03	62.31	68.75	62.96
O_2, wt%	5.58	5.99	5.92	5.39	5.82	5.74	5.34	5.89	5.41
H_2O, wt%	4.79	10.56	5.45	6.72	12.53	7.53	7.73	14.81	12.28
CO_2, wt%	17.11	18.29	17.87	17.25	19.12	18.31	16.94	18.48	17.66
CO, wt%	0	0	0	0	0	0	0	0	0
HCl, ppmw	0.58	56.1	20.0	0.748	16.9	7.9	0.71	12.4	4.2
SO_2, ppmw	296.2	5137	1324	328.1	2252	850	384.3	2137	397
Sulfuric Acid (equivalent SO_3), ppmw	0.32	19.4	4.4	0.04	0.31	0.3	0.01	1.01	0.25
NO, ppmw	165.9	374.6	200.5	160.7	484	214.0	151.2	459.3	175.6
NO_2, ppmw	13.4	30.2	16.2	13.0	39.0	17.3	12.2	37.1	14.2
NH_3, ppmw	0	2.4	2.4	0	2.5	2.4	0	2.5	2.4
Ar, wt%	1.11	1.19	1.18	1.07	1.15	1.14	1.06	1.14	1.07
Mercury Elemental, $\mu g/Nm^3$	1.4	4.74	2.73	8.07	13.7	10.32	9.55	22.64	12.66
Oxidized, $\mu g/Nm^3$	0.18	11.07	6.36	0.13	4.57	3.09	0.16	7.55	1.78
Total, $\mu g/Nm^3$	1.76	15.81	9.08	8.2	18.26	12.89	9.71	30.19	14.54

Particulate concentrations tended to be lowest when a wet desulfurization system was part of the pollution control scheme. In addition, the cold-side ESP removed more particulate than the fabric filter. Table 3-7 presents the estimated ranges of particulate

loadings in the flue gases of the various coal ranks. At this time, the ability of particulate loadings, at the magnitude indicated by the IECM, to overwhelm the Carbozyme HFCLM System, is unknown, but it will be important to minimize fine particulate that might affect the HFCLM permeator membrane operation.

While fly ash particulate can potentially cause physical blockage of the membrane, the particulate likely will also contain SO_3 aerosols. These small-diameter aerosols can pass through most SO_x removal systems, including wet desulfurization systems, since they do not have sufficient momentum to impact the water droplets. Once they pass through the APC devices, they could potentially impact the ability of the Carbozyme HFCLM System to separate CO_2 from the flue gas by acidifying the CLM. Selection of a pretreatment process will need to consider this issue. Carbozyme expects the HFCLM permeator to capture any SO_3 aerosols that escape the pretreatment process.

Table 3-7 Estimated Flue Gas Particulate-Loading Ranges

Coal	Power Plant Configuration	Particulate Concentration, g/Nm^3
Bituminous Coals		
Sufco	Cold-side ESP, wet SO_x scrubber	0.0297
All but Foidel Creek	Fabric filter, no SO_x scrubber	0.0349
PRB Subbituminous Coals		
North Antelope/Eagle Butte	Cold-side ESP, wet SO_x scrubber	0.0282
All	Fabric filter, no SO_x scrubber	0.0349
Lignites		
Falkirk	Cold-side ESP, wet SO_x scrubber	0.0274
All but Freedom	Fabric filter, no SO_x scrubber	0.0349

Carbozyme's Permeator Acceptance Criteria

Carbozyme identified flue gas contaminants that might have deleterious impacts on the performance of the HFCLM permeator, including particulates, strong oxidants, and water-soluble contaminants such as acid gases [Jensen et al., 2008]. Particulates have the potential to adsorb to the membrane surface and occlude micropores. Separately, they might be able to clog the bore of the hollow fiber. Strong oxidants or other highly reactive species have the potential to react with the polymer membrane, limiting its useful life. Acid gases and water-soluble oxidized metals will be absorbed in the CLM, which is a lightly alkaline buffer. Inasmuch as CO_2 capture is an acid-base process as the acids accumulate the performance of the HFCLM permeator will decrease because of a change in pH. Ionized divalent metals such as mercury (Hg^{++}) can act as inhibitors to CA. The Carbozyme HFCLM System acceptance limits are given in Table 3-8.

Table 3-8 Carbozyme HFCLM System Acceptance Limits

Contaminant	Acceptance Concentration	
HCl	7.08 ppmv	8.46 ppmw
HF	7.08 ppmv	4.64 ppmw
SOx (SO2 + SO3)	7.08 ppmv	18.57 ppmw
NOa	191 ppmv	195 ppmw
NO2b	20.4 ppmv	20.8 ppmw
Hg (as Hg2+)	3.54×10−6 ppmv	0.033 μg/m3
Hg (as Hg 2+) with 1 mM EDTA	>2×10−3 ppmv	>18.7 µg/m3

[a] Assumes 3.7% capture as HNO_3 and K_i = 100 mM.
[b] Assumes 34.7% capture as HNO_3 and K_i = 100 mM.

Comparison of Flue Gas Component Ranges with Carbozyme's HFCLM System Acceptance Requirements

The pretreatment approach that could apply to virtually all flue gases, derived from a rank of coal must produce a gas stream that is acceptable to the Carbozyme HFCLM System when the components vary within the ranges shown in Table 3-9. The table shows that the pretreatment system primarily will have to remove SO_2 in order to meet the Carbozyme HFCLM System acceptance requirements.

Table 3-9 Comparison of Flue Gas Component Ranges with Carbozyme HFCLM System Acceptance Requirements

Flue Gas Component	Minimum	Maximum	Median	Carbozyme HFCLM System Requirements	Typical Removal Required, %
HCl, ppmw	0.58	56.10	7.9	8.46	None
SO_2, ppmw	296.2	5100	1000	18.57	98.1
SO_3, ppmw	0.01	19.4	0.5		
NO, ppmw	151.2	484.0	200.5	195	2.7
NO_2, ppmw	12.2	39.1	16.2	20.8	None
Oxidized Mercury, μg/Nm^3	0.13	11.07	3.24	0.033	None (with EDTA[a])

[a] Ethylenediaminetetraacetic acid.

Candidate Pretreatment Technologies

Three commercially available technologies were evaluated for their ability to remove the contaminants of concern.

- **Condensing Heat Exchangers** - Condensing heat exchangers remove both sensible and latent heat from the flue gas by countercurrent, indirect contact, with a cooling fluid, typically cool water. As the flue gas temperature drops, acid gases condense on the tube surfaces. Ultrafine particulate can be trapped by the condensate. When they are large enough, the condensate droplets fall and are captured in the bottom of the

unit. This technology was not selected because it likely would not condense the SO_3 aerosols. In addition, certain fly ashes (such as those produced by PRB subbituminous coals) might form concrete when combined with the relatively small amount of water condensed from the flue gas.

- **Wet ESPs** - Wet ESPs capture ultrafine particulate and acid mists. They are often installed after a wet flue gas desulfurization system. Because the flue gas has been cooled to moisture saturation, the gaseous pollutants condense to form aerosols that are captured by the wet ESP. Wet ESPs are very effective in removing SO_3 mists and submicron particulate and provide additional mercury control. Unfortunately, they are probably not appropriate for all coal-fired utilities because those that burn coals that form Class C fly ash (e.g., PRB subbituminous coals) will form concrete in the wet ESP. Other coal-fired plants for which the operators want fuel flexibility might not use wet ESPs for the same reason.

- **Wet Scrubbers** - One of the simplest methods for removing acid gas components from flue gas is a wet scrubber. This technology is relatively simple to design and fabricate and can be tailored to the specific needs of a process by changing tray or packing design and altering properties of the solvent. This technology can be employed where ultrafine Class C fly ash is present because the volume of water present is significantly large in comparison with the amount of fly ash, thus eliminating any potential for forming cement within the pretreatment system.

EERC determined that a polishing wet scrubber would be able to produce a flue gas stream to meet the CLM permeator SO_x requirements. Addition of EDTA to the HFCLM permeator should permit acceptance of the predicted mercury levels. EERC and Carbozyme were unable to find a suitable, commercially available research-scale scrubber system. Thus, EERC designed and fabricated a polishing scrubber for this purpose and then installed it on the EERC's Conversion and Environmental Process Simulator (CEPS).

Scrubber Design Detail

The polishing scrubber was designed using a conventional chemical engineering approach for the design of a packed gas absorption tower as described in Treybal (1980) with additional information provided by Schifftner and Hesketh (1996). The scrubber was designed for an 11wt% $CaCO_3$ slurry flowing at 0.34 kg/min (0.75 lb/min). It was fabricated from acrylic - 10.16 cm (4 in.) in diameter with a packed height of 1.3m (4.28 ft). The polisher cylinder contained Norton Intalox ceramic saddle packing, 13mm (½-in.) (Figure 3-1).

During the testing to verify the ability of the scrubber to remove SO_x to the low levels required by the Carbozyme CLM the CEPS system was fired on natural gas to obtain a baseline SO_x value and then spiked with SO_2 at levels that were roughly equal to the high, low and mid-SO_2 concentrations estimated earlier.

The SO_x levels leaving the polishing scrubber were logged every 30 seconds during each test period. The scrubber slurry consisted of 11wt% $CaCO_3$ in water at a flow rate of 91 L/hr (24 gal/hr). Table 3-10 summarizes the conditions for each of the test

periods. Although the mechanical systems on the scrubber functioned flawlessly, challenges with the gas analysis system prevented the measurement of SO_2 below 50 ppm.

The SO_2 removal verification test was repeated with the CEPS infrared SO_2 analyzer replaced by an ultraviolet SO_x analyzer (AMETEK Model 921 Single Gas Analyzer) at the exit of the polishing scrubber. (Ultraviolet gas analyzers do not have the issues with interference from CO_2 and water at ultralow SO_2 concentrations, as is the case with infrared analyzers). The minimum detection limit for the ultraviolet gas analyzer was 4 ppmv for this test.

Figure 3-1. Close-up view of polishing scrubber during shakedown testing

Results and Discussion

The CEPS system was tested on January 14, 2009. The CEPS system was fired on natural gas for roughly 30 min to obtain a baseline SO_x value and then spiked with SO_2 to determine the ability of the polishing scrubber to remove SO_2 from the flue gas. We evaluated three different SO_2 levels: 860, 2600, and 3300 ppmv. Table 3-10 summarizes the test conditions.

Table 3-10 Verification Test Conditions

Test Period	Duration	SO2 Input Concentration
Baseline	30 minutes	–
Low SO_2 level	60 minutes	850 ppmv
Moderate SO_2 Level	50 minutes	2500 ppmv
High SO_2 level	35 minutes	3300 ppmv

Table 3-11 shows the mean and standard deviation for SO_2 concentrations at three points within the CEPS system (post-combustor, post-wet FGD, and post-polishing scrubber). As the low standard deviations indicate, the data are very precise; i.e. the data points tended to be close to the mean values for each test period at each analyzer.

Table 3-11 SO_2 Concentrations Recorded During Verification Test

SO_2 Concentration Leaving Combustor, ppmv		SO_2 Concentration Leaving Scrubber 1, ppmv		SO_2 Concentration Leaving Polishing Scrubber, ppmv	
Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev
859	28	56	1.5	5.09	0.14
2583	61	62	5	5.03	0.04
3298	82	53.5	1	4.82	0.14

Figure 3-2 plots the concentrations of SO_2 leaving the polishing scrubber during the three verification test periods. The data are shown as a logarithmic plot to better show the detail of the SO_2 levels exiting the polishing scrubber. The plot shows that the system was able to reach steady-state conditions during each of the test periods, meaning that the results are representative of operation at those conditions. The plot also shows spikes in the CO_2 concentration exiting Scrubber 1. These spikes, caused by cleaning of water from the gas analyzer filter, did not the result of sudden increases in SO_2 concentration at that point in the system.

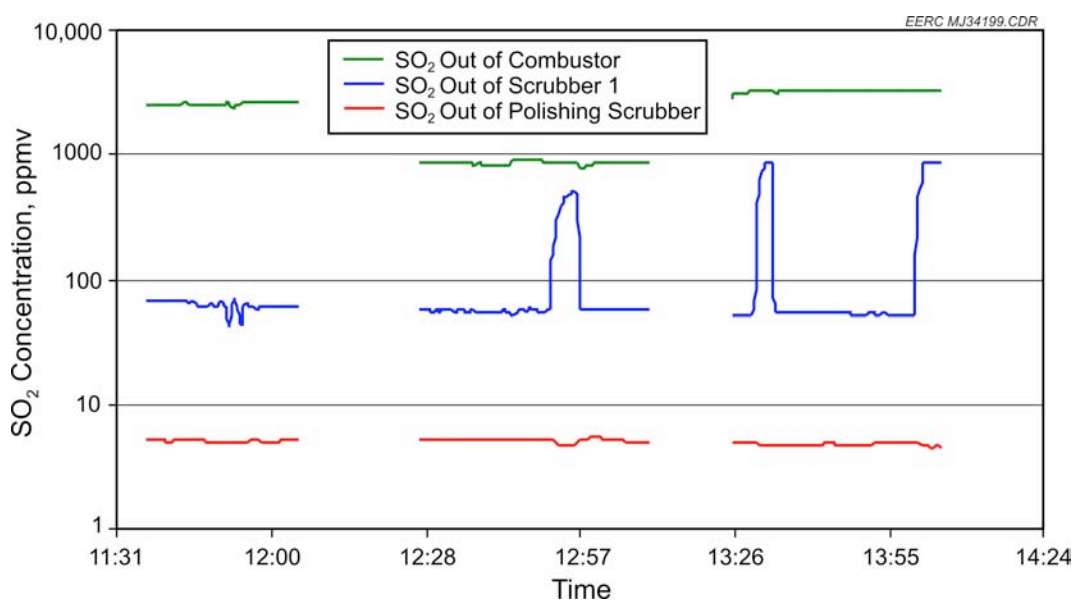


Figure 3-2. SO_2 concentrations. Polishing scrubber verification test

Conclusions

Acceptance values for flue gas pollutants were generated for the permeator taking into consideration two factors. The first was the pH change of the CLM as a function of

time, given the fact that it is refreshed only slowly to compensate for any loss of water. The level of SOx proved to be the only acid gas of significance. For 90 days of continuous operation, per preferred permeator performance the maximal SOx level desired was <10ppmv. pH sensitivity is an issue applicable to every acid-base chemistry absorption process. The second issue was the sensitivity of the enzyme to candidate flue gas pollutants. In this case the only contaminant of possible importance was ionized mercury (Hg^{++}). This can be managed with mercury capture equipment or by addition of EDTA to the CLM.

Analysis of the flue gas composition derived from a large number of power plants combusting a wide variety of ranks of coal by means of many different burners provided a clear idea of the emission levels that would be encountered. On this basis we designed experiments to spike the CEPS output in order to determine the efficacy of SOx removal by the FGD and the polisher unit.

The polishing scrubber whose design was based on estimated flue gas concentrations and using standard chemical engineering scrubber design principles, demonstrated its ability to remove SO_2 to the low levels required by the Carbozyme process, *i.e.* <10ppmv, more specifically it achieved a SO_2 value of ~5ppmv.

4. TASK 2 - ENZYME DEVELOPMENT AND SELECTION

Goal

Task 2 – Enzyme Development and Selection addressed the development of a preferred enzyme catalyst. The catalyst selected is the enzyme carbonic anhydrase (CA - E.C. 4.1.1.1) the fastest known catalyst for the conversion of CO_2 to bicarbonate and the reverse. However, for it to be used effectively in this engineered system numerous components, subsystems and processes have to be integrated in a specific manner. This task was focused on the following items:

- Development of a specific isozyme that operates at high temperature and exhibits high turnover. In the event that the isozyme created does not meet performance criteria in the $0.5m^2$ HFCLM permeator, then modify the isozyme as needed to meet the programs needs. (Isozymes - enzyme variants – are referred to as isoforms by geneticists, to recognize differences in family structural organization, *e.g.,* monomer vs. dimer, etc.)
- Development of a method for immobilizing the enzyme on the polymer surface at the gas-liquid interface such that the enzyme exhibits high stability, long lifetime and that the immobilization system exhibits high mass transfer efficiency.
- Selection an expression system, *i.e.* a host cell and growth system, to express the enzyme that exhibits high yield and ease of capture of the product.

This Task was a joint effort of Carbozyme (testing and qualification) and Novozymes (design, development, manufacture). It also enjoyed input from Prof. J. G. Ferry of the Pennsylvania State University (PSU). Inasmuch as the project was terminated before completion, the selection of an expression system for isozyme production was not undertaken to any meaningful degree and will not be discussed.

Approach

Development of a High Efficiency Expression System for a Thermophilic Enzyme

The goal of this subtask was to select a preferred isozyme that had a high turnover, operated well at elevated temperature, and was stable. A first consideration was the format of the preferred isozyme, *i.e.* would it be provided as a purified material or as a crude product (technical grade - TG) - a partially cleaned material derived from a cell exudate, a cell lysate or a cell paste. This consideration is important because a crude product would be expected to be far less expensive but have a greater likelihood of wetting the polymer membrane and, as it consists of many different proteins it would be difficult to determine how much of the CA would be immobilized on the polymer membrane surface when using standard protein assays.

A - Enzyme Source

Candidate enzymes that exhibit preferred properties can be obtained in one of three ways: 1) identification of a preferred wild type, 2) rational design to change the known amino acid sequence in a logical manner using modern molecular biology methods, or

3) directed evolution wherein the operating conditions under which the expression host live are modified to favor selection of a host cell that contains the enzyme with preferred properties.

In prior work, we had identified a wild type thermophile – CAM – that operated effectively to a temperature as high as 85°C. It had two limitations. The first was that its activity was an order of magnitude lower than the fastest mesophile CA - α-BCA II. Second, large-scale expression was difficult in *E. coli* most probably because it is a multimeric protein and does not assemble well when expressed in this organism.

For these reasons we sought an alternate approach. Prior work examined rational design starting with a mesophile protein. However, we achieved only modest increase in operating temperature. We decided therefore to start in this project with a new path, directed evolution, and we selected Novozymes, NA, to undertake this responsibility. Inasmuch as many of the thermophilic enzymes are multimers and many of the high turnover enzymes are monomeric, we suspect that Novozymes decided to use a monomer to start the directed evolution program. Novozymes' web site and patents indicate that their preferred host is a bacillus and that the enzyme would be harvested as a by-product of natural exocytosis. The primary material supplied to Carbozyme by Novozymes was referred to as Technical Grade (TG) enzyme - a crude cell exudate that contains many other proteins and cytoplasmic components.

Novozymes provided several different isozymes (NS81074, NS81103, NS81104) to Carbozyme for testing. Sample NS81074 was delivered both as Purified Grade (PG) and as TG. The TG material introduced several concerns. First, would other constituents in the mixture decrease the hydrophobicity of the polypropylene, *i.e.* wet the membrane. Second, would the presence of other constituents, including proteins, make it difficult to measure specific enzyme activity, as the background amino group reactions could not be separated from those attributable to CA. Third, when using a polyamino acid immobilization method would non-CA proteins and other cell debris occupy sufficient fraction of the free volume to make it difficult to achieve the enzyme density that might be desired.

Carbozyme tested Novozymes TG enzyme at a variety of concentrations and temperatures. Each of the enzyme samples we had – various Novozymes PG or TG samples, Sigma BCA II, and PSU CAM - was tested in bulk solution, in contact with native membrane samples and in contact with membrane materials that had been activated by means of exposure to chromic acid. Testing was carried out under four conditions: a) at room temperature, b) at 50°C, both at 1atm, and c) under a hydrostatic load of 5kPa in the presence of water or d) in the presence of CLM. The objective was to measure the time that elapsed before the liquid leaked through the membrane. All TG samples failed Leak Testing within a few minutes. Only Novozymes PG enzyme was acceptable for development efforts. TG proved unacceptable, later, for a second reason, namely that it was impossible, using ordinary protein assays to determine how much CA was present as compared to the total protein level in the mixture. The CA/protein fraction could be determined by use of zinc analysis but this specialized test was neither convenient nor inexpensive and certainly not commercially viable.

Carbozyme purchased α-BCA II from Sigma-Aldrich to continue development of the program. At the same time Carbozyme searched for an alternate enzyme provider.

Sigma-Aldrich derives its BCA II from erythrocytes (human or bovine) using standard lysis and resin binding purification methods. This monomeric isozyme is a mesophile with very high activity - ~1.4e6 mol/mol-s. However, it has a maximal operating temperature of <45°C. Further, it is inordinately expensive and thus would have no commercial future given the current purification method.

As the program progressed the importance of having an operating thermophilic enzyme grew. We purchased some purified CAM from Prof. J. G. Ferry at PSU. This isozyme was produced in *E. coli*; the crude cell lysate was then purified by means of an adsorption column. CAM had originally been isolated from *Methanosarcina thermophila* [Alber and Ferry, 1996]. To guarantee greater supplies we contracted a production source at PSU to provide additional enzyme for later experiments.

B - Enzyme Activity Test Methods

Each isozyme sample was subjected to a variety of qualification tests to determine which would be preferred for this project. Some of the test regimens were novel and necessitated development and qualification. While it would appear *a priori* that the α-BCA II enzyme would be disqualified due to its thermal profile it was the only isozyme readily available during the early part of the work and it had been used for many years in related work, thus it formed a baseline against which all other enzymes were compared.

Selection of a new isozyme required that the enzyme kinetics demonstrate performance that would be desired under the preferred operating conditions. This statement assumes that such relevant performance can be measured readily, *i.e.* that an assay exists that is appropriate. The measurements made under such unique conditions must be reliable. However, the operating conditions used for the capture and enrichment of CO_2 are far different than those used for standard assays – ice temperature and a weak buffer solution. To obtain operating case specific measurements necessitates corrections to compensate for the physical-chemical properties, *e.g.,* use of fugacity and activity vice concentration and consideration of any operative interactions with other species. It also requires a mathematical representation of the kinetics as a basis for predicting performance.

A first issue is to distinguish between thermostabile and thermophilic isozymes, *i.e.* those that do not denature at elevated temperature or would renature on return to mesotemperatures and those that would operate at elevated temperature. Validating that an isozyme is thermophilic requires that it operate at elevated temperature. This implies that there is a test to validate such a statement. Validation and characterization of the preferred isozyme properties involves measurement under the selected operating conditions.

Enzyme assays

Enzyme assays used for CA are of two classes – end-point and dynamic. End-point assays are run at fixed temperature and use specific reagents. CA dissociates water to generate an hydroxyl ion (bound to the zinc) and a proton (released to the bulk solution) a convenient way to measure activity is to determine the time required to achieve a given pH change, *i.e.* to achieve an end-point at given temperature and

solution chemistry. The end-point assays are commonplace and routine and thus used for everyday measurement. The rationale for 0°C measurements is to maximize the time difference between the catalyzed and uncatalyzed rates. This does not provide information about enzyme performance at elevated temperature, *e.g.,* >50°C. End-point test are not thermally variable and hence not applicable as thermophilic performance measures. Standard tests, carried out in established buffer systems, do not correspond to the chemistry of the contained liquid membrane (CLM) or of the mass transfer fluid (MTF). For these reasons they are indicators and correlates but are not a true measure of performance under defined operating conditions.

CA activity can be measured by a wide variety of tests. In Table 4-1 we list the end-point assays (4 on left) and the dynamic assays 5 on the right). For our purposes two changes are needed in the enzyme assay – to be able to be run at any given temperature and with any given solution chemistry. To this end we examined and developed several different assay procedures.

Table 4-1 Development of an Activity Test to Measure Performance at Elevated Temperature

CA Test Options									
	Manometric /N-CON Respirometer Activity	Maren	Wilbur-Anderson	p-NPA activity	Fluorimetric end-point and dehydration rate	pH-stat hydration rate	dynamic pH	Membrane Contactor - VSP, μmod	MIMS (membrane inlet mass spectrometry)
Temperature									
0 - 4°C	X	X	X	X					
Variable					X	X	X	X	X
Test Solution									
Prescribed	X	X	X	X					
Variable					X	X	X	X	X
Mechanism		pH change	pH change		fluorescence of an inclusion complex	pH change			
Measurement		colored dye; pH meter	colored dye; pH meter	colored dye	fluorometer	Amount of acid or base added to maintain pH	removal or addition of CO2 or bicarbonate	removal or addition of CO2 or bicarbonate	removal or addition of CO2 or bicarbonate
Special Requirement					dansylamide in cell	pH Stat apparatus	RGA or Ion Analyzer; temperature	RGA or Ion Analyzer	stable isotope
Note				indirect; measures esterase not proton change					

We examined four end-point analysis methods: Maren [1940], Wilbur-Anderson (W-A) [1948], manometric N/CON [Milburn and Beadle, 1960; Taha et al, 1966], intracellular fluorometry, and para-nitrophenyl acetate (p-NPA) [Pocker and Stone, 1968], and a pH-stat method [McIntosh, 1968]. The Maren and W-A assays use a colorimetric (or pH electrode) measure of pH change in a weak buffer solution. The manometric method measures changes in gas pressure as a function of consumption or production of gas, here CO_2. The Manometric / N-CON Respirometer test, developed by Novozymes was soon abandoned. Intracellular fluorometry is an effort to insert a pH sensitive fluorometric reporter into a cell that is producing CA to indicate the magnitude of CA production. It can be used to determine whether the CA is operative under the temperature at which the cells are growing. The p-NPA assay measures esterase activity, not CO_2 hydration, and is thus not a direct measure of CA activity.

Ultimately the Wilbur-Anderson (W-A) assay became the preferred first line evaluation tool.

We considered three different dynamic assays – pH stat, Dynamic pH, and MIMS (membrane inlet mass spectrometry) [Tu and Silverman, 1975]. The pH stat assay [1968] titrates base into a reaction solution to compensate for the induced acidification.

To deal with the need for a simple dynamic measurement applicable to a wide range of temperatures and operating solutions we developed what we named the Dynamic pH method as a candidate alternative to MIMS. The dynamic pH test differs from the Maren or W-A assays in that it provides a quantitative measure of changes in pH in the under conditions of varying temperature and solution chemistry to determine the influence of these variables on the activity of a particular CA isozyme. Additionally, the dynamic pH method can measure activity in both the CO_2 absorption and CO_2 desorption (stripping) modes. The idea was to measure simultaneously changes in pH and gas composition, the latter by means of RGA. This would allow the use of any temperature and any MTF. However, this new method needed a series of calibration curves to compensate for ion fugacity and gas activity at different temperatures and in different solutions. MIMS uses an RGA in conjunction with stable isotopes to determine the rate of formation or destruction of bicarbonate.

Dynamic pH Measurements

Detailed analysis of the initial data being returned by the Dynamic pH Method tests were at variance with expected pH values calculated by means of the DOE [1994] chemistry model. This necessitated the need for corrections for gas solubility at temperature and in the presence of various ions. A mathematical representation was made to seek the basis for the discrepancy. Among the approaches we examined were: 1) transformation of the dynamic pH data to CO_2 capture and release rates, 2) regression of the no-enzyme data to obtain estimates of kinetic parameters for a 0.5 M $NaHCO_3$ solution, and, 3) addition of gas-liquid mass transfer terms to the kinetic model. This last required confirmation that the current method is not gas-liquid mass transfer rate limited – *i.e.* validation that the Dynamic pH Method is reaction rate limited. This last required regression to the experimental data. Use of literature data proved inadequate and erroneous.

Incorporating the gas phase CO_2 measurement into the Dynamic pH Method test data yielded the basis for the discrepancy between the model calculations and the observed pH values for a given gas phase composition. To evaluate the potential validity of this hypothesis we carried out a series of measurements of equilibrium pH for solutions in contact with a range of gas phase concentrations of CO_2 and compared them to values calculated using two different, published, aqueous chemistry models – the DOE chemistry model and the OLI Systems StreamAnalyzer software. We found the OLI model to be superior in predicting the pH data. In specific, with OLI pH values differed by only 0.05 to 0.17 pH units from those observed. In contrast, the DOE model pH values differ by 0.15 to 0.41 pH units from those observed. Thus, the OLI model proved to be 2.5-3 times more accurate. Ultimately, the Dynamic pH Method and Membrane Contactor tests proved most valuable for demonstrating and quantifying CA activity at a given temperature and when using a given CLM fluid.

We did not go forward with MIMS studies [Tu and Silverman, 1975] due our inability to provide the stable isotopes central to this measurement method.

C - Enzyme Kinetics Modeling

The objective of the enzyme kinetics modeling effort was to better understand the interactions between solution chemistry, enzyme kinetics and HFCLM permeator performance. These models are also needed to evaluate the results of immobilization experiments. Initial work focused on evaluation of experimental data from the dynamic pH tests that were conducted using a solution of 0.5M $NaHCO_3$ at 50°C, without enzyme.

The approach used to develop the model was to begin with a non-catalyzed condition before including the enzyme catalytic step. As noted above, the initial data indicated a discrepancy between the pH values calculated by the chemistry model we were using [DOE, 1994] and the values we found experimentally which necessitated the inclusion of regression corrections.

As noted, the equilibrium chemistry of the DOE Model 1 exhibits a substantial deviation (0.15-0.41 pH unit) from our experiment measurements. Initially, we decided that when experimental data were not available, we would regress our own equilibrium constants on the basis of either the experimental measurements or the results of the OLI stream analyzer analysis. As shown in Figure 4-1, the values for Keq1 = 1.1×10^{-6}, Keq2 = 4.5×10^{-10} match quite well with the OLI analysis. These data values were used in our kinetic simulation of the 0.5 $NaHCO_3$ solutions. We were aware from previous studies that the OLI prediction typically deviates slightly (0.05-0.17 pH unit) from experimental data.

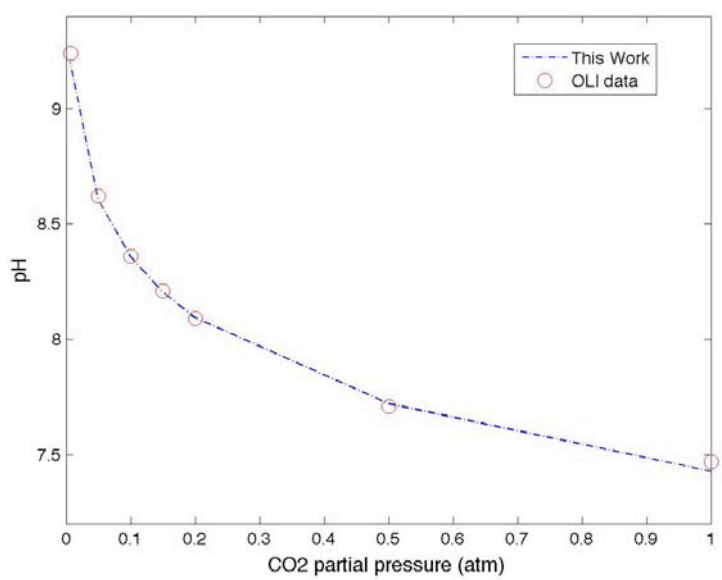


Figure 4-1. The regression equilibrium constants from the OLI stream analyzer

In an open system, it is critical to have a good estimation on the gas-liquid mass transfer for any practical model. The total CO_2 mass transfer at the gas-liquid surface can be expressed as equation (1).

$$\frac{d[DIC]}{dt} = kla\left([CO_2]_{surf} - [CO_2]\right) \quad (1)$$

DIC is the total dissolved CO_2 concentration, $[CO_2]_{surf}$ is the CO_2 concentration at the gas-liquid interface and can be calculated from gas-liquid equilibrium (e.g., $[CO_2]_{surf}$ is in equilibrium with 0.67% CO_2 at 1 atm in gas phase). *kla* is the mass transfer coefficient. In principal, with considerable experimental effort, *kla* can be accurately measured; alternatively it can be correlated. Our data suggested that we could use a single reasonable approximation as the predictions are not overly sensitive to the value of *kla*, here 0.1 s^{-1}.

With the equilibrium coefficients and *kla* held constant we could then regress the experimental data for the enzyme-free condition to set the non-enzymatic rate coefficients k1, and k4. These forward rate coefficients are the only adjustable parameters in our model. k-1 and k-4, the reverse rate coefficients, are calculated directly from the forward rate coefficients and the equilibrium constants. Figure 4-2 shows three separate experimental measurements compared with model calculated predictions using the regressed values for k1 = 0.037 s^{-1} and k4 = $4.05 \times 10^{3.3}$ These curves illustrate that the theoretical model provides an acceptable level of agreement with the experimental measurements.

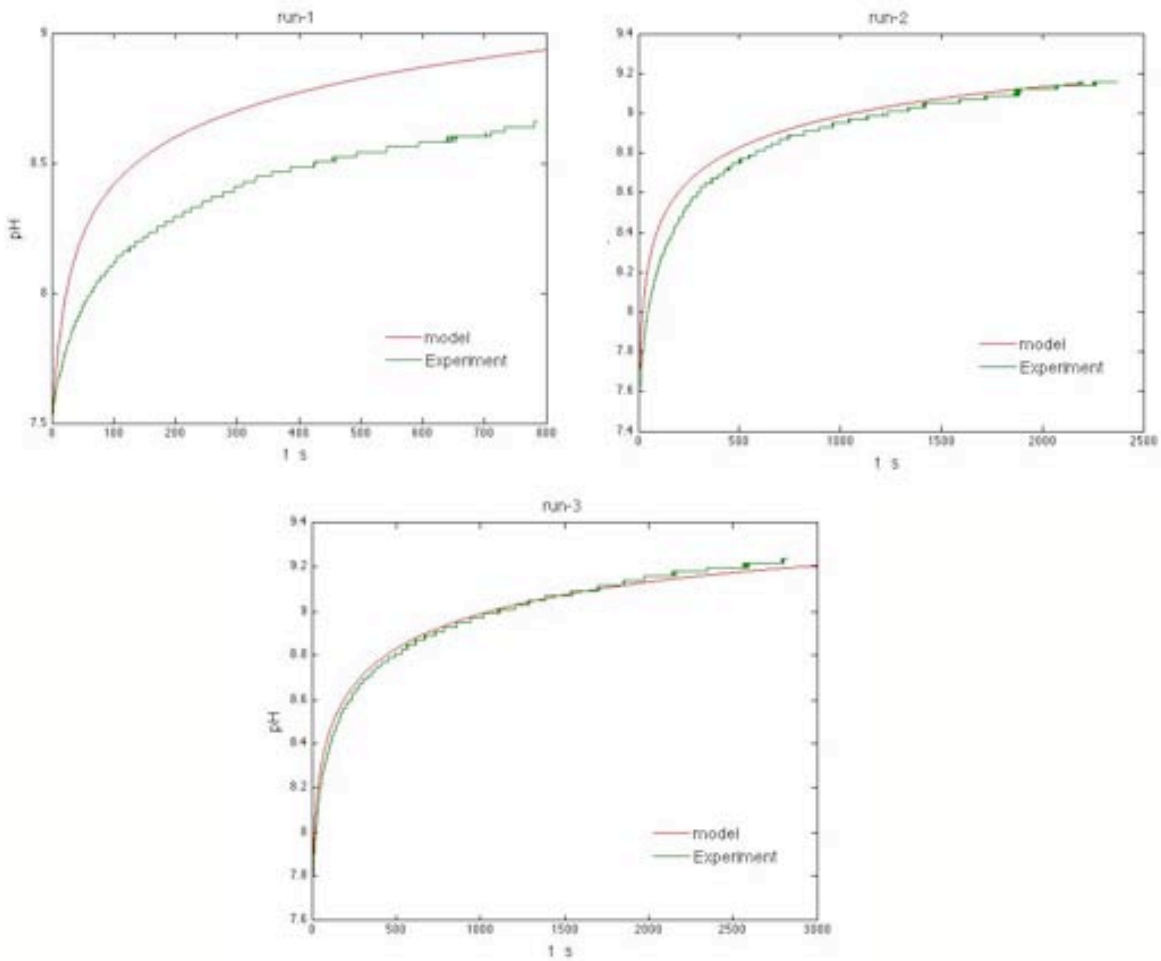


Figure 4-2. A comparison between the pH dynamic experiment and theoretical modeling

In 2008 Wylock and colleagues [2008] proposed a new model schema that introduces a static diffusion-reaction model to calculate CO_2 flux at an interface. To obtain a dynamic model we developed an iterative calculation, based on these reactions to update the bulk concentration values. We used the Comsol Multiphysics software both to construct the static diffusion-reaction model and to set up the iterative calculation to update the bulk concentration values.

The advantage of the diffusion-reaction model is that the transport diffusion coefficient no longer shows up explicitly as it does in Equation 1. *kla* is generally treated as a constant [Wylock et al, 2008], but here it is a variable whose value changes as a function of temperature, bubble size, and other parameters. In our model all the physical parameters - bd (bubble diameter), G (gas-liquid relative velocity), tc (contact time), and Se (gas-liquid interface area) - can be measured or can be estimated from the carefully designed experiments. Importantly, the dynamic value is incorporated in our modeling.

Figure 4-3 illustrates the results from using the physical parameters from the work of Wylock, et al [2008] and the non-enzymatic rate parameters from the DOE 1994

water chemistry model. The plot illustrates our preliminary simulation results for a 0.5M $NaHCO_3$ solution undergoing CO_2 desorption by stripping of the solution previously saturated with 20% CO_2 in air by means of a gas stream containing 1% CO_2 in air at 323K. Because the solution chemistry and system set up used by Wylock et al differed from ours (as noted above), the physical parameters they used were not applicable. As shown in Figure 4-3, we can simultaneously plot both the pH and DIC curves. This is the great advantage of this method; it provides two independent measures of dissolved CO_2. Using this approach we achieved a simulation that is consistent with the type of experimental data we collect using the dynamic pH method.

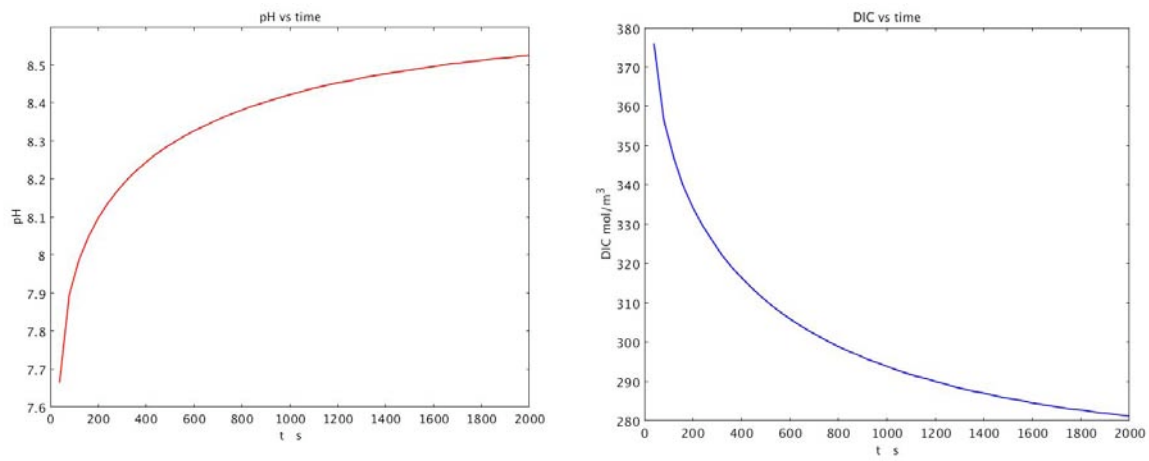


Figure 4-3. Simulated changes in pH (top) and DIC (bottom) as a function of time for reactions with no enzyme present. The scale value mirrors those used under experimental conditions

The next step was to incorporate Rowlett's [1984] enzyme kinetic model into the COMSOL modeling environment. In Rowlett's mechanism six intermediate enzyme forms and eight distinct reactions are used to represent the process of CO_2 hydration/dehydration in the presence of CA. A second buffer, other than $NaHCO_3/Na_2CO_3$, is used to accept the protons in solution. We first validated our model by reproducing the concentration profile calculated by Rowlett's program. Then, we removed the second buffer, and incorporated the enzyme kinetics, in coordination with the non-enzymatic kinetics, to generate a solution whose chemistry is close to that used in our experiments. Doing this retained the behavior shown in Rowlett's model. Figure 4-4 shows the reaction rate increases as the CA concentration increased. By these steps we could replicate the published results, modify the model to use the non-enzyme kinetics model in place of Rowlett's "buffer", and demonstrate that the response of the kinetics model was consistent with the previous findings.

This kinetics model was incorporated into the 1-D HFCLM permeator model (Task 5). The results from the Task 5 section are relevant towards optimization of CLM composition and enzyme activity. Inasmuch as these results are more relevant to permeator design and performance they are reported in that section.

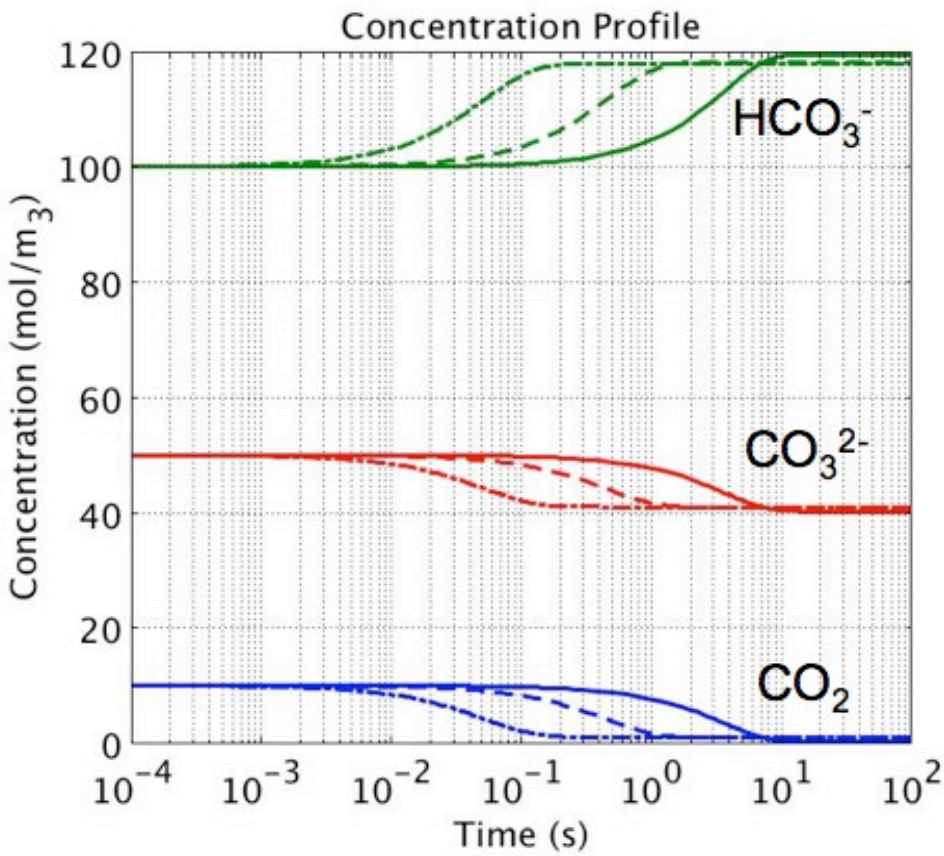


Figure 4-4. The dissolved CO_2, HCO_3-, and CO_3^{2-} concentration as a function of CA concentration at 0 (solid), 0.03 g/L (dash), and 0.3g/L (dash dot) mol/l. (Effectively 0.2 M $NaHCO_3$ solution.)

Figure 4-5 shows a comparison between experimental and model data for CO_2 dehydration at 50°C and 0.5M $NaHCO_3$. The solid (measured) and dashed (calculated) response curves demonstrated good agreement. The CO_2 fraction in headspace measured by RGA was plotted as a function of time in the same Figure 4-5. The model prediction of the CO_2 concentration is comparable (data not shown).

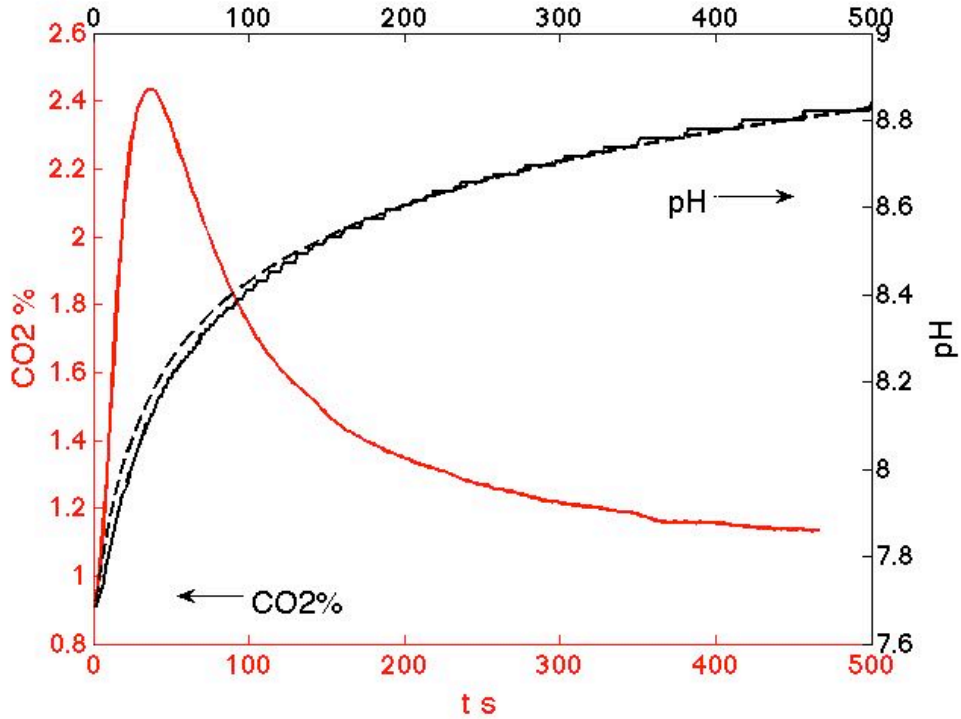


Figure 4-5. Comparison of measured (solid) and predicted (dash) pH change in solution for a dynamic pH CO_2 desorption experiment. The CO_2 concentration (red) in the headspace is also plotted for comparison

Figure 4-6 shows the inverse relationship between CO_2 in the headspace and pH in the CLM illustrating the very close tie between the two.

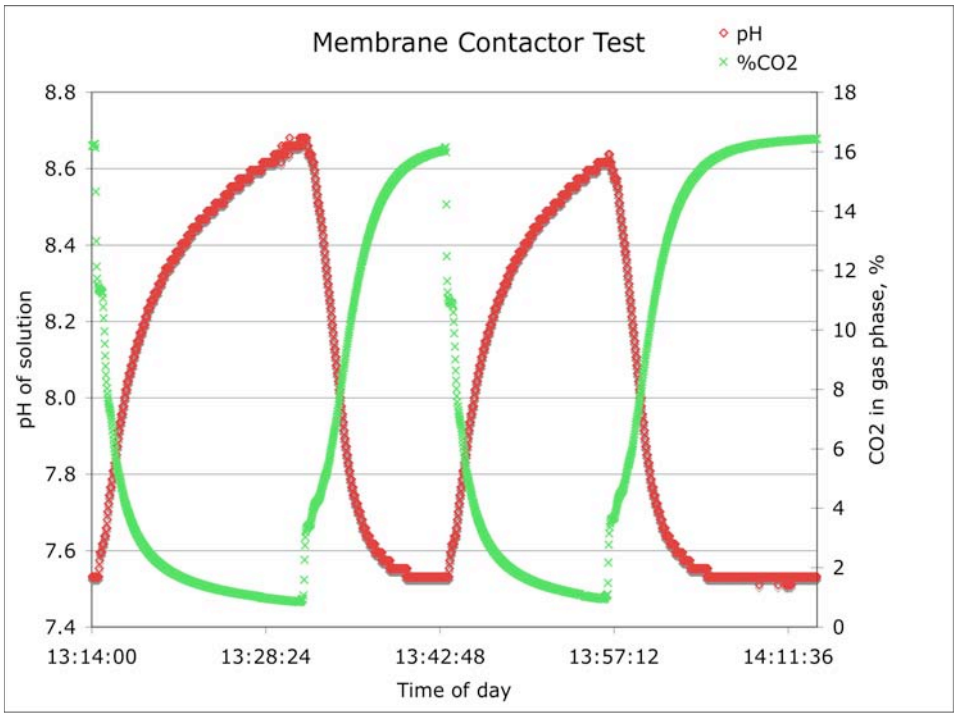


Figure 4-6. pH and CO_2 concentration values from a dynamic membrane contactor test (25°C, 0.1 M CLM buffer, No enzyme)

Development of a Robust Immobilization Linking System Rationale

The heterogeneous catalysis approach studied here has several potential advantages: most effective, least expensive, and most cost effective means of using an expensive catalyst. Its efficacy derives from the fact that the catalyst is at the gas-liquid interface guaranteeing the least diffusion delay, fewest solubility limitations, and most rapid transformational contact. It is least expensive because it minimizes the amount of material required. However, to achieve these benefits it is necessary to immobilize the catalyst onto the interfacial surface, here a microporous, hydrophobic, polymer membrane. This necessitates two actions – careful activation of the polymer surface and development of an immobilization procedure to meet key performance and longevity requirements.

The relative lifetime of the enzyme vs. that of the membrane is another issue that must be factored into the design and implementation of the immobilization method. Even a target lifetime of as much as 1 year for the enzyme will be far less than the 5 years or more for the polymer. Consequently, it will be necessary to develop a process that allows the enzyme to be removed and replaced, preferably *in situ*, to minimize removal and replacement of the modules. This requirement necessitated development of a method to remove and replace (R&R) the enzyme periodically. In so doing we would be immobilizing the enzyme by electrostatic bonding. As such we could encounter the possibility of elution of the enzyme or the immobilized polymer from the immobilization matrix. Among the ways to address this issue are the following: a) non-linked adsorption of the enzyme to the polymer, usually involving some denatured protein as a binder, b) covalent (hard) immobilization, c) immobilization via fusible link

such that one portion is covalently bound to the surface but the enzyme is modified to hold a link to the base material that can be broken given the correct chemistry, and d) an ionic immobilization where the enzyme is entrapped.

Option a) was explored by using polymer beads that had not been surface activated. Preliminary results indicated some immobilization of enzyme. However, it was not stable, washed off easily and was likely non-specific. The amount of enzyme needed for this approach would be cost prohibitive. Option b) was not explored, as it did not satisfy the R&R requirement. Option c) was enacted by means of the well-known nickel nitrilotriacetic acid (Ni-NTA) method. Here the enzyme is modified to add a tail consisting of numerous histidine residues (poly-His), which effectively bind to the nickel metal and which can be displaced by a wash containing imidazole. While Novozymes succeeded in preparing lab samples of a nickel adherent CA via a His-type tail, due to schedule and legal issues, this material was never examined or used. For these and other reasons our focus in this work was on option d).

A - Membrane Surface Activation

Polypropylene is a hydrophobic, non-reactive material, meaning that there are no surface groups available for reaction, thus the immobilizing agent cannot bind by means of covalent, ionic or electrostatic linkages to this material. This makes it necessary to activate the surface to create reactive groups.

Chromic Acid Activation

Initial studies used chromic acid as the activation reactant primarily because it operates well with the epoxy used for the tubesheets. Our epoxy supplier (Masterbond) provided a procedure and process applicable to polypropylene. Developmental studies targeted the Very Small Permeator (VSP) membrane samples, *i.e.* 25mm diameter circles of Membrana-Charlotte Celgard X2400 polypropylene. The membrane material was exposed to chromic acid for periods up to 30 min. at 25°C. Prolonged exposure yielded a yellow, then a brown color which correlated with progressive embrittlement of the polymer as evidenced by the resulting fragility and cracking. The goal was select a time and temperature for activation sufficient to provide reactant groups but not so long as to incur physical damage to the polymer.

We tested the treated membranes for possible structural compromise by subjecting them to leak testing, *i.e.* a hydrostatic load was imposed across the membrane. A time-concentration-temperature curve was generated to define the activation process that imposed the least damage while still supporting immobilization. The surface, examined by means of FTIR, showed that activation resulted in the formation of hydroxyl groups that could be used as attachment sites. This protocol could now be used on flat sheet (FS) and hollow fiber (HF) material. Membranes subjected to the preferred treatment regimen were candidates for later enzyme immobilization studies, specifically using the polyethyleneimine (PEI) method (see below).

The chromic acid activation method was particularly sensitive to the exact exposure time. Despite initial success several residual problems continued to plague this method. One was that the activation process could continue despite washing. A second was that the chromic acid activation process was not commercially viable due to the adverse

environmental impact of large-scale chromic acid use and the cost associated with its safe disposal. This latter concern promoted examination of other, greener methods.

Plasma Activation

We explored several different plasma treatment conditions as applied to both FS and HF. These varied in terms of duration, power and the presence of various chemistries in the reaction vessel. A first observation was the difference in surface properties of the FS and HF materials. This turned out to be due to the addition (by the manufacturer) of various chemicals to the FS material. The result was that it reacted quite differently than did the HF. Consequently the results using the two different materials were not readily comparable.

For this reason, initial studies of enzyme immobilization on FS plasma activated surfaces were abandoned in favor of testing on HF directly. This decision, in turn, required production of a new test bed. In response, we created MiniModules (Fig. 4-11), *i.e.* a small roll of HF that could be tested directly and in a manner similar to that previously used for the FS (see below) and later MicroModules (μMod – Fig. 4-12) which consisted of a length of HF in a casing, provided by Membrana-Charlotte. While the FS could be organized to function as a permeator, an absorber or a desorber (stripper) the MiniModule or μMod, as designed, could only operate in absorber or desorber modes.

The first control was to determine if the plasma treatment changed the fundamental pore properties of the membrane. We compared gas permeance between untreated and plasma treated HF. No change was detected. This control allowed the next step – Enzyme Immobilization. Details of membrane testing are given below (Performance Analysis with MicroModules).

The results shown in Figure 4-7 indicate that all three modules were about equivalent suggesting that membrane plasma activation had neither an adverse nor a beneficial effect.

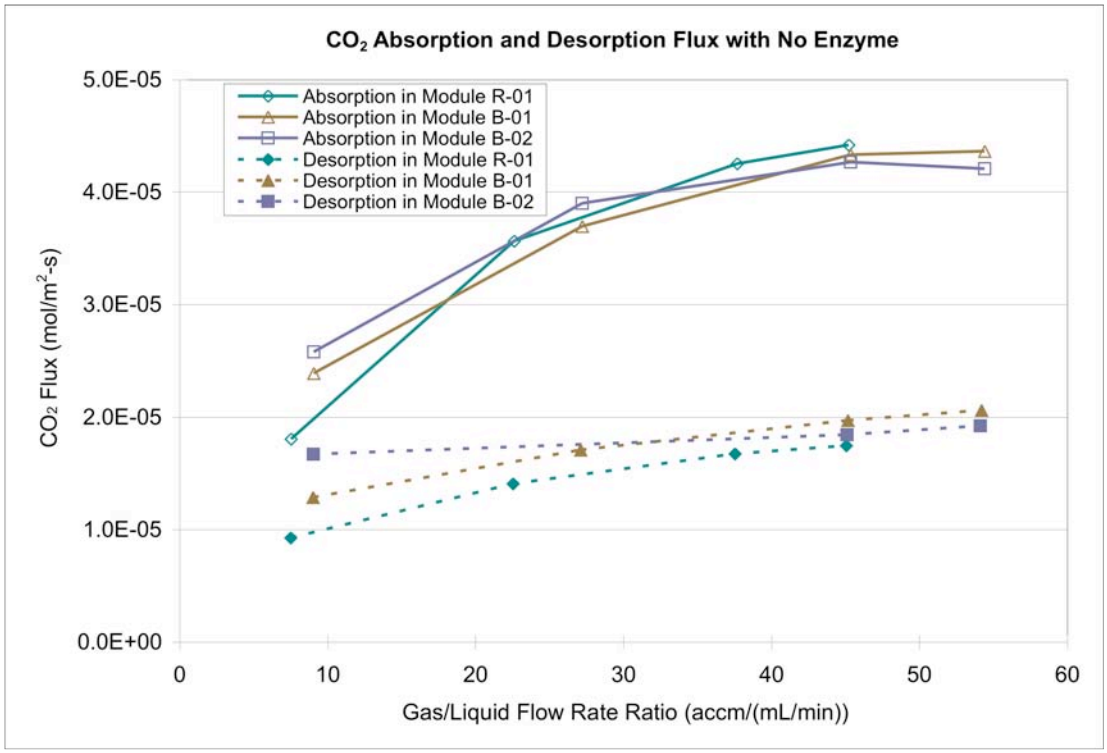


Figure 4-7. Absorption and desorption flux as a function of gas to liquid flow rate ratio in MicroModules operated under no enzyme conditions

B - Immobilized Enzyme Activity Test Methods

A first step in quantifying immobilization efficacy is to determine the amount of enzyme immobilized. There are several principal concerns – 1) how much enzyme is immobilized initially, 2) how much remains attached, 3) how active is it over time, 4) how active is it under given operating conditions, and 5) how well does it perform under test conditions similar to those that will be encountered during use.

We carried out End-point and Performance analyses for both the chromic acid activated material and the plasma activated material.

These analyses commonly used the W-A test method. A first object was to determine the enzyme activity on the day that the immobilization occurred as a means of evaluating the efficacy and utility of that particular procedure as compared with others we had tried. The immobilized material was tested repeatedly using the W-A method the object being to evaluate the amount of enzyme activity after a given period of time when the immobilized material was exposed to storage under various conditions of temperature and fluid composition. Inserting immobilized CA into a test bed that is an analog of that for later scale-up provides the most effective means to judge the expected performance under operating conditions.

C - Development of a Robust Immobilization Linking System

Polyethyleneimine (PEI)

Initial studies used the polyamino acid (PAA) polyethyleneimine (PEI) to form a thin film as the basis for immobilization. The film was estimated to be less than 10μm in thickness. PEI was selected as it had previously been used to immobilize CA to a cellulosic material. The enzyme was mixed with the PEI and the activated membrane dipped into the solution as a means of coating.

The W-A assay was used to measure enzyme activity. The initial activity was about 65% of the bulk phase enzyme. We observed as much as 100% of the activity during the initial 30 min. wash in 0.5M CLM buffer. However, the activity level decreased by day 2 leaving a remainder of only 28% of the initially immobilized activity.

Following the initial measurement the material was stored at 4°C in water or CLM and activity from discrete samples was measured daily. The object was to plot loss of activity over time. Loss of retained activity can be due to denaturation or to elution. To distinguish between these the buffer solution was collected and its activity measured. We observed, unfortunately, that a sizable fraction of the enzyme eluted into the buffer.

To attempt to limit leakage we crosslinked the enzyme and the PEI by means of glutaraldehyde. Glutaraldehye is known to decrease activity and this was observed. However, despite exploring numerous variants in application process the cross-linking did not decrease elution substantially.

The inability to retain significant activity levels obviated the need to carry out a Performance analysis. From these data we concluded that the PEI method was not viable for continued study. It was abandoned.

Layer-by-Layer Immobilization (LBL)

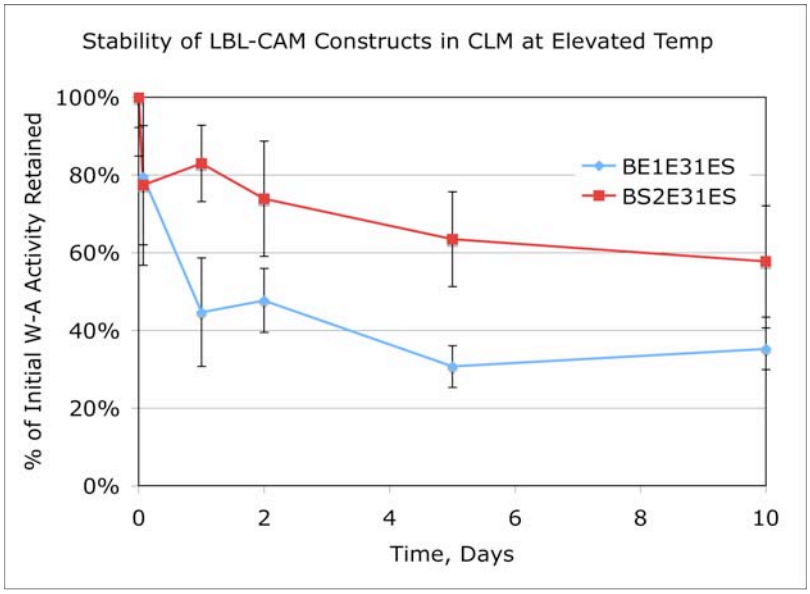
Despite the failure of a single polyamino acid – PEI – to adequately immobilize CA we were confident of the PAA method. We consulted Prof. Dibakar Bhattacharrya of the University of Kentucky to gain advice on the LBL method, an alternative approach to using a single PAA. Benefitting from his advice we utilized plasma activation of the PP HF to generate amino or carboxyl groups on the surface. To these we attached a base layer of a neutral PAA. On top of this we constructed a series of layers of acid and basic amino acids into which we had mixed various concentration of CAM.

We tested many different LBL-CAM assemblies. LBL-CAM assemblies BE1E31ES and BS2E31ES were constructed on plasma activated flat sheet PP membranes. The effectiveness of the enzyme immobilization was tested using the W-A assay to measure enzyme activity. The membranes were incubated in CLM solutions at elevated temperature for up to 10 days. The results are shown in Error bars represent +/-1 standard deviation for triplicate analysis.

Figure 4-8.

Construct BS2E31ES shows greater retention of the initial activity (60% over 10 days). Constructs similar to these were then tested for functional performance (i.e. absorption and desorption flux) using plasma activated hollow fiber membranes that had been potted as MiniModules. Note, the phenomenon of immediate loss is well

known. In commercial use the design requirement is for the initial 80% value (normalized for loss). Thus, the controlled retention is about 80%.



Error bars represent +/-1 standard deviation for triplicate analysis.

Figure 4-8. Stability test results of 2 sets of LBL-CAM constructs over 10 days in CLM solution at elevated temperature

Continued experience led to improved immobilization. Figure 4-9 illustrates (red triangles) successful long-term immobilization of enzyme. We succeeded in achieving 80% retained activity for 60 days.

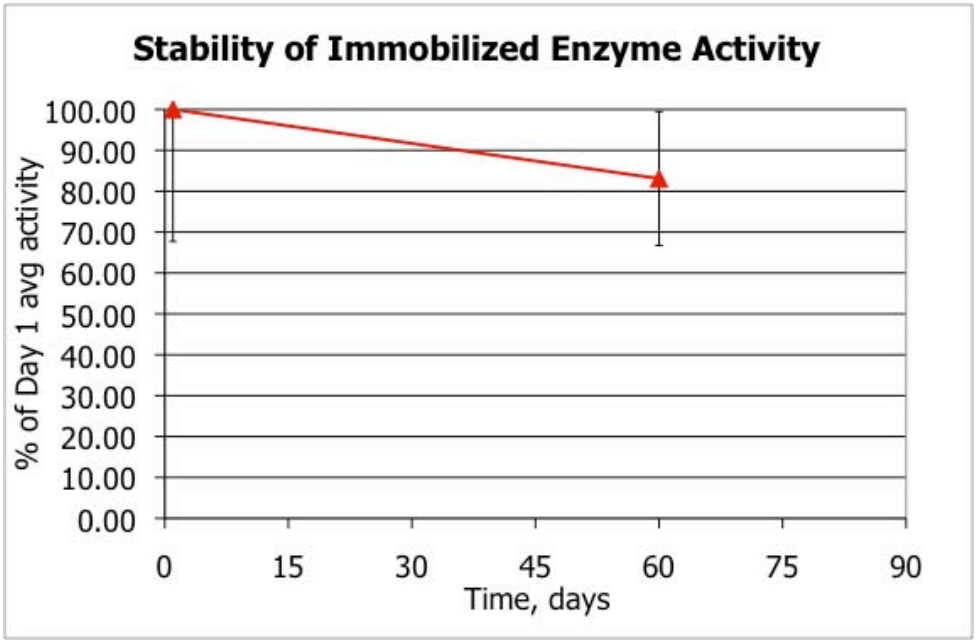


Figure 4-9. Normalized W-A activity of LBL-CAM Assembly ALS1E31ES1 over 90 days of measurements

Test Apparatus

The Very Small Permeator (VSP), Figure 4-10, is an FS analytical tool. It consists of two small diameter (25mm) membranes separated by a washer of known thickness (*e.g.,* 300µm). Gas is provided into the top half and gas is extracted from the bottom half. Gas flow is radial but countercurrent. This test apparatus was used for the FS chromic acid PEI and FS plasma activated PAA layer-by-layer (LBL) studies.

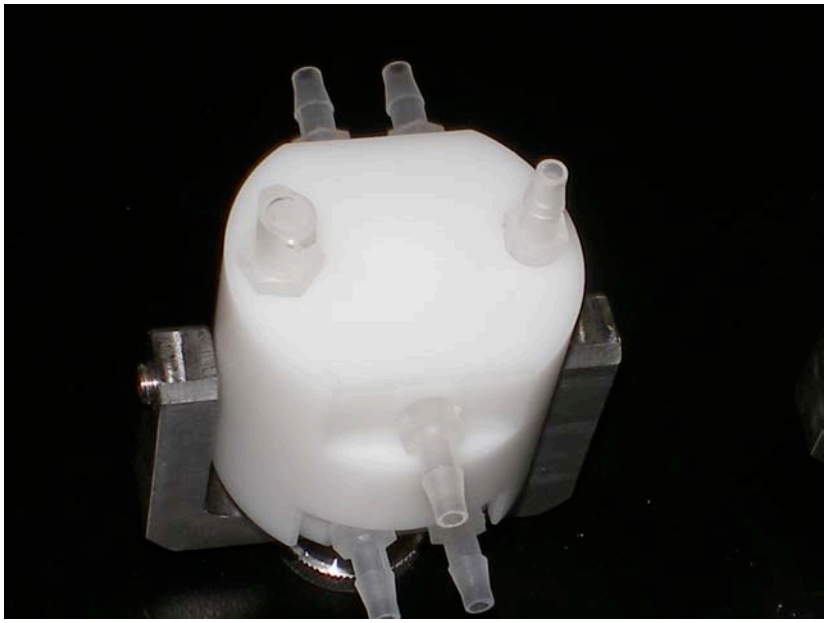


Figure 4-10. VSP for use in enzyme acceptance testing, CLM chemistry optimization and testing of immobilized enzymes.

The MiniModule (Figure 4-11) is a small HF array organized as a permeator, an absorber or a desorber. The module is a larger version of the same with a surface area is $0.5m^2$ for the permeator or $1m^2$ for the absorber or desorber.

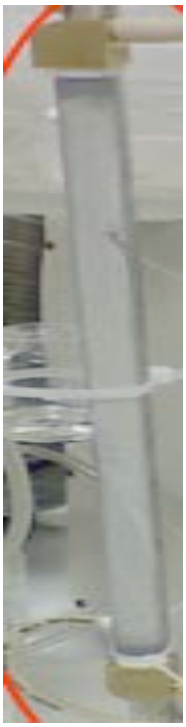


Figure 4-11. Mini-module.

The μMod, Figure 4-12. , consists of a HF wrapped around a flat plate for a small number of turns such that feed gas can be delivered to the bore and the liquid on the shell can be used as a sink for CO_2 equivalents (Ce); the gas composition is measured by RGA to determine the amount of CO_2 extracted from the feed. The surface area is $100cm^2$.

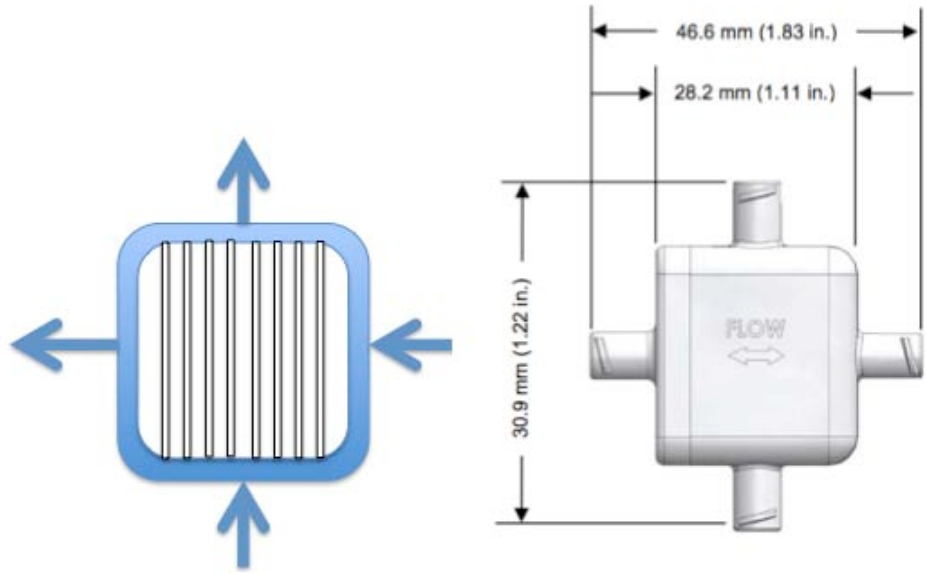


Figure 4-12. Membrana micromodule. (cross-section on left; shell on right).

Results and Discussion

Enzyme Qualification/Acceptance

We used four criteria to qualify enzyme materials: 1) turnover rate (kinetics) under controlled conditions, 2) stability in CLM, 3) membrane wetting (enzyme-membrane interactions), and 4) CO_2 capture performance in the VSP.

1) Turnover Rate: The results of the Maren, W-A, and protein assays for several different isozymes are given in Table 4-2. They show that W-A activity of BCA II from bovine serum is 5-times that of one thermophilic enzyme while the second was not active. The preferred thermophilic enzyme has a kcat of $10^4 s^{-1}$, two orders of magnitude lower than the $10^6 s^{-1}$ of BCA II. However, the ability of thermophilic enzyme to function at higher temperature coupled with better thermal stability compensates for the lower activity.

Table 4-2. Results of Enzyme Activity and Protein Content Assays

	Maren Activity (U/mg)	Wilbur-Anderson Activity (U/mg)	Protein Content or Conc. by BioRad Assay (%)
BCA II from Sigma (Powder)	591	2529[1] (2710)	97%[2]
Thermophilic-1 (Supplier 1)	122	566	71.2 g/l[3]

Thermophilic-2 (Supplier 2)	0	0	70%[2]

1 – This agrees well with the manufacturers value of 2710 U/mg for this batch of enzyme.
2 - Protein content is weight % of the protein dry sample.
3 – Supplier reported 100g/L protein. Difference in measurement method may account for this.

2) Stability in CLM: Figure 4-13 illustrates data for enzyme activity vs. time. The plot includes data for two different CLM conditions for the thermophilic enzyme from one supplier and the two technical grade CA isozymes from another. The enzyme solutions were placed in sealed vials and incubated at 65°C. Samples were removed periodically and assayed by the Maren assay. The results show that the longest lifetime observed was for the thermophilic isozyme in CLM Buffer 2. Eighty percent activity was retained for 11 days under these conditions. This is consistent with the needs for the 250-hour tests planned for scaled-up apparatus.

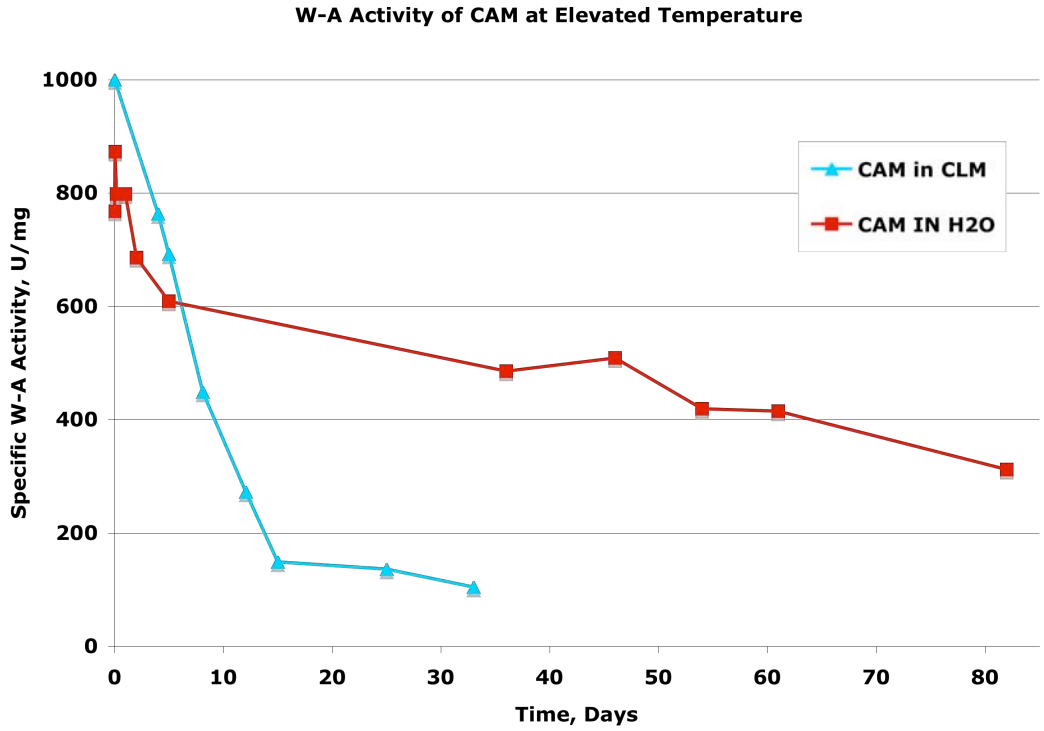


Figure 4-13. Enzyme activity as a function of time with repeated measurements

3) Membrane Wetting: As noted, a principal concern was whether a given enzyme sample would wet the membrane under control and operating conditions, *i.e.* convert the membrane from being hydrophobic to hydrophilic. Control testing used water, CLM, or purified enzyme solutions in CLM at room temperature and at elevated temperature.

All of the Novozymes TG enzymes failed the wetting test at elevated temperature. Two approaches were taken to resolve this problem as Novozymes preferred to provide TG material. One was that Novozymes made efforts to "clean up" the sample. The

second was that CZ dialyzed samples to remove production surfactants. While, ultimately we did find some TG material that did not fail a wetting test over a modest period of time the duration was sufficiently short to make the use of TG material unacceptable. Several of the Novozymes PG enzymes and BCA II and CAM each passed the wetting test.

4) CO_2 Capture Performance: Each sample that passed the kinetic and wetting tests was introduced to the VSP as a homogeneous catalyst, *i.e.* dissolved in CLM, to measure the rate and magnitude of the beneficial effect of adding the enzyme.

Performance data for the Novozymes PG enzyme are shown in Figure 4-14 where it is clear that this enzyme provided reasonable performance in the permeator under these conditions. Data show the presence of the enzyme provides for much higher CO_2 permeance and selectivity versus N_2 and O_2.

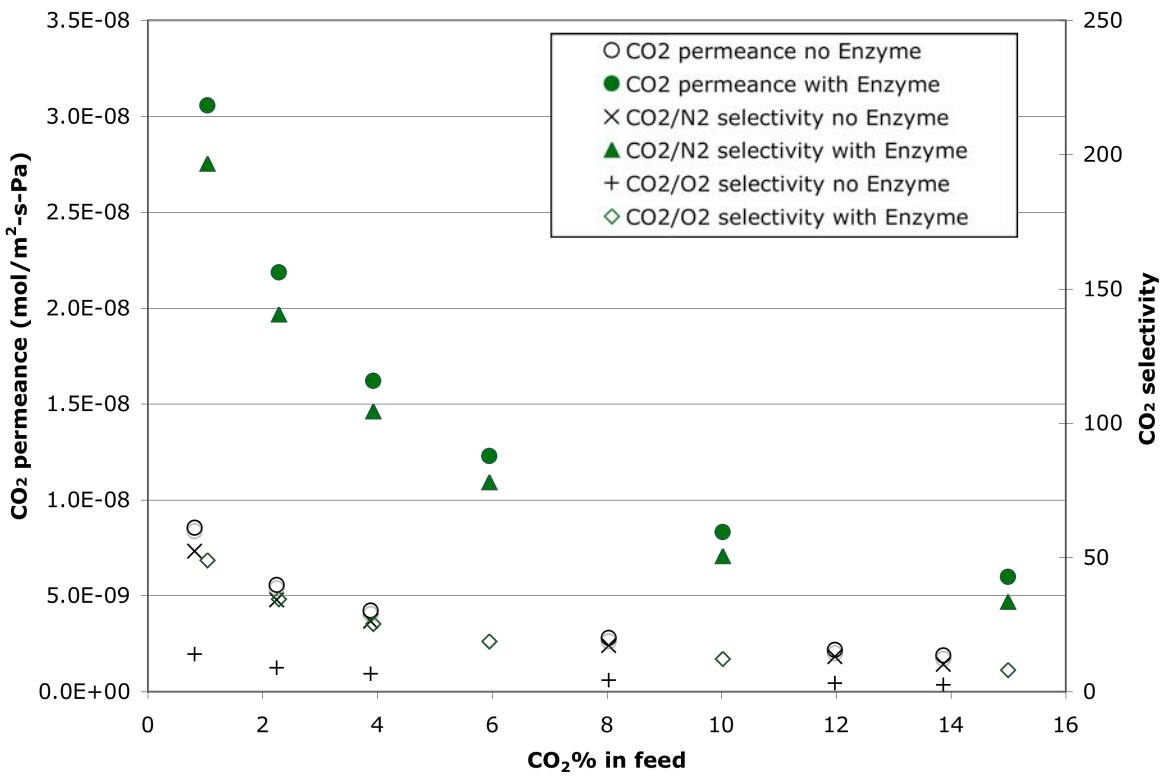
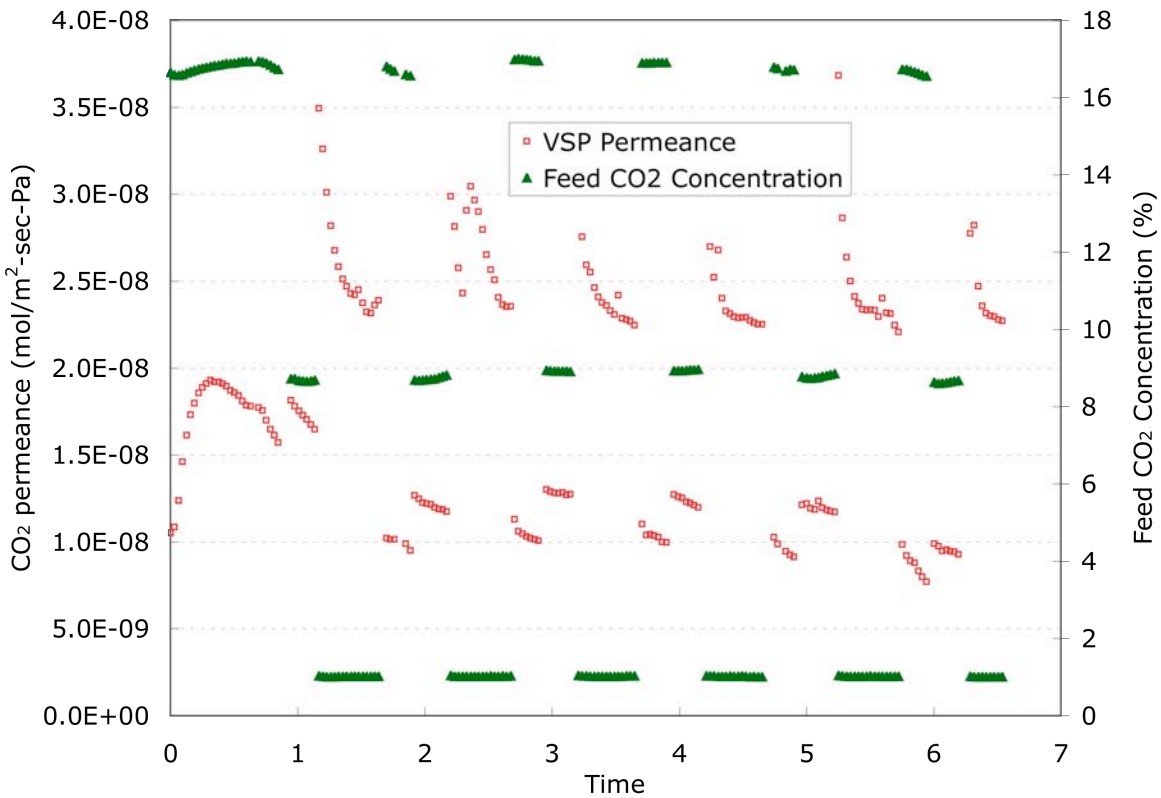


Figure 4-14. Performance data for use of specific enzyme at 40°C in 0.5M CLM

A series of VSP tests were run to characterize the lifetime of non-immobilized enzyme in bulk buffer solutions. The experiments were conducted at 50°C using two discrete permeator systems with $NaHCO_3$ buffer concentrations of 0.5M and 1M, respectively. Novozymes NS81074 enzyme solution (1.5mg/ml) was introduced to each permeator. CO_2 was provided at about 1%, 4%, 10% and 15%, in successive and repeated cycles. The gas composition of the feed, sweep, permeate and retentate are each routinely recorded by the RGA for later processing using a Matlab program to

derive permeance and selectivity. The Novozymes PG and PSU CAM tested successfully in the VSP at 50°C for 48h. This VSP experiment was run for 6 days, Figure 4-15. The CO_2 permeance observed was 1.0e-8 +/- 0.2e-8 mol/m^2-s-Pa for a feed CO_2 concentration of 16.75+/-0.05%. This is commensurate with that typically observed with other enzymes at the same temperature. Evidence that the enzyme was stable in the test was obtained by measuring the enzyme activity in the CLM removed at the end of the experiment. These measurements revealed that 85+/-5% of the enzyme activity remained. Additional comparative data under these test conditions are shown in Table 4-3. Under elevated temperature and pCO_2 conditions CAM gave superior performance.



Note: The higher values for the early time after switching to the 1% condition are due to the gradual loss of excess CO_2 remaining in the CLM from the 8.8% condition.

Figure 4-15. Performance of VSP with thermophilic enzyme at elevated temperature

Table 4-3. Summary of VSP performance results from experiments with thermophilic enzyme.

Feed CO_2	1%	5%	8.5%	16.5%
No Enzyme	0.56	0.22	0.17	0.15
BCA II	3	2.5	2.5	1.7
Novozymes	3	1.5	2.1	2.0
CAM – 50°	3	NA	2.1	1.9
CAM – 65°	4.1	NA	2.8	2.5
Permeance, mol/m^2-s-Pa (units x 1e^{-8})				

Maximum performance was observed for use of CAM at the highest temperature. Near maximum performance was maintained for more than 6 days. Figure 4-16 shows the performance of the VSP at the highest design temperature. Very high CO_2 permeance values (the highest ever seen for operation of the VSP at these feed concentrations) were observed from day 1 through day 6. An upset condition occurred after which performance values declined. On recovery the values were the same as those seen at lower temperature. The experiment was terminated after 10 days.

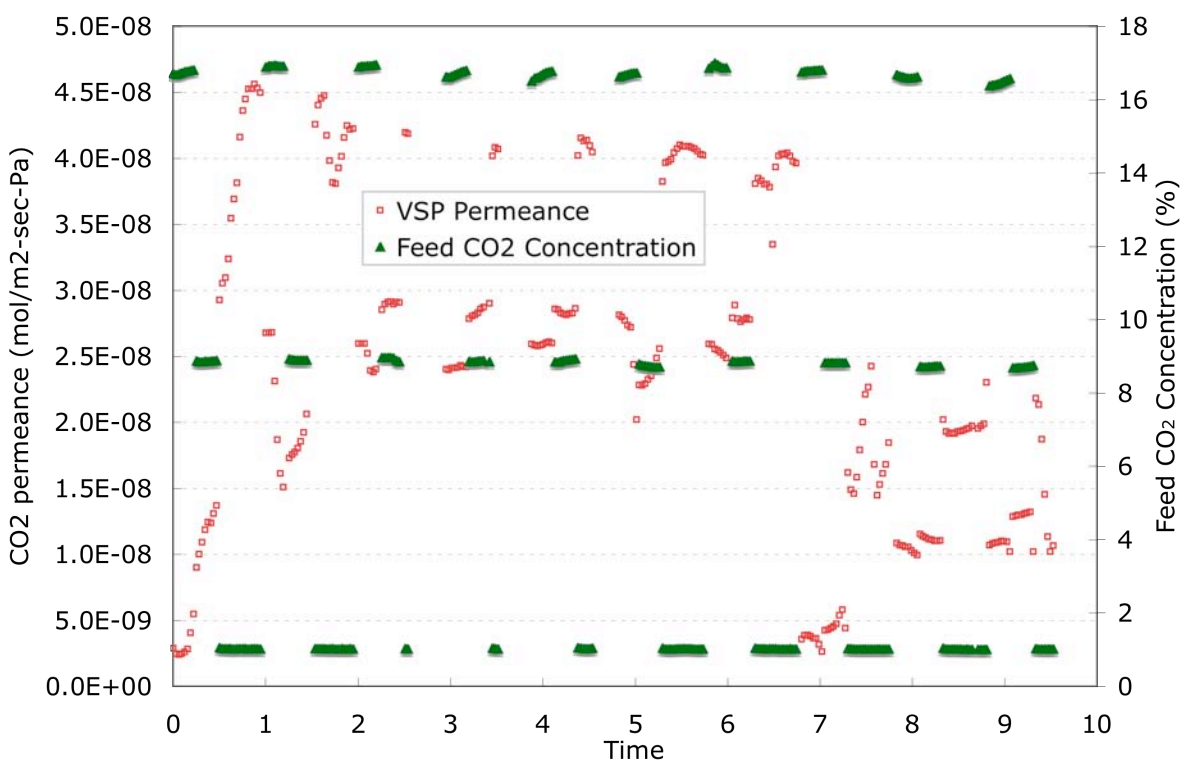


Figure 4-16. High temperature enzyme testing in the VSP

Module Performance Analyses

A - VSP and MicroModule Performance Analyses - Control

As noted above, a first control was to test membranes after they had been activated but prior to immobilizing enzyme on the surface. This served to verify that the various surface activation methods did not adversely affect membrane performance. The data revealed no discernable effect of the presence of surface functional groups in terms of CO_2 permeance for the no-enzyme condition. The same CO_2 permeance value was obtained for both the no-enzyme normal flat sheet membrane and no-enzyme plasma activated flat sheet membranes (operated under maximum design temperature conditions).

B - Performance Analyses with MicroModules

We constructed 16 different HF μMod with four different enzyme-PAA combinations. These were tested in absorption and desorption modes, all at room temperature. For each condition we measured flux with and without enzyme present and carefully noted the mass balance with respect to percent closure. The data showed a 100% benefit of enzyme presence for the absorption data. The absorption flux achieved mean values of $1.3*10^{-4}$ mol/m^2-s.

Note that the pH of the MTF was always alkaline thus favoring absorption. This was evident in the desorption mode where the addition of the CAM provided about a 60% benefit, as would be expected as there was modest effective driving force to be amplified.

It is important to note that these μMod are very small; thus, the percent closure for assessing mass balance had considerable range. The mean value was 100.86% but standard deviation was 47.1%. This is due to the very small scale of each component – membrane area, tubing diameter, and numerous connections, all served to amplify the effect of small leaks.

The tests run for absorption in the same modules showed fluxes around 6e-5 without enzyme and 1.3e-4 with enzyme. These values are 1,000 to 10,000-times better than was seen for the flat sheet and the HF arrays using spontaneous surface adsorption. These data speak very strongly to the value and benefit of immobilization.

Two performance test plots (Figure 4-17 and Figure 4-18) summarize the results obtained from operation of μMod under room temperature conditions with the standard MTF. Figure 4-17 shows the absorption performance observed under these conditions; Figure 4-18 the desorption performance. All of the data presented are from experiments run in crosscurrent μMod. The light blue, brown and green hand drawn curves are provided to show the performance observed for the two different immobilization patterns attempted (brown line = rejected method, green line = accepted method) and the no enzyme condition.

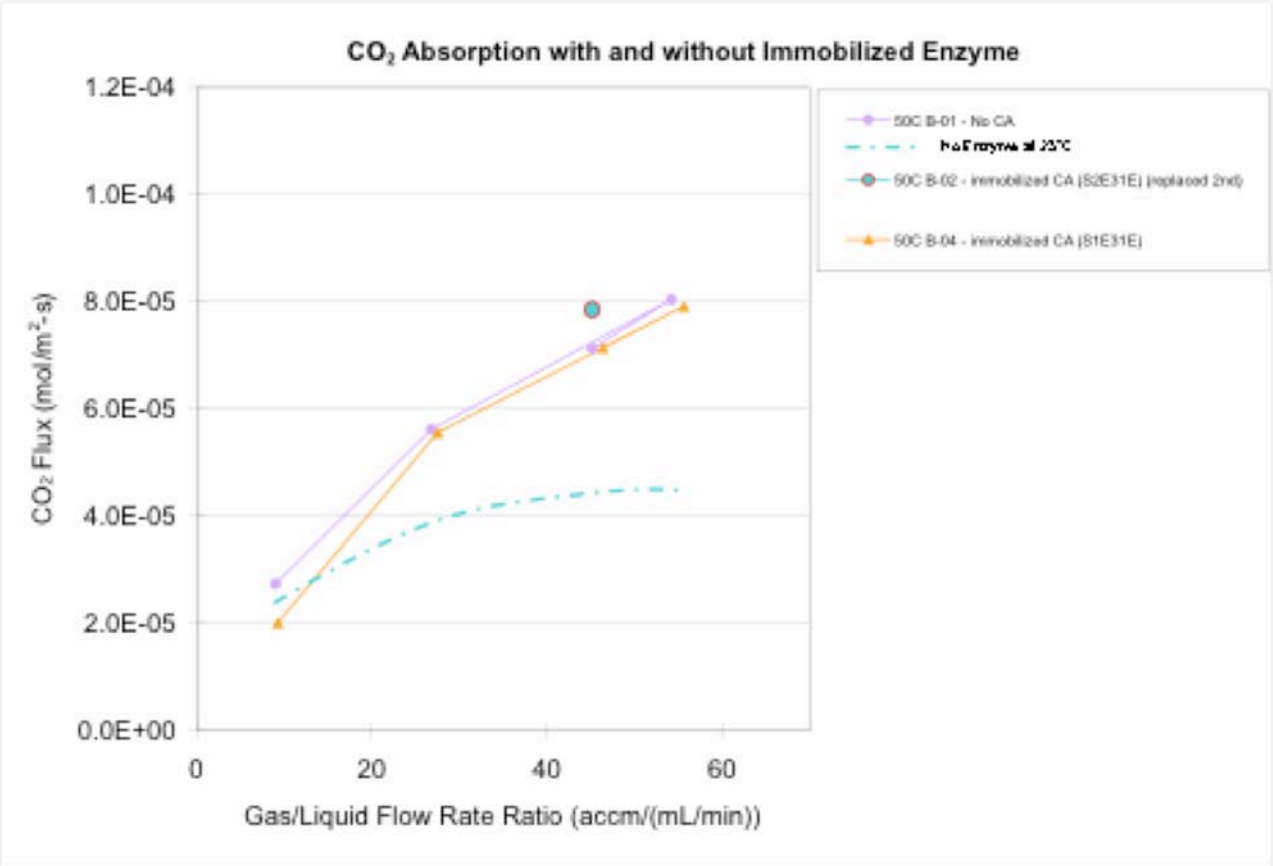


Figure 4-17. Absorption flux performance for µMod B-02 at gas/liquid flow ratios near 45 accm/(mL/min)

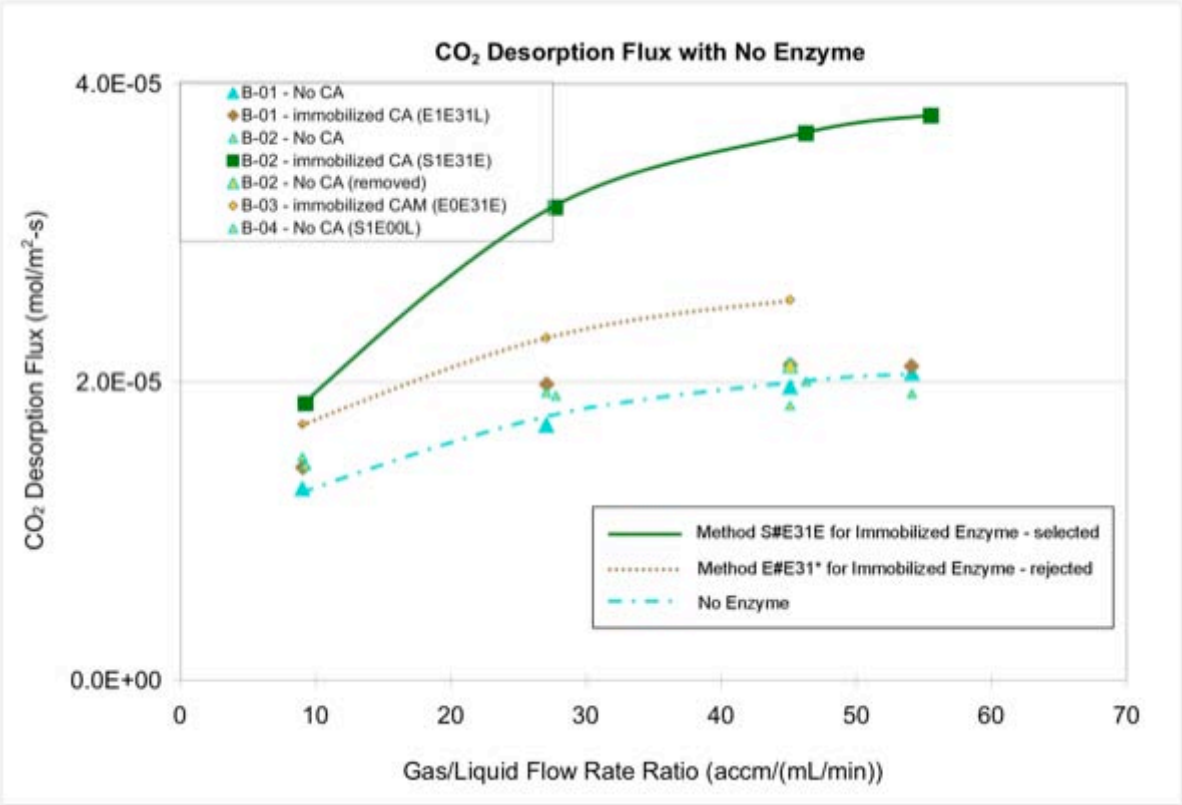


Figure 4-18. Experimentally Measured Desorption Flux for CO_2

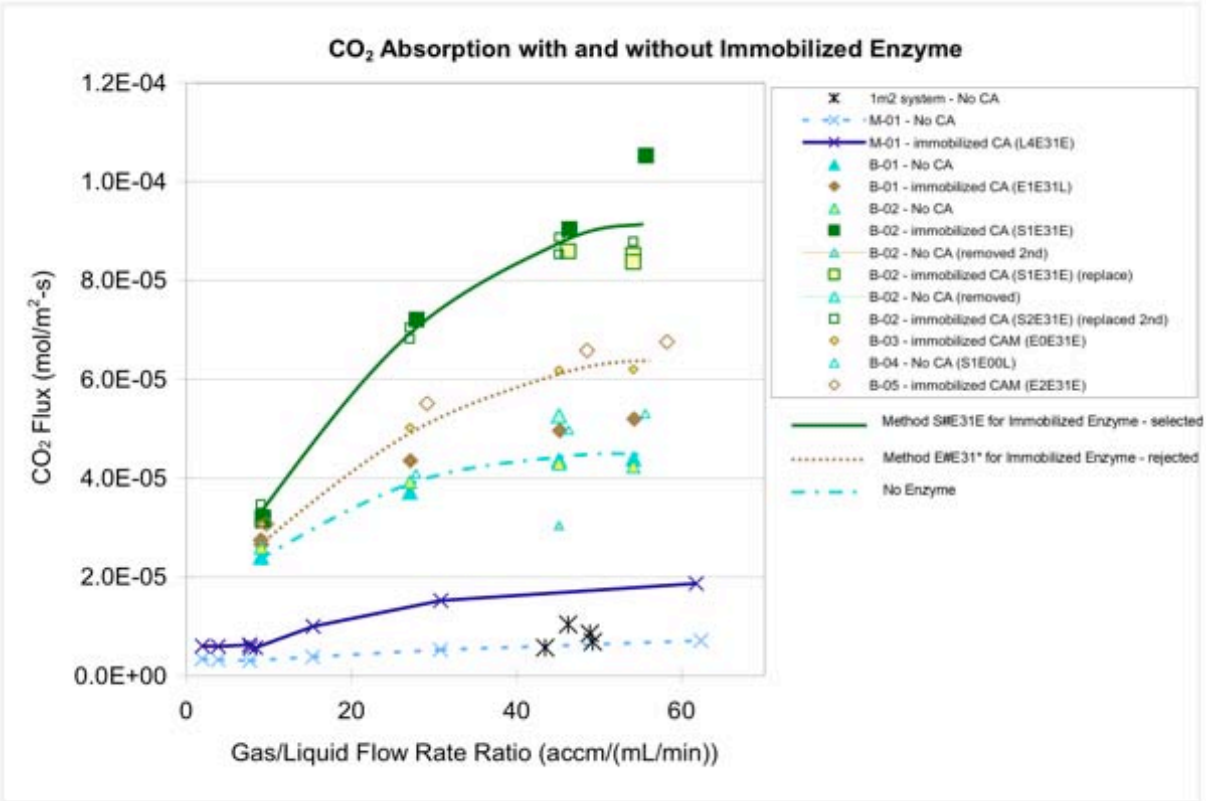


Figure 4-19 compares CO_2 flux under conditions of no enzyme vs. immobilized CA in plasma activated micromodules. The gain is about five-fold. Two sets of data are presented: 1) crosscurrent experiments run in µMods, and 2) countercurrent experiments run in MiniModules and large modules (M-01 = mini; 1m^2 system = large). The data show significant improvement when using the µMod. In this case the enzyme is immobilized to the membrane surface. The light blue, brown and green hand drawn curves are provided to show the performance observed for the two different immobilization patterns (brown line = rejected method, green line = accepted method) and the no enzyme condition.

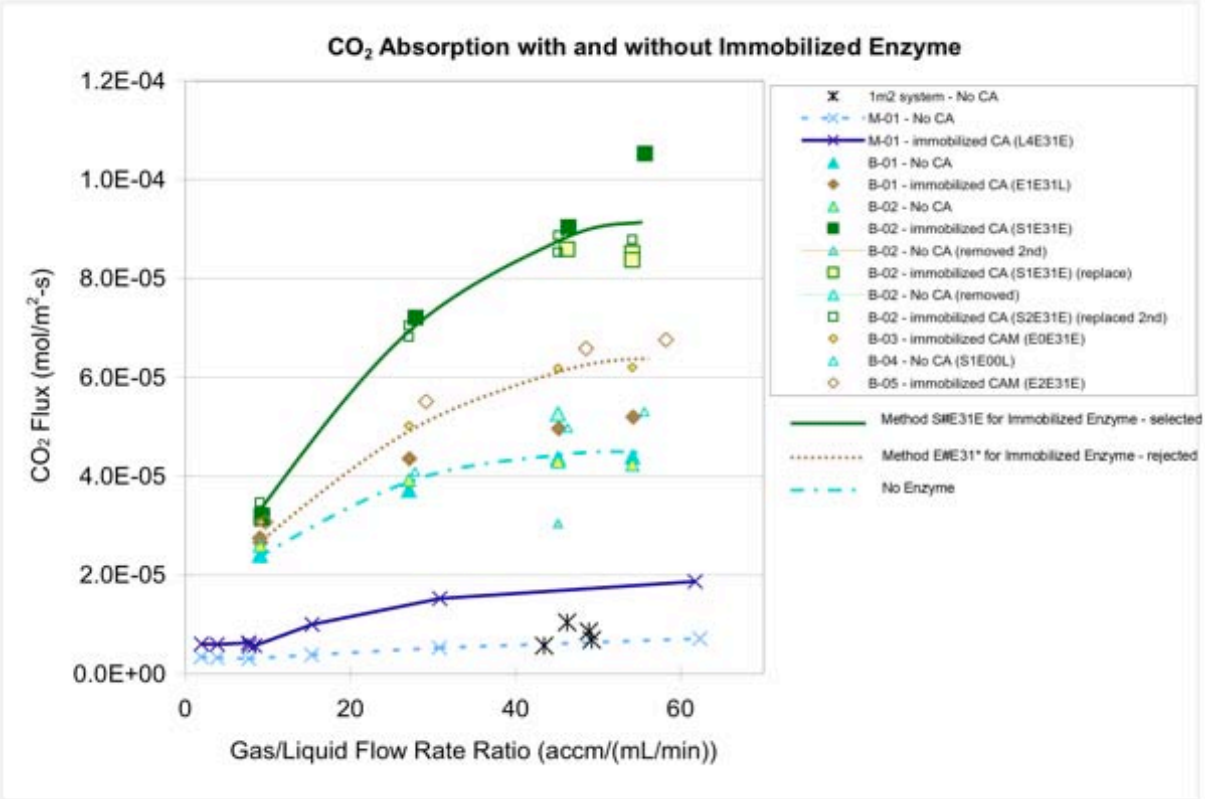


Figure 4-19. Experimentally Measured Absorption Flux for CO_2

K - Performance Analyses with Removal and Replacement of Enzyme

As was noted above the lifetime of the enzyme and of the membrane differ significantly. The target for the former being 1 year or less, while we anticiapte 5 years or more for the altter. Thus, it was critical to develop a method to remove and replace the enzyme without having to take the system apart or to remove and replace entire modules. To this end we developed the LBL method to allow shedding of the PAA but not of the base layer so that a new PAA layer could be attached to the remaining base layer.

We measured CO_2 flux with and without enzyme immobilized to the membrane. These data are illustrated in Figure 4-20. They show the success of the R&R studies for gas/liquid flow ratios near 45, a value that was selected because it is closest to the design condition. The first bar, labeled No Enzyme, was collected before any immobilization work was done but after the hollow fiber was activated for use in enzyme immobilization (μMod B-02). The first enzyme immobilization (Enzyme (1)) illustrates *in situ* application of one layer of enzyme. The data collected after the first *in situ* removal are labeled as Remove 1 – No Enzyme. The second application of immobilized enzyme (first replacement) is labeled Replace Immobilized Enzyme (2) indicating the second application of enzyme to this module (a single layer of enzyme). *In situ* removal of this enzyme resulted in the bar labeled Remove 2 – No Enzyme. The next *in situ* replacement was performed using two layers of enzyme. The bar is labeled Replace Immobilized Enzyme (3).

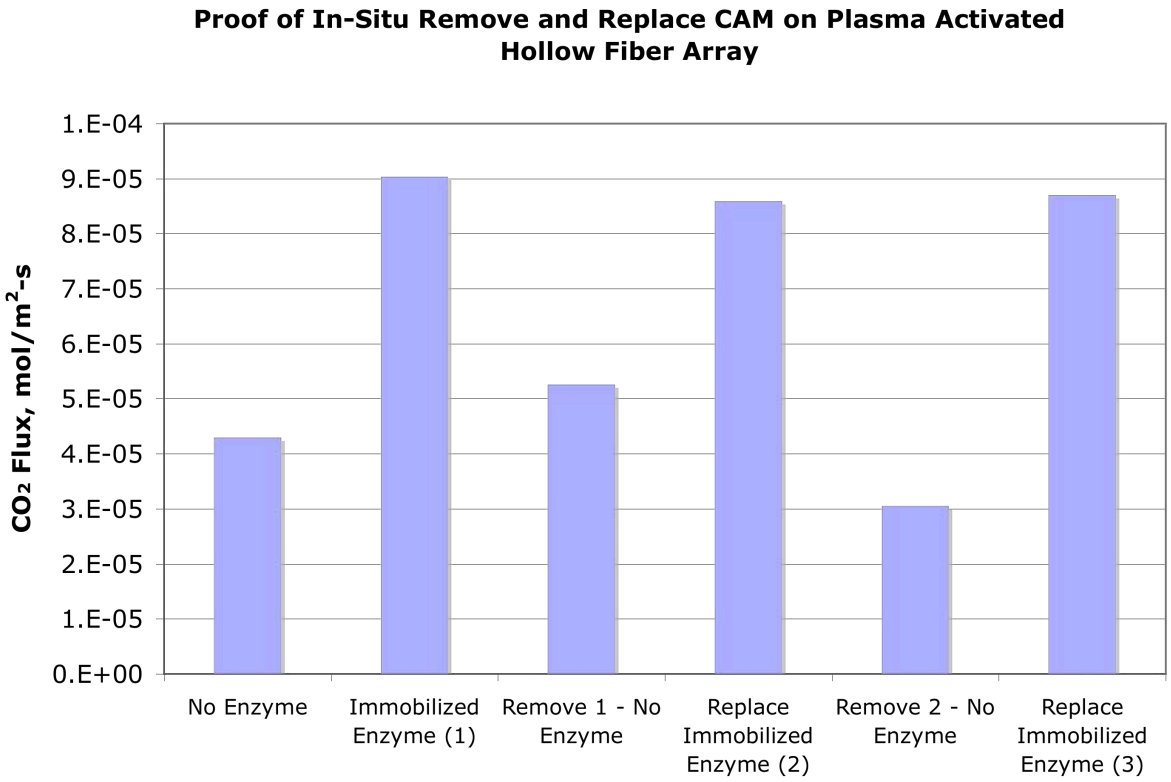


Figure 4-20. Absorption flux performance for µMod B-02 at gas/liquid flow ratios near 45 accm/(ml/min).

Conclusion

A bullet summary of the data reported indicate the following:

1. Enzyme – CAM was the preferred enzyme being superior to the Novozymes materials.
2. Surface activation – Plasma activation proved superior, easier, more controllable, and more environmentally friendly than did activation by means of chromic acid.
3. Immobilization – The LBL method proved superior to the use of a single PAA, viz. PEI. The LBL method strongly supported the remove and replace requirement thereby providing a vehicle for enzyme replacement *in situ* while maintaining the membrane system intact. We removed and replaced enzyme 5-times.
4. Modules – The HF modules, of any design, proved easier to use and performed better than did the FS modules.
5. Flow – Countercurrent flow yielded better performance than did crosscurrent flow.
6. Absorption vs. Desorption – Desorption, driven conjointly by vacuum and a thermal shift yielded better performance per unit area than did the absorption modules.

5. TASK 3 - IDENTIFICATION AND SELECTION OF A MEMBRANE MANUFACTURER

Goal

Task 3 – Identification and Selection of a Membrane Manufacturer addressed the identification and selection of a membrane manufacturer that could fabricate spiral wound hollow fiber membranes and perform module fabrication.

Approach

Carbozyme used the following approach to select our membrane material, module and manufacturer:

- Define the requirements for membrane selection
- Define Carbozyme's module requirements
- Identify membrane and module manufacturers
- Down select among the companies that manufacture membranes based on the satisfaction of our requirements and performance

Define the Requirements for Membrane Selection

The Carbozyme hollow fiber permeator design has several unique properties that are supported by various patents received or pending. Figure 5-1 is a schematic to illustrate the fundamental elements of the design – two microporous, hydrophobic hollow fibers (HF) are arranged adjacent to, but separated from, one another by a thin liquid film known as the contained liquid membrane (CLM; referred to as the MTF for the absorber/desorber design). The values in Figure 5-1 represent the CO_2 concentrations at each point. The apparatus, a HFCLM permeator operates such that when it is fed a CO_2 containing stream it extracts this gas by converting the CO_2 to a bicarbonate species at the first gas-liquid interface and then converting the bicarbonate back to CO_2 at the second gas-liquid interface. Operation of this apparatus extracts >90% of the inlet CO_2 and provides an outlet (permeate) that when dried meets the criterion concentration appropriate for insertion into a pipeline as a super critical gas, i.e. >98% CO_2.

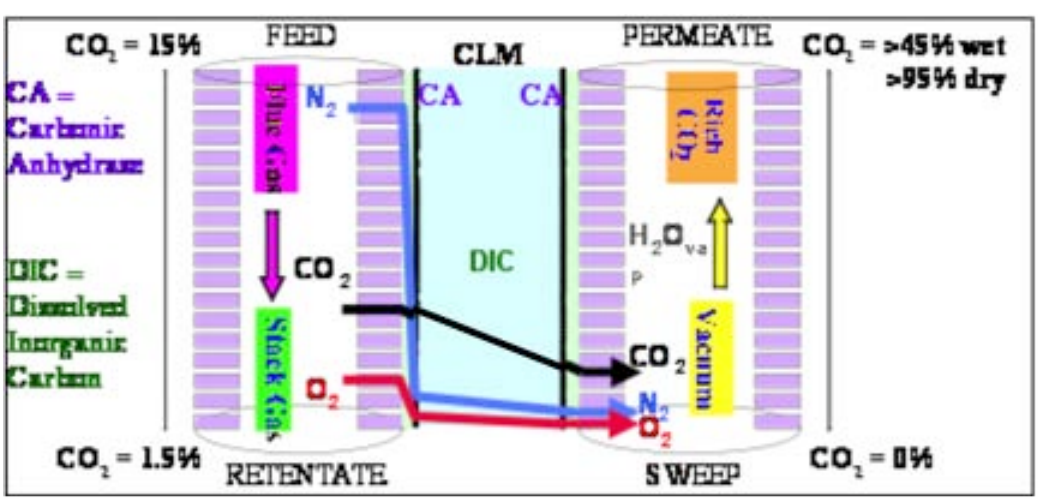


Figure 5-1. Schematic illustration of the Carbozyme permeator design.

One key features of the polymer membrane is that it must create and maintain, by physical means, multiple separate spaces – gas space(s), liquid space(s), etc.
The polymer membrane must be microporous and hydrophobic to allow the gas and liquid phases to interface, via diffusion, without allowing them to mix.

- A gas-liquid interface is formed that allows rapid transport of the gas to the liquid surface. The membrane pores must be gas filled to achieve 1) faster transport because gas diffusion is rapid while liquid diffusion is slow, and 2) physical separation to avoid liquid leakage into the gas flow. This is necessary to allow use of vacuum conditions on the CO_2 product side and serves to minimize liquid handling and gas/liquid separation requirements.

The polymer membrane must be made from a material that is available (or can realistically be anticipated to be available) in very large quantity, at a reasonable cost.

- This relates to the material of construction. A large-scale power plant, e.g. 400MW plant, will require tens of millions of square meters of membrane. Low cost is a reason to focus on polypropylene rather than other much more expensive polymers like PTFE or PVDF.

The material and format must be available in dimensions consistent with the anticipated design and operation of the permeator. The dimensions of the fibers, i.e. ID, wall thickness, porosity, length, etc., must support the performance of the Carbozyme permeator.

- The preferred length and inner diameter are a function of the pressure drop anticipated given the flow rate of gas passing through the fibers (note: this is a function of performance goals – the greater the unit area of transport of CO_2 the greater the flow per fiber). Carbozyme calculated preferred length and diameter targets based on anticipated performance and used these in the evaluation of HF with the understanding that various tradeoffs could be made to more closely fit the available materials. For example, higher porosities and lesser wall thicknesses may be preferred because these would minimize the mass transfer resistance presented by the HF membrane.

HF, if supplied apart from a module, must be delivered as an array, preferably on a reel.

- The object of the Carbozyme design is to maintain a rigid geometry such that the spacing between the polymer membranes creates a CLM of known dimension that separates the CO_2 from other gases in the mixture.
- Assemblies using individual hollow fibers are known to have problems such as dead zones, short-circuiting and flood zones that are prevented by array formation.
- Bias wound assemblies of individual hollow fibers cannot be used for multiple tubesheet formations.
- A rigid geometry is achieved by assembling membranes, preferably HF arrays (knitted assemblies of HF that function like a sheet) into modules by rolling layers of membrane in a jellyroll manner. A woven array can be handled as a fabric to allow manufacture of a spiral wound module by a roll-up process.

In summary, to realize the unique properties of the Carbozyme apparatus design, we generated the following set of requirements for the product fibers and arrays:

The membrane must be hydrophobic
The membrane must be microporous

The membrane must be available as hollow fiber with acceptable physical dimensions and properties

The membrane must be available (or can realistically be anticipated to be available) in very large quantity at a reasonable cost.

The membrane must be available as a woven array or available as spools containing very long runs (kilometers in length) of continuous fiber such that it could be made into a woven array.

Carbozyme's spiral wound, HFCLM (SW-HFCLM) design places the following requirements on the module manufacturer.

1. The capabilities of the module manufacturer must be consistent with the construction of a multiple tubesheet permeator having overall dimensions consistent with the scale-up plans outlined in the SOPO.
2. The module manufacturer must be complaint or willing to work with Carbozyme to effect design modifications needed to satisfy Carbozyme's essential requirements.
3. The module manufacturer must be capable of scaling modules for progressively larger operation.
4. The module manufacturer and Carbozyme must work together to achieve a viable product, which, in operation, would be appropriate to satisfying the DOE CO_2 capture objectives.

Identifying Membrane and Module Manufacturers

Membrane is available with a number of discrete features and properties. These include: format - flat sheet and hollow fiber; water acceptance – hydrophobic and hydrophilic; physical openness - porous and non-porous, as well as porosity; assembly of hollow fiber – filament and woven; and, material – cellulose, Teflon, polypropylene, etc. Membrane is also available as a standalone product or assembled into modules of many different designs. The most common design formats are plate and frame, skeins and spiral wound.

We search for manufacturers of microporous hydrophobic hollow fiber membranes. We found well over 120 firms that manufacture membranes, and greater than 45 that make hollow fiber membranes and modules. From these we determined which could provide hollow fibers that might meet our specifications and which of those firms would supply us with samples of microporous hydrophobic hollow fibers and/or hollow fiber array made with microporous HF. This reduced the number of firms considered to a total of six.

Candidate manufacturers of membrane and modules were found searching web, journals, product literature, supplier directories and consulting industry associations. Some of the sources we used were:

- Consulting industry source lists, specifically: Filtration and Separation 2006 Buyers' Guide (Elsevier 2006).
- Using the Online Membrane Supplier Directories listed in Table 5-1.
- Conducting web searches using search terms such as microporous polypropylene, hydrophobic hollow fiber, and degassing.
- Searching for suppliers using the supplier link service Alibaba.com to find and interface with suppliers.

Table 5-1 Online Membrane Supplier Directories

Gateway to Membrane World	www.geocities.com/faisal_hai/companies
Filtration and Membrane World	www.membraneworld.com/manlinks.html
Plastic Material Manufacturers and Distributors	www.plastic-materials.com/?source=google
Membrane Manufacturers Directory	www.membrane-guide/english/index.htm
Manufacturers of Membrane and Module	www.tcn.zaq.ne.jp/membrane/english/ManufactE.htm
N. Am. Suppliers from Medical Device Link	www.devicelink.com/company98/category/Filters_and_IV_Components/index
WBX's Membrane Index Page	www.waterdrop.com/mp.htm

One of the most useful sources we found was the Manufacturer List of Membranes and Module (http://www.tcn.zaq.ne.jp/membrane/english/ManufactE.htm). When it was accessed on June 29, 2007 it had a list of 111 membrane manufacturers with contact information and tables indicating the types of membranes and modules they supply and an indication of whether or not they made equipment (e.g., skids).

Web searches were conducted throughout the project period using Google and other search engines and a variety of search terms including the phrases microporous, polypropylene, hydrophobic, hollow fiber, and degassing. All attempts were made to obtain as comprehensive of a useful list of membrane and module manufacturers as possible.

Samples were received from 6 firms (one US manufacturer and 5 Chinese manufacturers). All of these samples were evaluated for their potential use in a Carbozyme permeator. Only Membrana-Charlotte provided loose fibers that could be applicable for use in making hollow fiber array. Inasmuch as Membrana-Charlotte manufactures hollow fiber array, this eliminated the option of obtaining hollow fiber and having it woven appropriately.

Down Select among the Companies that Manufacture Membranes based on the Satisfaction of our Requirements and Performance

Early interviews with module suppliers showed a surprising reticence to manufacture multi-tubesheet design or to invest the time or money needed for the manufacturing modifications. In specific, market considerations such as alternative economic opportunities, manufacturing capability, time availability, R & D interests, perceived market risk, and many others, are critical to the willingness of a module manufacturer to commit the resources and accept the risk of new product development. In addition, the SOPO described a specific scale-up order for modules starting at $4m^2$ and ending at $400m^2$. Implicit in this plan was an increase in the physical size, diameter and length, of the module to accommodate this surface area. (As described below, this assumption, while valid across the industry was not valid for any individual provider).

The low level of module manufacturer cooperation, at that time, forced Carbozyme to consider the different "make/buy" decisions. Several candidate paths were considered to deliver appropriately designed spiral wound hollow fiber membrane modules. Each path dealt with a different aspect of the "make/buy" decision. The different paths are described below.

1. Carbozyme could make or purchase fibers and then make or have made arrays and modules. While this would not be in the spirit of Task 3.1 it might be needed if we were unable to find an appropriate provider of arrays or modules.
2. Carbozyme could manufacture or have manufactured fiber arrays or purchase them from a vendor? These would then be assembled into modules by Carbozyme or by a provider.
3. Carbozyme could obtain arrays and assemble them or have them assembled into modules.
4. Carbozyme could purchase modules and have them modified by a module manufacturer (subcontractor) to achieve a design that is acceptable?

The preferred path would be a single vendor that provides modules of appropriate size, design and materials to comply with a "buy" strategy. This alternative would be the least risky alternative to Carbozyme and the FACA program, as there would fewer components, relationships and considerations to manage.

The steps performed in the evaluation of these options were as follows:

1. Determine the cost and effort to purchase and operate a hollow fiber extrusion and dry stretching operation pilot plant. Turnkey pilot plants appear to be available from several suppliers.

   CONCLUSION – The cost and time to execute on this option were too great. In addition running a hollow fiber manufacturing operation is not part of Carbozyme's corporate plan nor is it in the area of expertise of Carbozyme. Result: Buy hollow fibers.

2. Examine the purchase of a weaving machine or having the weaving done.

   CONCLUSION – The cost and time to execute on this option were too great. In addition running a hollow fiber weaving operation is not part Carbozyme's corporate plan nor is it in the area of expertise of Carbozyme. Result: Buy arrayed hollow fibers.

3. Examine the ability to make modules from purchased hollow fiber arrays. Carbozyme had developed methods for hand rolling membrane array into modules. This provided a guide on the efforts and approach needed for in-house manufacture.

   CONCLUSION – The absence of a reliable supply of arrayed fibers and difficulties encountered in small-scale construction decreased the viability of this approach. The cost and time to execute on this option were also too great. The reality of scaling our methods to handle master rolls of hollow fiber array the fabrication of specialized equipment that was outside the scope of our capability. Result: Find a one-stop vendor/partner to supply the membrane, array, module manufacture, reliability and quality control.

Market conditions changed dramatically in late 2008 reversing the situations described above, making candidate providers more cooperative and willing to take greater risks. A key change was the realization that CO_2 capture was likely to be enacted in law thus creating a market that did not exist earlier.

Results and Discussion

The first decision point in our evaluation related to which material would be used. Microporous hollow fiber is available as polypropylene, Teflon (PTFE) and PVDF. PVDF is at least 10X more expensive and its availability is limited due to worldwide demand for use of PVDF in pipe manufacture. Teflon is also much more expensive than polypropylene. The principal suppliers of microporous hollow fiber Teflon are W.A. Gore Co. and Mykropolis. Note that the Teflon hollow fibers are not woven. Further, in view of the cost differential among the various candidate hollow fibers that met this criterion only polypropylene was of low enough cost to be used for this application. Further, of these materials only polypropylene is available as a woven array. Price consideration and material availability on large scale were satisfied only by polypropylene

The decision to use polypropylene limited our search to a small number of companies located in the US, Germany, Japan, Korea and China. Pursuing the option that we might have to have polypropylene hollow fiber woven for later assembly we obtained samples of loose fibers from all companies that would supply them. The fibers were evaluated for quality, uniformity, consistency, and the likelihood they could be made into array. Table 5-2 lists the loose fiber materials that were tested. Table 5-3 lists the hollow fiber array that was available at the time from Membrana.

Table 5-2 Firms that provided samples of loose hollow fiber for evaluation.

Company Name					
Name	SongQiao Company	Hangzhou H-Filtration Membrane Tech. & Eng. Co., Ltd.	Shandong Zhaojin Motian Company, Ltd.	Tianjin Jinghai Yunda Industry and Trade Co. Ltd.	Sheng Liu Company
Location	Hangzhou, China	Hangzhou, China	Shandong, China	Tianjin, China	Ningbo, China
Property					
Material	PP Hollow fiber	PP Hollow fiber	PP Hollow fiber	PP Hollow fiber	PP Hollow fiber
OD (μm)	480	400 - 450	300 - 400	500	
ID (μm)				350 - 400	300~400
Thickness (μm)	47	40 - 45	30 - 40		40~60
Pore size (μm)	0.1~0.2	0.02 x 0.2	0.02 ~ 0.04	0.01 - 0.2	0.1~0.2
Open area (porosity)		40 - 50 %	50 - 65%	~55%	>50%
Gas flux (cm3/cm2*s*cmHg)	>7.06-2	> 7.06-2			>8.56-2
Tensile strength (MPa)	>120	120			120
Array	Not available	Not available	Not available	Not available	Not available
Price					
$/m2	3		RMB 200 (~$25)		3.52
$/1000 m	3				4.4
Minimum order		10 kg			
Supply ability		1000 kg			
Production Capacity		200~300 million meter/year			50~60 million m/month
SAMPLES	yes	yes	yes	yes	yes
COMMENT	lowest quality	medium quality	high quality	high quality	medium to low quality

Table 5-3 Firms that provided samples of hollow fiber array for evaluation.

Company Name			
Name		Membrana (PolyPore)	
Location		North Carolina, USA	
Property			
Material	PP Hollow fiber (X-30)	PP Hollow fiber (X-40)	PP Hollow Fiber (X-50)
OD (μm)	300	300	300
ID (μm)	240	200	220
Thickness (μm)	30	50	40
Pore size (μm)	0.04 X 0.10	0.03 x 0.2	0.03 x 0.3
Open area (porosity)	40%	25%	53%
Tensile strength (MPa)	> 175 grams/filament	> 175 grams/filament	> 175 grams/filament
Array	50 HF/inch	53 HF/inch	53 HF/inch
m2 fiber/m2 array	1.8	1.8	1.8
Price	in modules only	In modules only	in modules only
Weaving capability	yes	yes	yes
SAMPLES	yes (fiber)	yes (array)	yes (array)

Quality control was an important consideration in evaluating loose HF received from the various suppliers. A yet more important consideration was the ability to assemble the fibers into arrays. Ultimately this consideration was not congruent with the basic manufacturing method used to create the micropores on the hollow fibers. That process eliminated all of the loose fiber materials and manufacturers that supplied samples. Unknown to us, until we received the HF samples, most firms that make dry stretch microporous hollow fibers use a batch method. This batch method results in damage to sections of the hollow fiber. Figure 5-2 and Figure 5-3 show examples of this damage. This type of damage does not present a problem when the loose fibers are used to make a simple, short, two tubesheet module, but it does eliminate the ability to use the fiber to make hollow fiber array.

Figure 5-2. Picture of damaged hollow fiber from batch dry stretch. Flattened fibers and clear sections indicating nonporous nature. These fibers are from membrane supplier 1.

Figure 5-3. Batch dry stretch hollow fiber from membrane supplier 2. Damage at the ends shows overstreched fibers with very small diameter, a split fiber and flattened fibers.

The batch dry stretch process used by most of the firms involves wrapping non-porous hollow fiber filament around two widely spaced pipes or dowels. These are moved away from each other in a controlled manner (ideally in a controlled

environment). This stretches the hollow fibers along its axis between the pipes thus forming the micropores. This process tends to damage the part of the hollow fiber that is wrapped around the pipe or dowel leaving some fibers in that region unstretched, and others over-stretched and/or compressed flat (see Figure 5-2 and Figure 5-3).

At the time of our research, we were only able to find one US based firm that used a continuous dry stretch process (US Patents 4,405,688, 4,541,981, 5,013,439) to make microporous polypropylene hollow fibers; Membrana-Charlotte (at their facility in North Carolina – their German manufacturing facility uses a different process).

While Membrana-Charlotte had provided samples to us for very small-scale development work, they would not agree to provide larger quantities. They agreed only to provide modules. Membrana-Charlotte has an extensive series of patents on the design and manufacture of their specific module design. This extensive patent portfolio meant that any other module provider would have to make a different design. Other candidate providers had the capability of laying down individual fibers but did not have the capability to assemble arrays, essentially a two-dimensional cloth rather than filaments.

Figure 5-4 illustrates membrane surface SEM, hollow fiber, hollow fiber array and a small permeator module assembled from he array.

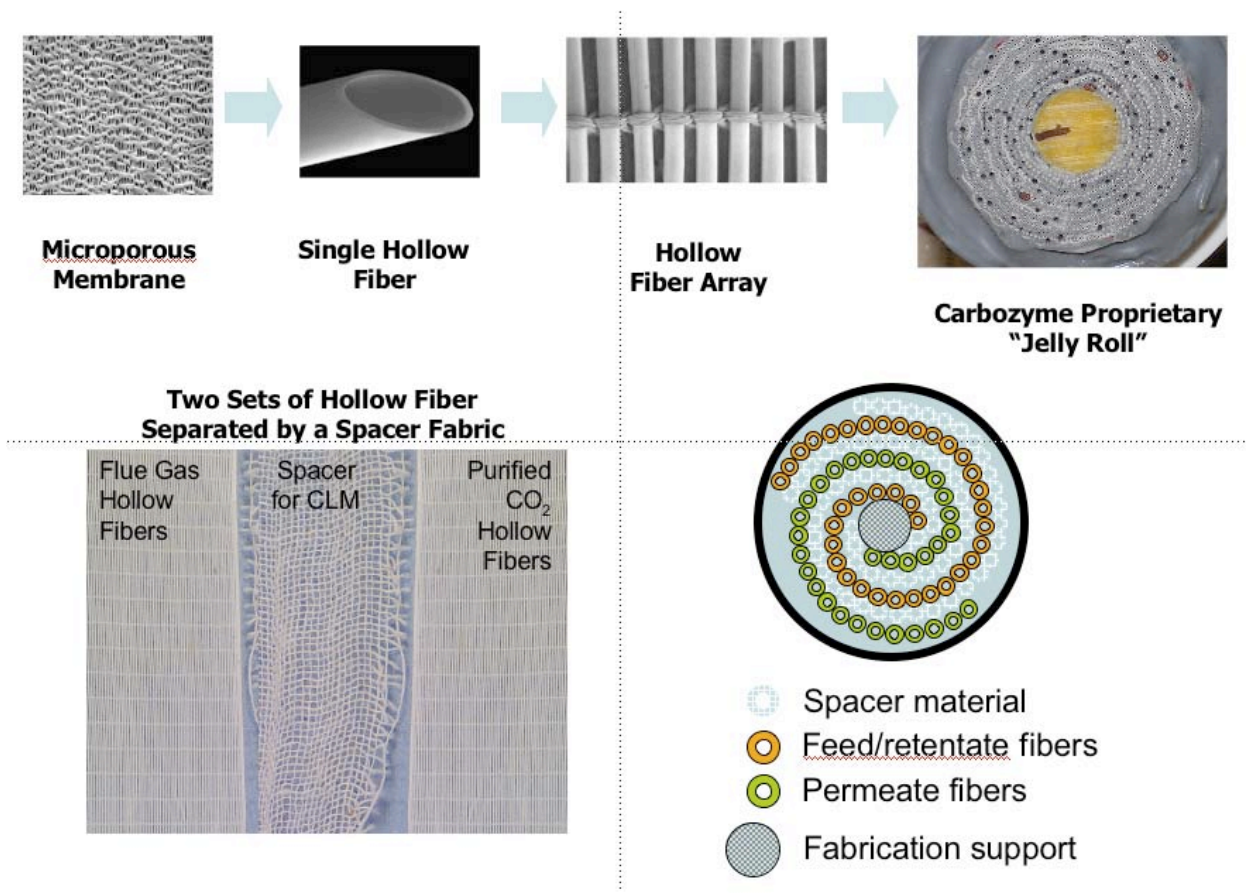


Figure 5-4. Illustration of the materials and assembly process for developing a permeator. A cross-section of the permeator is shown on the lower right.

Conclusion

Carbozyme's only practical solution was to purchase membrane and modules from a single vendor with the full range of capabilities needed to achieve the project goals - fiber production, fiber array knitting, modules design and fabrication, and the quality control. Carbozyme designed, developed and demonstrated certain improvements on the basic hollow fiber module design considered critical to the success of our product. One is the ability to layer multiple hollow fiber arrays. Membrana-Charlotte has this ability. Second, we wished to mix layers of microporous and non-porous fibers. Again, Membrana-Charlotte when approached exhibited willingness to make this modification. Third, Carbozyme has targeted a specific scale-up program to make progressively larger modules and module arrays. Membrana-Charlotte is experienced in this regard and has expressed willingness to satisfy these goals. As noted, a key consideration was that the vendor had to have both the requisite capabilities and an interest in making modifications to satisfy the Carbozyme design needs. Since this effort was a step on a path to commercialization a further requirement was that the vendor have the ability to scale-up the module to the largest possible size to achieve benefits of scale and to minimize the number of external connections, i.e. plumbing, valves, gauges, sensors, etc. Membrana-Charlotte displayed such a desire.

Upon completion of the evaluation, Carbozyme begun negotiated a contract with Membrana-Charlotte to manufacture modules for this contract. Additionally, Carbozyme requested from the DOE approval to add Membrana-Charlotte to the program as the module manufacturer. Upon termination of the contract, Carbozyme was still awaiting this approval.

6. TASK 4 - ELECTRODIALYTIC (EDI) TEST CELL DESIGN, CONSTRUCTION AND TESTING

Goal

Task 4 - Electrodialytic (EDI) Test Cell Design, Construction and Testing addressed the evaluation of the technical feasibility of using an electrochemical system (referred to below by the acronym RW-EDI) with the biocatalyst carbonic anhydrase (CA) to facilitate CO_2 capture for coal flue gas while exhibiting a smaller energy penalty than is the case with temperature swing (TSA) or vacuum swing (VSA) approaches. The goal is to examine a pH swing design (pHSA). The effort focused on developing and demonstrating a proof-of-concept of the process.

Approach

Electrodeionization (EDI) is an industrial process that incorporates ion-exchange (IX) resin beads in an electrodialysis (ED) stack. ED is an electrically-driven, membrane-based separation process. Commercial EDI systems are constructed by filling the diluate channel in an ED stack with loose IX resin beads. Argonne National Laboratory (ANL) has developed and patented a process for immobilizing the loose IX resin beads with polyethylene resins to form a porous resin wafer (RW) material.

The RW-EDI platform enables *in situ* pH control by using the water splitting reaction eliminating (or minimizing) the need for acid/base additives. This capability has significant promise for capture and release of CO_2 as bicarbonate. Carbozyme has developed a membrane-based platform that uses the enzyme catalyst carbonic anhydrase (CA) to convert CO_2 into bicarbonate in basic solution and back to CO_2 using TSA and VSA. In the current approach task, we combined the ideas of enzyme catalysis and RW-EDI under pHSA conditions to generate a new apparatus – CA/RW-EDI; the object being to absorb CO_2 under mildly alkaline conditions and desorb bicarbonate under mildly acidic conditions, with the reactions facilitated by CA

RWs are fabricated from commercial grade, gel-types of strong-acid cation and strong base anion exchange beads (Figure 6-1a). RWs with different cation/anion mixing ratios were fabricated using ANL's patented process (US 6797140, 7306934, and 7452920). Commercial polymeric ion-exchange membranes were used in assembling the RW-EDI stack. Different membrane configurations were tested during process development. A commercial ED stack was used as the base template to assemble the EDI stack. Two different ED stacks sizes were employed: 14cm^2 and 195cm^2 membrane size. ANL's in-house gasket material was used to seal the resin wafers in the stack (Figure 6-1b). The ability to scale-up the process is supported by ANL's bench scale and commercial scale facilities (Figure 6-2).

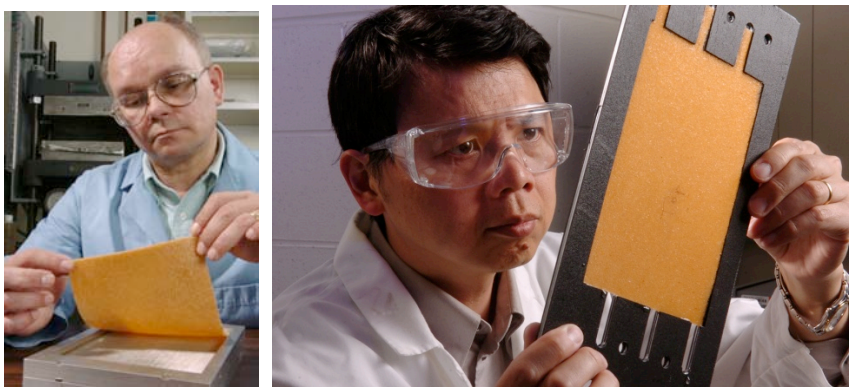


Figure 6-1. a) Resin wafer (195cm^2) as it is removed from the fabrication mold and b) inspected in its sealed gasket system

Figure 6-2. ANL's bench scale (195cm^2), pilot (0.2m^2), and commercial (0.4m^2) ED systems

Due to the novel challenge of delivering gas to the ED stack as well as the increased complexity of the process design, we constructed single cell pair arrays for the current experiments. In contrast, for desalination or organic acid recovery, a stack contains 5-10 cell pairs (a pair of ion exchange membranes with a diluate and concentrate channels). A pilot scale ED stack would typically include 20-50 cell pairs at 0.2m^2 and a commercial stack will typically include >100 cell pairs at 0.4m^2.

A variety of ionic carriers were used to provide counterions and/or buffer operations. These included NaCl, phosphate buffers, and potassium carbonate at concentrations of 3mM to 1M. Gas concentration was either 10% CO_2 in N_2 or 15% in air, each at 101.3kPa (1 atm). A total organic carbon (TOC) analyzer was used to analyze bicarbonate solution concentration. Gases were analyzed by means of a residual gas analyzing mass spectrometer (RGA). All the samples were conditioned with NaOH and kept in sealed sample vials to avoid atmosphere exchange of CO_2.

An EDI stack setup, built by ANL, was sent to Carbozyme for calibration and testing. Figure 6-3 is a photograph of the EDI setup running at Carbozyme. The test cell is the large silver rectangular device on the left. While the intent of the EDI setup was to provide data that would allow closure of the mass balance while accomplishing separate analysis of the absorption and desorption capacity of the system, as a function of solution chemistry, current, and enzyme we were aware that the use of such small stacks would make closing the mass balances difficult. As it turned out, overall there was a 50% variance in mass balance, which for this small system was considered quite acceptable.

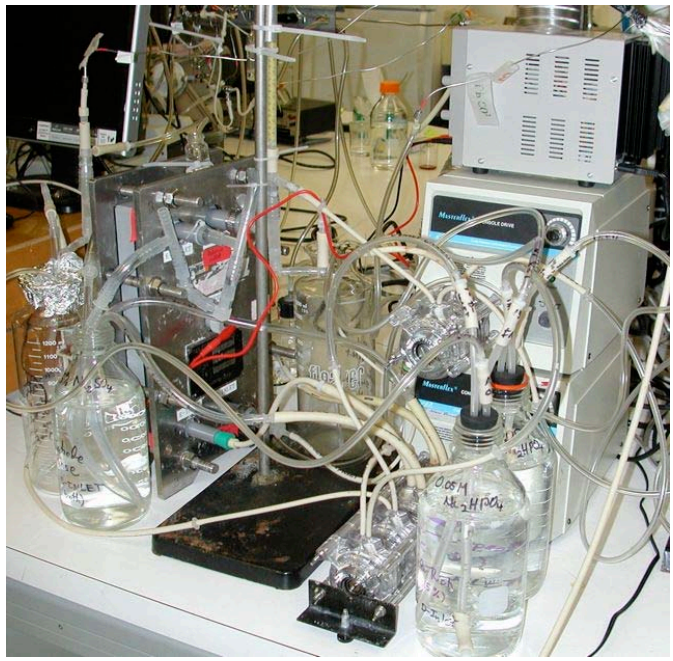


Figure 6-3. CO_2 capture EDI apparatus with pumps, solution reservoirs and power.

Four different test paradigms were examined – a) no enzyme / no current, b) no enzyme / current, c) enzyme / no current, and d) enzyme / current. These conditions were run under a variety of closed-loop and open-loop scenarios for both absorption and desorption stages. The variables considered included gas and liquid flow rates, flow distribution in different cell-pairs, buffer composition and concentration and current density, and measurement of pressure drop and product purity, all leading to a calculation of effective parasitic load. Importantly, these experiments involved a single or, at most, 2 cells while a commercial apparatus would involve a minimum of 100 cells, thus the energy losses in the electrode compartments would be significantly reduced and the apparent efficiency would be much greater.

Results and Discussion

Design EDI bioreactor with in situ pH control to create different pH zones for CO_2 absorption and desorption

Two different designs were evaluated for their capability to create local pH zones for acidic and basic pH. Figure 6-4 (a) and (b) show the schematics and examples of the RW of these designs. In design I, acidic and basic zones were separated by the ion-exchange membranes. In design II, the different pH zones were placed in the same EDI compartment and separated by a porous barrier.

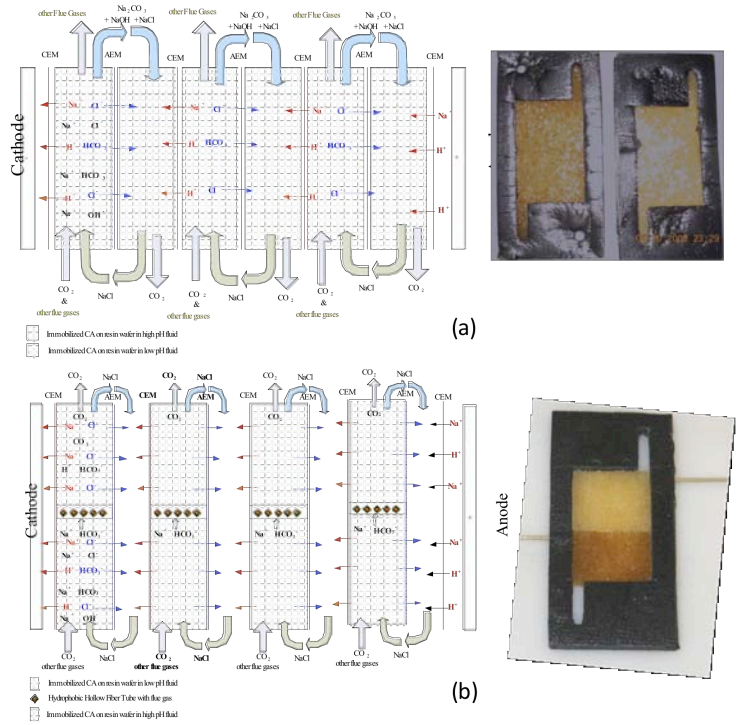


Figure 6-4. EDI configurations of design I (a) and II (b)

NaCl provided shuttling counterions for water splitting during operation to generate the different the pH zones. The basic pH zone would be used for CO_2 capture and the acidic pH zone used for CO_2 release. The data in Figure 6-5 verify the ability to create different pH zones. The pH could be as high as 11 and as low as 3. NaCl solutions were circulated through the basic pH compartment and then the acidic pH compartment before returning to the recirculation tank. Many variables affected the pH of the solution in different zones. Among these were feed flow rate, applied current and the mixing ratios of ion-exchange resin beads in the resin wafer.

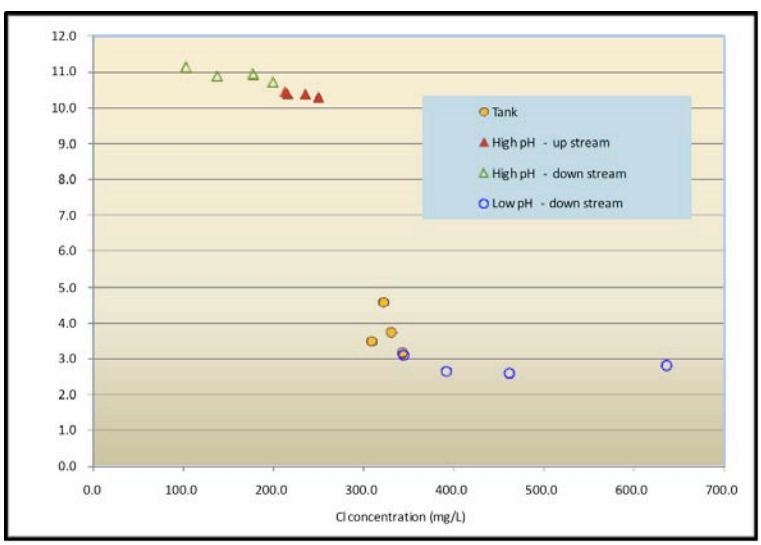


Figure 6-5. Solution pH in different EDI compartments

Consideration of different EDI designs for CO_2 absorption and desorption

We used a "half-cell" to evaluate each the pH-dependent CO_2 capture and release processes. Figure 6-6 illustrates the EDI membrane configurations for each half-cell. In each process, resin wafers with different cation/anion mixing ratios were used to generate the proper local pH in the RW compartment. Five RW conditions were compared – 1) anion excess, 2) pure cation, 3) pure anion, 4) cation excess, and 5) no RW. NaCl was used to shuttle counterions for the conversion of CO_2 into bicarbonate in the capture step or neutralization counterions during conversion of bicarbonate to CO_2 in the release step.

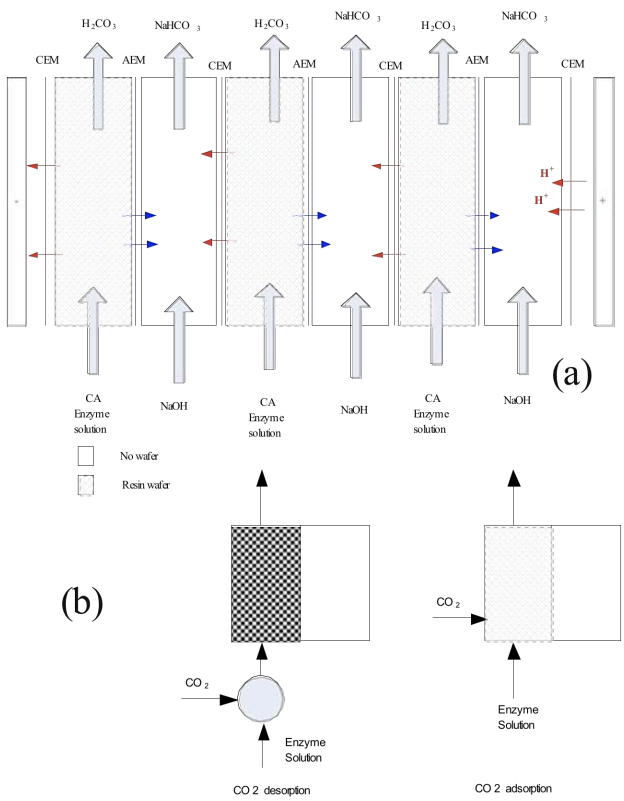


Figure 6-6. (a) Configuration of the "half-cell" EDI stack; (b) Schematic of CO_2 gas and solution feeding in capture and release experiments.

To evaluate CO_2 desorption from solution we simulated the CO_2 capture fluid by use of a feed solution that had been saturated with CO_2, before introduction to the RW-EDI stack (Figure 6-6a). Figure 6-7 shows the CO_2 release rate, using different kinds of IX RW compositions, and the power consumption needed to achieve the CO_2 release. The results show that mixed cation/anion resin wafers performed better than pure resin wafers. Anion-excess resin wafers had better performance and overall lower power consumption (around 0.4kWh/kg CO_2 release) than the other resin wafers. ED performance without the resin wafer was inferior; it exhibited a 500% increase in power consumption in comparison to the best RW-EDI format. This result highlights the significant advantage of RW-EDI for CO_2 release.

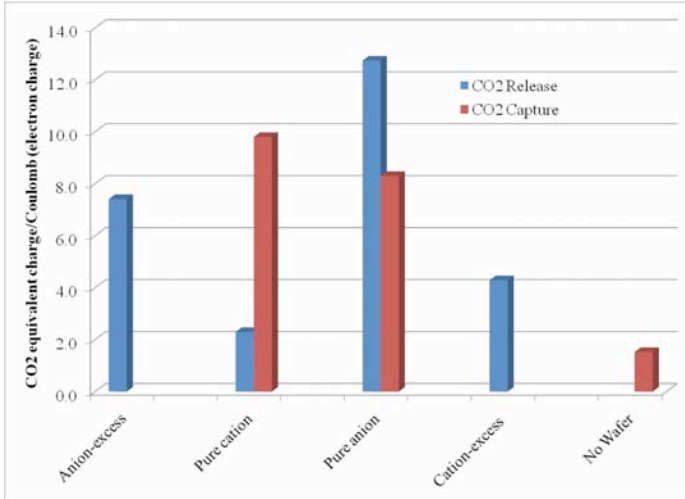


Figure 6-7. Electrical efficiency of capture and release of CO_2 based on resin wafer composition.

Feasibility evaluation of CO_2 capture/release from liquid-gas mixing zone in RW-EDI-Half-cell test for CO_2 Capture (absorption)

A similar setup (Figure 6-6a) was used to evaluate the CO_2 capture behavior with CA/RW-EDI. CO_2 was fed directly into the resin wafer compartment in the EDI stack and contacted with the capture solution. Figure 6-8 shows the results for CO_2 capture and power consumption with pure resin wafers. Similar to the results from the CO_2 release evaluation, the CA/RW-EDI provided significant performance advantages over ED. Figure 6-9 summarizes power consumption for CO_2 capture and release using the CA/RW-EDI technology.

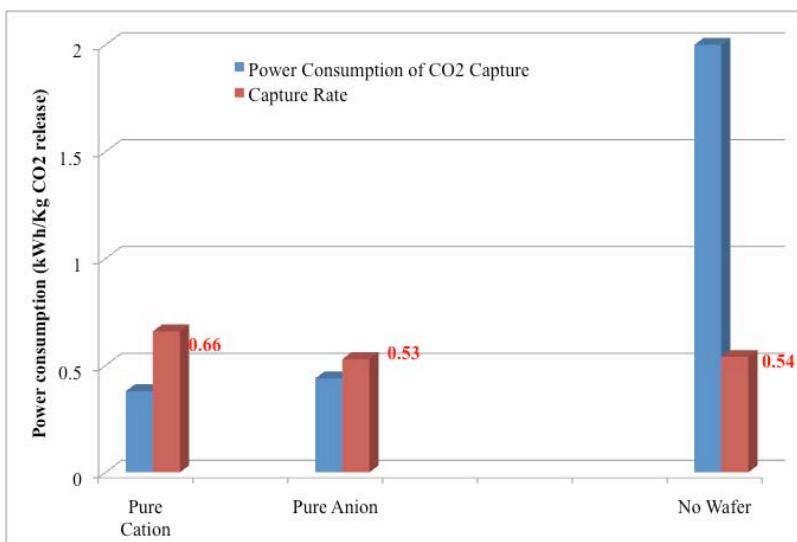


Figure 6-8. Power consumption and CO_2 capture (absorption) rate using different resin wafers.

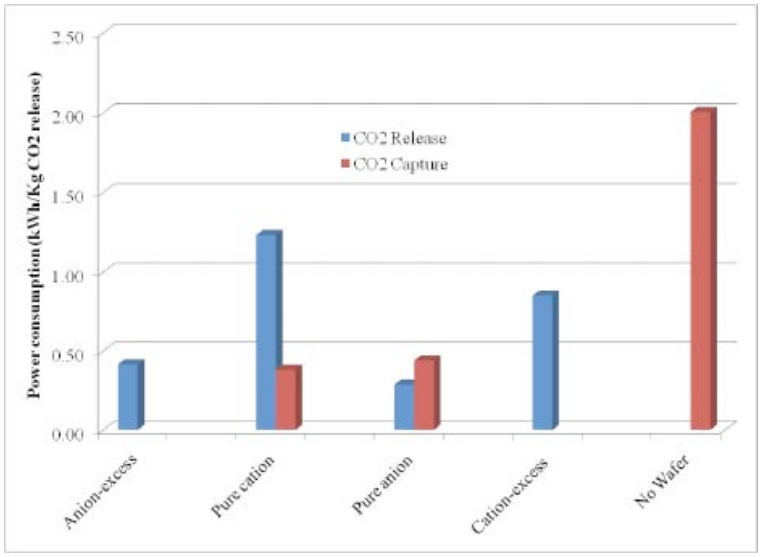


Figure 6-9. Comparison of CO_2 captures and release using different types of resin wafers.

Feasibility evaluation for CO_2 capture and release using a full RW-EDI cell with liquid-gas mixing resin wafer

A full RW-EDI cell was assembled (Figure 6-10) such that the counterion shuttles were recirculated between the CO_2 capture and release compartments. Note that CA was in the bulk solution; it was not immobilized.

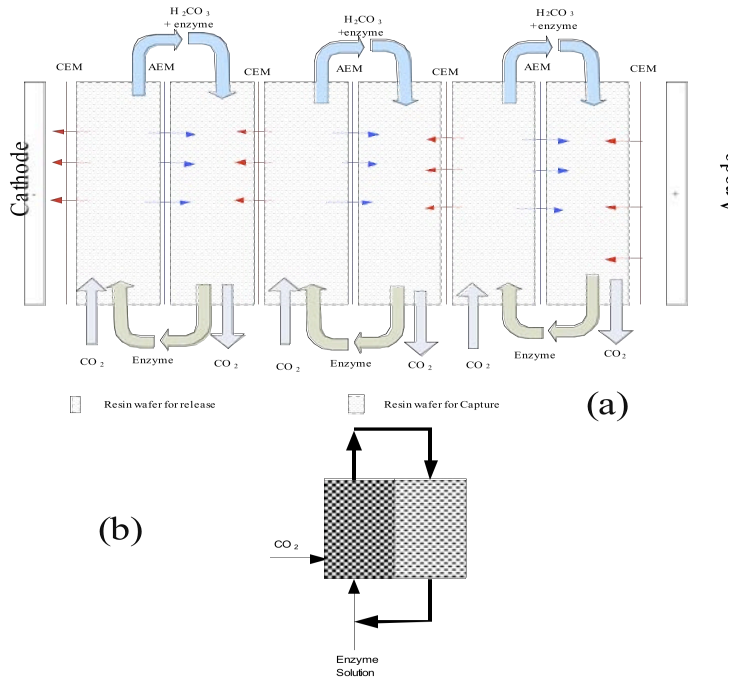


Figure 6-10. Configuration of a single EDI stack for CO_2 capture and release.

Figure 6-11 is a schematic representation of the gas and liquid flows and the sample locations.

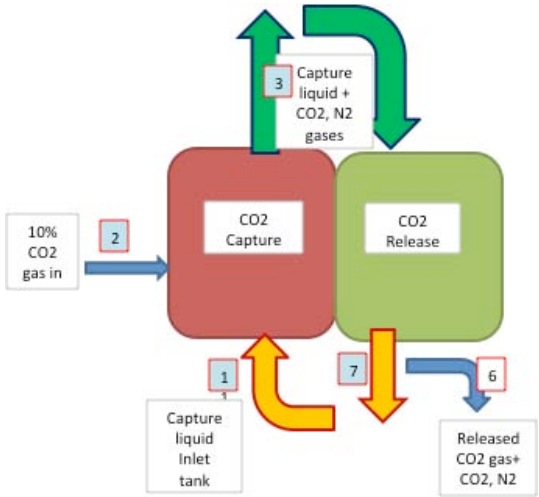


Figure 6-11. Schematic of EDI experimental setup for single-stage CO_2 capture and release.

Testing employed a 10% CO_2 gas (balance N_2) fed directly into the capture compartment where it was converted into bicarbonate. The bicarbonate solution was fed into the CO_2 release compartment to be converted back to CO_2. Several IX membrane configurations were assembled and tested for the performance. The best membrane configuration was selected to demonstrate feasibility. Table 6-1 shows the results of CO_2 capture from the 10% CO_2 (balance N_2) gas stream. Phosphate buffer (10–50mM) was used as the counterion solution. A relatively stable 80% CO_2 capture/release efficiency was achieved in with the RW-EDI with CA. Without CA, the RW-EDI had an overall efficiency of only 40% CO_2 capture/release. The RW-EDI/CA system also reduced power consumption by 50% as compared to the RW-EDI without CA.

Table 6-1. CO_2 capture and release with a single cell pair with RW-EDI system.

Conditions	Operation time	CO2 Capture Ratio in Captrure compartments	CO2 Release Ratio in Release Compartments	Overall CO2 Captured/Release in EDI	CO2 Captured/Release Power Consumption (kWh/kg CO2)
Resin Wafer EDI	Without CA enzyme				
	60 min	77%	74%	57%	2.1
	120 min	70%	57%	40%	2.7
Resin wafer EDI	With CA enzyme				
	60 min	108%	69%	74%	**2.2**
	120 min	97%	92%	89%	**1.4**
	180 min	94%	83%	78%	**1.3**

The power consumption in the presence of different anion and cation mixtures is shown in Figure 6-12. Anion materials were the more effective.

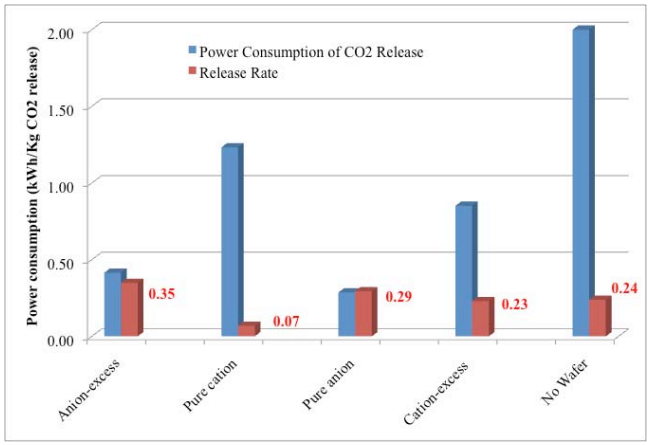


Figure 6-12. Power consumption and CO_2 release (desorption) rate using different resin wafers.

Evaluation of different EDI RW designs for CO_2 absorption and desorption

The effective dry composition of the product gas derived from a feed gas of 15% CO_2 in air, and generated under room temperature, and atmospheric pressure conditions, was 91.9% CO_2, 5.1% N_2, 3.0% O_2, and 3.0% water vapor. For purpose of comparison, the initial HFCLM product gas was released at ~50°C, 0.2atm, ~54% water vapor. Following mild compression the effective dry composition product was 93.6% CO_2, 3.6% N_2, and 2.7% O_2.

The EDI experiments indicated that an EDI system can be designed, prototyped and operated in a manner where it will achieve ~90% removal of CO_2 from a flue gas and could produce a CO_2 product of ~92% purity, dry. The current data, from proof-of-concept experiments without optimization, indicate that the power consumption for CO_2 capture, is around 1.4-1.5 kWh/kg CO_2, equivalent to ~$65/tonne CO_2 at a cost electricity of $0.05/kWh. We believe an optimized system could achieve an energy cost of <0.2kWh/kg CO_2. Our preliminary economic model of the optimal process operations predicts <$20/tonne CO_2 capture and release. Current estimates are that the size of this device, without process optimization, is quite large and the gas flow pressure drop is too high to be acceptable. The device that was achieved was useful for proof-of-concept. The limitations of the design are:

(1) The prototype system was only a single-cell-pair stack – the result being a significant parasitic load in the electrode cells therefore the efficiency of energy use was limited. Note that the commercial EDI stack will have more than 100 cell-pair stack, which will significantly enhance the energy efficiency of this system. In addition, because our design does not require the captured ions to be transported across the ion exchange membrane, we can use thicker resin wafers.

(2) The gas distribution in the prototype system, i.e. gas-liquid contacting, was done in the simplest possible manner and was designed only for proof-of-concept. This means there was a relatively high gas flow pressure drop through the system and a low and unquantifiable gas/liquid mass transfer area per unit volume. The observed pressure drop was 8.4-8.6kPa (1.20-1.25 psig) for this small system, which was operated at a moderate gas/liquid flow rate ratio. While this pressure drop may appear modest one has to recognize that the

length of the flow path was small and gas flow pressure drops are expensive. We estimated that a 13.8kPa (2 psi) pressure drop would cost 10MWe for an EPRI 7c (approximately 500MWe) power plant (i.e. 2% parasitic load, for this small pressure drop). The volumetric CO_2 capture rate observed was ~30kg/m^{4-}day (based on the resin wafer volume). [Note: The volumetric absorption and desorption rate based on current flux values.

The net result of this analysis is that a significant improvement in the design and construction of the EDI system is needed before it can be determined if it can be scaled up to a commercially viable system. The system must achieve a much higher volumetric CO_2 absorption rate and a lower electrical power use before it could be considered viable.

Because the electrical cost observed is already $65/tonne and the volumetric capture rate is low, it is unlikely a more detailed economic analysis will provide any benefit but would entail considerable cost. An economic analysis would be justified for an optimized system.

Conclusion

We demonstrated the technical feasibility for CO_2 capture and release in a RW-EDI using CA in with a counterion shuttling solution in the proof-of-concept demonstration. The presence of CA increased the rate of CO_2 absorption by 5-fold. The overall efficacy of using the CA/RW-EDI system was almost 10x vs. the no enzyme / no current condition. Overall, our results indicate that adding current provides a 70% increase in CO_2 capture and a 155% increase in CO_2 release. The power consumption for CO_2 capture and release is around 1.4-1.5 kWh/kg CO_2, about $65/ton CO_2 at the cost of $0.05/kWh electricity.

7. TASK 5 - PERMEATOR SCALE-UP DEVELOPMENT

Goal

Task 5 – Permeator Scale-up development addressed the design, fabrication, testing, analysis and demonstration Carbozyme's CO_2 Capture System. This task was setup to scale-up the SWHF-CLM module design in two stages. Initial validation of the design would be done on 0.5m^2 SWHF-CLM permeator. This will be followed by the incremental development of a 40m^2 module that would benefit from the previous empirical performance testing.

As the design of Carbozyme's CO_2 Capture System changed, this task was modified on June 23, 2009 substituting an 11m^2 system rather than a 40m^2 module.

These successive size scaling developments and demonstrations are a necessary prelude to yet greater scale to be delivered to the EERC for testing, using actual, albeit heavily scrubbed, PC flue gas in Task 8.

Approach

Test Plans for Carbozyme's System

The first step in the engineering development was to develop standardized test plan procedures to qualify modules, i.e. to control for gas, liquid or vacuum leaks in the fibers, tubesheets or fittings.

Two plans would be developed. The first plan would be directed towards module qualification and laboratory scale demonstrations developed by Carbozyme. The second would target the 42MJ/h (40,000 BTU/hr) tests using the Conversion and Environmental Process Simulator (CEPS) at EERC. The EERC test plan addressed the various performance aspects expected to fully understand the capabilities of the module during upset and non-upset conditions.

Carbozyme developed a qualification test plan applicable to each module. The details are:

1. Water pressure test of the liquid handling section: Pressurize the system to 207kPag (30 psig). Look for leaks in fibers (sealed & semi-permeable), tube sheets and fittings.
2. Water pressure test of the gas handling sections: Pressurize the system to 207kPag (30 psig). Look for leaks in fibers (sealed & semi-permeable), tube sheets and fittings.
3. Fill the CLM space with water pressurized to 207kPag (30 psig) and pull a vacuum on gas sections to -96kPag (720mmHg), a value slightly below the vapor pressure of the water. Hold the vacuum looking for a pressure rise in gas sections. If the vacuum cannot be maintained, determine the leak site and repair if possible.
4. For Permeators, set up as in 3, pressurize the Feed side and provide a vacuum on the Sweep side. Set the Feed pressure at 101.3kPag and the Sweep to -96kPag (720mmHg). Observation of an increase in the vacuum pressure of the sweep side or a fall in pressure of the sealed feed side from atmospheric pressure indicates a failure.

5. Pressurize any impermeable fibers to 207kPag (30 psig) and look for a fall in pressure and for leaks.

Carbozyme's system test plan employed the following steps:

1. Complete integrity testing of the permeator test bed assembly at room temperature without the permeator being placed in external insulation.
2. Repeat testing at room temperature with Permeator installed inside a 6" urethane insulated shell.
3. Insulate the permeator external systems to allow operation at design temperatures.
4. Perform no-enzyme performance testing at design temperature.
5. Perform performance testing at design temperature using enzyme.

EERC's CEPS will be used to produce the combustion gases for the short-term tests of the Carbozyme permeators. The CEPS system will be set up with the 42.2MJ/hr (40,000-Btu/hr) combustor followed by a selective catalytic reduction (SCR) reactor for reduction of NO_x, a baghouse for particulate removal, a wet flue gas desulfurization (FGD) unit for SO_x removal, the specially designed polishing scrubber to meet the Carbozyme permeator flue gas acceptance requirements, a continuous mercury monitor (CMM) to measure mercury concentration, and the skid containing the three 40m^2 (*i.e.* total of 120m^2) Carbozyme permeators. The layout is shown in the Figure 7-1 schematic.

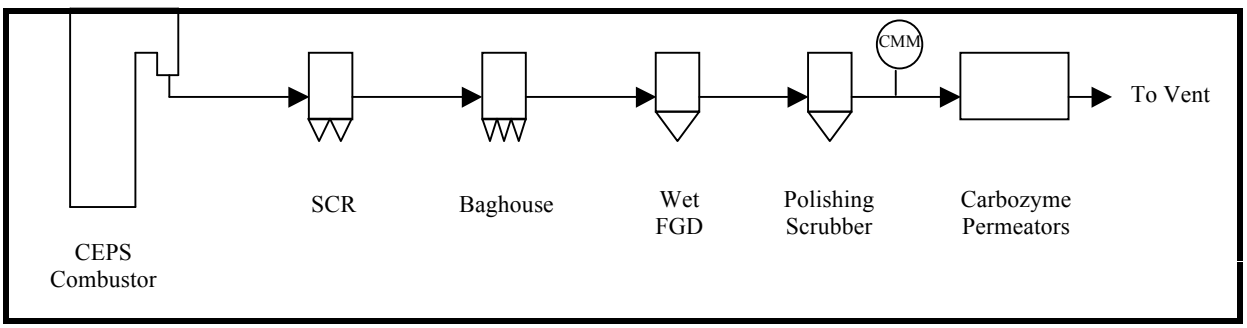


Figure 7-1. Schematic of CEPS as it will be set up for the Carbozyme System testing.

The Carbozyme System will be tested during four 250-hr tests. One test will be conducted using natural gas, another using a North Dakota lignite, a third using a Powder River Basin subbituminous coal, and a fourth using a bituminous coal. To permit the direct comparison of data for the various combustion feedstocks, all of the tests will be conducted using the experimental matrix outlined in this document.

Steady Conditions Test Plan (Duration 0–250 hrs)

The first, and lengthiest, portion of each 250-hour test will examine the operation of the Carbozyme permeators under normal, steady-state conditions.

- The polishing scrubber operating parameters will be set so as to achieve a SOx output of less than 10ppmv. (This end was achieved and is described above – Section 3).
- The coal feed, in coal combustion tests, will be held at a steady rate based on the furnace exit gas temperature. This temperature will be about 1093°C (2000°F) for

the lignite and subbituminous coal tests and about 1204°C (2200°F) for the bituminous coal test.
- The furnace static pressure and eductor/vacuum pump will be held at steady operation.
- The baghouse will be pulsed every 20 minutes.

Upset Conditions (Test Hours 201–250)

Various upset conditions that are likely to occur during operation at a power plant will be evaluated during the final 50-hour of each test. Upset conditions that will be tested include the following:
- SO_2 concentration spikes
- CO concentration spikes (from 5 to 100ppm)
- Furnace static pressure changes (i.e. Δp spikes)
- Particulate spikes (i.e. more-frequent baghouse pulsing)
- Power failures in the polishing scrubber, the eductor/vacuum pump, and the coal feed systems

We hypothesized that power failures could conceivably permanently damage the Carbozyme permeators. Therefore these tests would be limited to the final 15 hours of testing. We'd pulse the baghouse every 10 minutes during the testing. Five SO_2 concentration spikes were to be tested, as would ten furnace pressure spikes, and 20 CO concentration spikes. While one upset condition was scheduled occur every hour, the specific upsets would be randomized over the remaining 35 hours of testing.

Permeator Instrumentation Development and Testing

The next step in the engineering development was the design, selection, procurement, installation, and testing of the necessary sensors and controls for data collection and operation monitoring. The design included the necessary data points required to fully evaluate the systems performance during the testing protocols developed in all the test plans. Programmers at the EERC worked to ensure that the sensors, control hardware, and data collection and monitoring software would be compatible with the EERC's testing platforms (*i.e.* the CEPS and the ash fouling unit). EERC programmers developed the necessary computer code for computer-controlled operation of the system during testing at the EERC.

Carbozyme assembled a management and data acquisition system. The principal pieces of equipment are an Extrel Residual Gas Analyzing Mass Spectrometer (RGA) outfitted with a 16-port rotary valve, an Environics computerized Mass Flow Controller (MFC) and a National Instruments LabView data acquisition system. We wrote programs in-house for the NI LabView system. The system was instrumented with a series of thermocouples inbuilt to allow sampling of temperature throughout the apparatus. Inlet and outlet gas and liquid flow rates and pressures were monitored.

This system was programmed so that the MFC stepped through a series of feed gases to provide, successively 5, 10 and 15% CO_2 gas streams to the system for the testing of different systems as part of Task 2. In parallel the feed gas was monitored by the RGA as were the permeate and retentate gases. As noted, 14 temperature readings were also captured.

This final design evolved from manual to a fully automated process during the course of the project. Under the last condition experiments could be run 24/7 with no attendance. The data set was accessible from off-site locations. Remote video

monitoring allowed an off-site technician to view the apparatus in operation to determine if manual maintenance was needed.

Figure 7-2 is an illustration of the data display available in the laboratory and available online. . The traces illustrate the temperature profile within the permeator in addition to several key control that support operation of the permeator. Note the variability of the room temperature

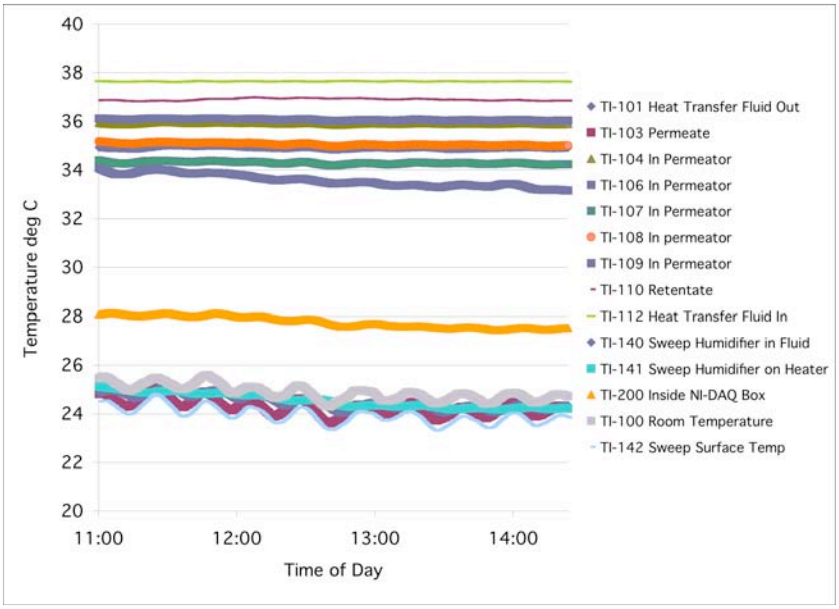


Figure 7-2. Example of temperature data collected during permeator operation.

Design of 0.5m2 SWHF-CLM Modules

Carbozyme originated in-house design and construction of a 0.5m^2 permeator. There were two key tasks - a) the structural layout of the multi-tubesheet design and b) the development of a Heat and Materials balance.

To manufacture these devices, Carbozyme had to consider such issues as tube sealing methods, roll-up procedures, spacer elements, epoxy management methods, shell design and components. Lastly, we generated a process and instrumentation diagram in order to measure key values permeator performance values during operation.

The original design consisted of two inlet and two outlet hollow fiber arrays and a CLM path to yield a 4-tubesheet pattern (Figure 7-3). Membrana-Charlotte ultimately provided a 5-tubesheet design model for use as the desorber portion of an absorber/desorber pair.

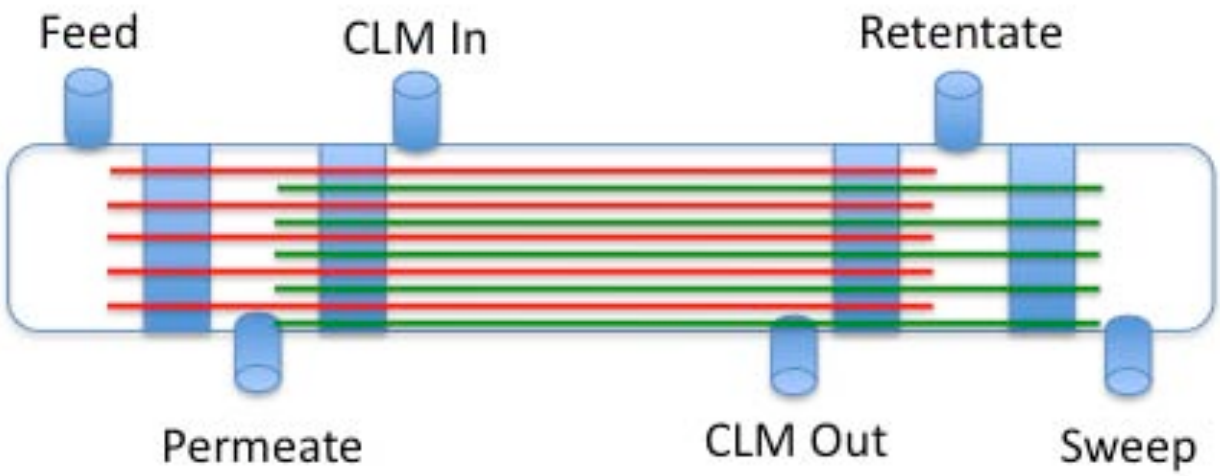


Figure 7-3. Four-tubesheet permeator.

Fabrication of 0.5m² SWHF-CLM and Module

We fabricated a permeator based on the accepted design developed for 0.5m² SWHF-CLM module. Fabrication required the procurement of materials, assembly, and acceptance testing of a 0.5m² SWHF-CLM module, in accordance, with Carbozyme's internal module and system test plans. Iterative design modifications and fabrication were required to achieve acceptable CO_2 capture performance.

The first process we needed to develop was a method for sealing fibers. We experimented with two methods – heat sealing and chemical coating. Heat sealing proved very delicate and required a very well controlled oven as the PP fiber could shrink or become fragile if not handled properly. Chemical coating required initial surface activation by chromic acid followed by surface coating with a UV-curable epoxy (Henkle Loctite). Surface activation is a common requirement of PP due to the absence of reactive groups on the surface to enhance binding of the epoxy to the fibers. This process could also be applied to the HTF fibers.

The assembly development process took place step-wise by constructing a 1-, 2-, and 4-tubesheet design.

A related task was the design and construction of the module housing, i.e. the shell. The initial design was in clamshell formation. Subsequent designs consisted of cylindrical arrays joined by couplers. Several iterations of the coupling scheme were needed before settling on one that worked consistently, easily and without shell leaks.

A large insulation shell was needed to surround the permeator due to the large surface area to volume ratio of these small diameter systems. Addition of the shell would allow detailed study of heat transfer occurring within the permeator. We constructed several different shell models before standardizing on a process that was easy to manufacture and gave uniform insulation.

Three problem areas arose several times in the process.

1. The hollow-fibers broke during assembly, a situation that is not unusual for such assemblies. The repair strategy was to detect which fibers are broken by means of a water test and then to seal those fibers so that they do not contribute to performance compromise.
2. The tubesheets leaked. The usual solution is to increase the width of the tubesheet, paying considerable attention to the initial sealing step, as failures occurred at the rollup rod.

3. The shell assembly broke during pressure testing. Several iterations in design eliminated this issue. We moved to CPVC for the shell materials, as the operating temperature exceeded the temperature rating for PVC.

Figure 7-4 illustrates a multi-tubesheet permeator before being encased in insulation.

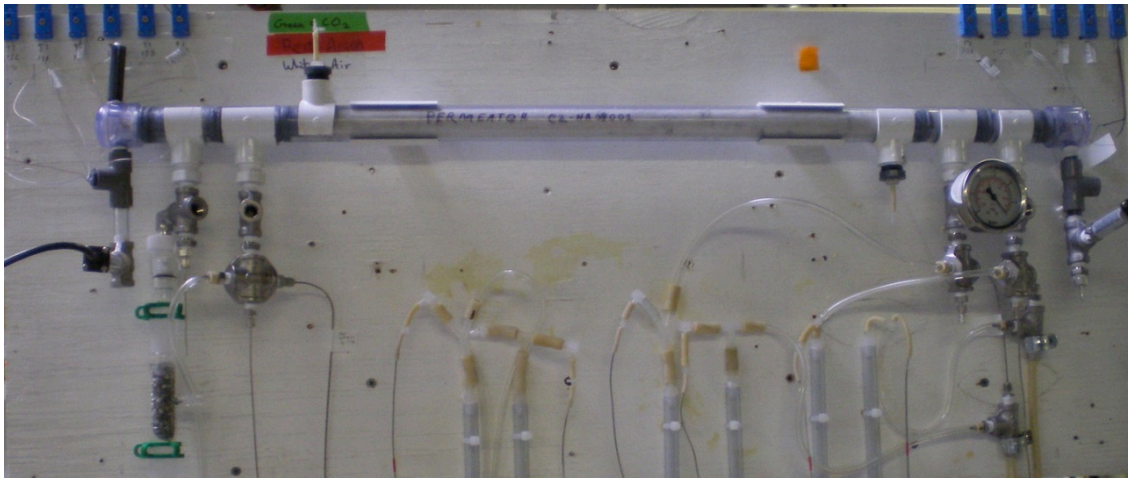


Figure 7-4. Permeator being assembled onto a test bed.

Figure 7-5 is a cross section of a similar design. The dark dots are thermocouple wires.

Figure 7-5. Cross-section of an assembled permeator.

Short term parametric testing of the 0.5m^2 SWHF-CLM module using natural gas or CO_2-spiked air was performed successfully in our laboratories.

Design of 11m^2 SWHF-CLM Modules

Upon completion of the testing and analysis of the 0.5m^2 SWHF-CLM module, Carbozyme began to design a 40m^2 SWHF-CLM module. Carbozyme and its membrane/module manufacturer (Membrana) considered lessons learned from such

issues as module design and operation, pore sealing methods, spacer design and manufacture, and to explored the successes and challenges encountered during the 0.5m^2 module construction. Membrana constructed an11m^2 CLM module for testing (Figure 7-6). Membrana provide data regarding two types of testing performed on these modules to demonstrate that they are structurally sound and can provide gas transport (degassing) across each set of fibers (feed-retentate and sweep-permeate). The performance was consistent with what is expected. (Note: this is not gas permeance testing but water degassing testing consistent with a standard module testing method used to qualify 3-tube sheet fluid degassing modules).

The existence of the 11m^2 design coupled with the extensive redesign, retooling and inherent delays associate with moving to an alternate design led to the expedient decision to use this apparatus as a basis for further studies. In addition, this design could be retrofit to operate in an absorber/desorber format.

Membrana went on to test the 11m^2 CLM module under a set of design conditions provided by Carbozyme to baseline apparatus performance. Initial testing was designed to evaluate the integrity of the design followed by data on CO_2 uptake into water followed by a $KHCO_3$ test. In the latter Membrana demonstrated an ability to extract as much as 65% of the CO_2 from a feed containing 15-20% CO_2, using a liquid temperature of 27°C. Figure 7-6 shows the apparatus setup in Membrana's lab.

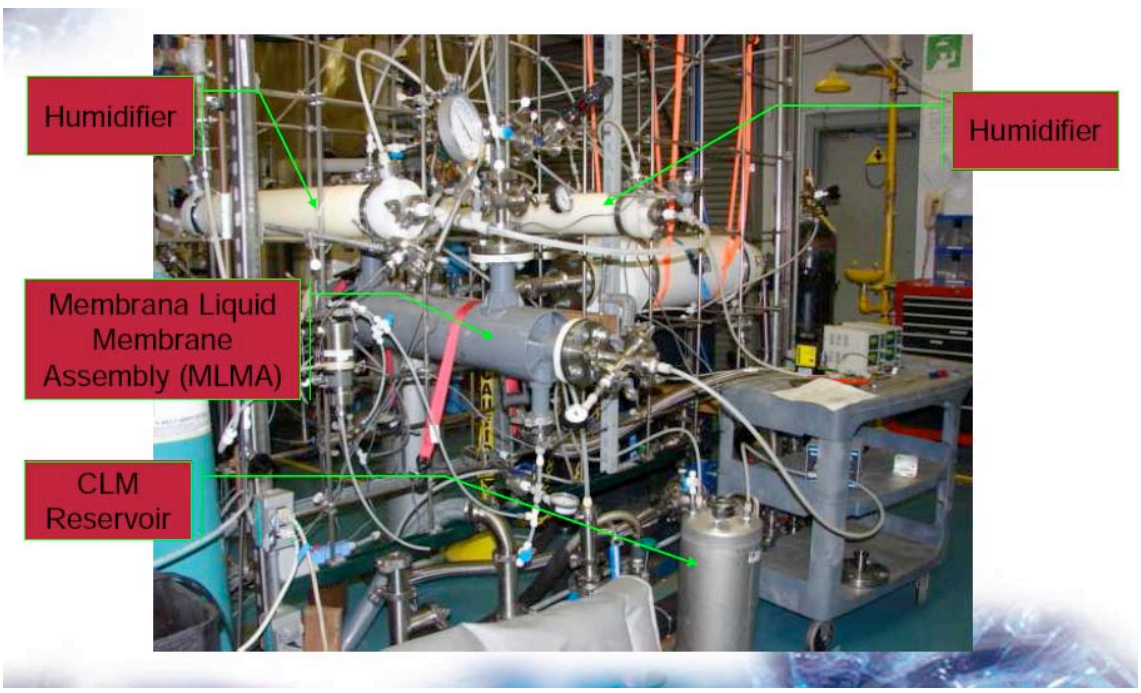


Figure 7-6. Illustration of the Membrana test rig.

Per revision of the SOPO, the original 40m^2 development effort was replaced by a 42m^2 absorber to be used conjointly with two 11m^2 desorbers (Figure 7-7). The permeator design was replaced by an absorber/desorber design to more closely fit the manufacturing capabilities provided by Membrana-Charlotte.

We developed a simulator for the design and construction of a complete system that included flue gas conditioning, through quench, cleanup, capture, flue gas reheat, CO_2 purification, trace O_2 removal, compression, drying and final pressurization to 16.5MPa (2400psi). The process used in the development of the simulator was to setup a PFD of

the flue gas treatment system that incorporates the lessons learned from the previous development of the permeator and modified to accommodate the new configuration.

The process integrated the flow sheets, the heat and material balance and a variety of new consideration developed for the separation system. The data acquired are used to replace the theoretical values to improve our modeling. The new model was used to define the flow rates/size/specifications for equipment (*i.e.* pumps, blowers, humidifiers, pipes/tubing), instruments (*e.g.,* flow tubes, temperature indicators, pH meters, pressure sensors) and sizing of the 11m^2 test module.

Figure 7-7 is a schematic representation of the layout of the absorber/desorber system under development. The stripper modules will be run in parallel. The modules will be constructed by Membrana-Charlotte using their hollow fiber array that has been plasma activated for use in enzyme immobilization. This three-module system is expected to capture quantities of CO_2 equal to that originally envisioned for a 40m^2 SWHF-CLM module.

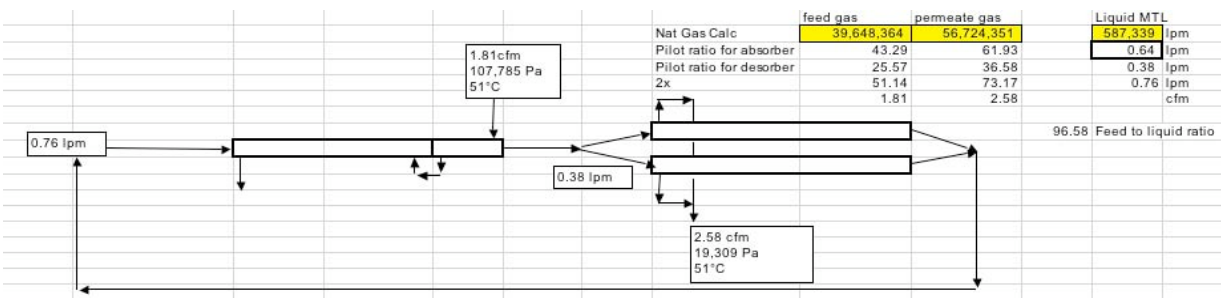


Figure 7-7. Schematic diagram of the one absorber, two parallel desorber system including module flow rates for test package.

Figure 7-8 is a PFD schematic representation of the absorber/desorber system that was designed. The numbered flows correspond to stream numbers in the heat & material balance. We performed extensive calculations on the new absorber/stripper design to predict the operational performance of the system. The calculated results, based on an EPRI 7C sized power plant, 462MW without CO_2 capture, shows a power generation of 407MW with CO_2 capture. This represents a parasitic load of <15%.

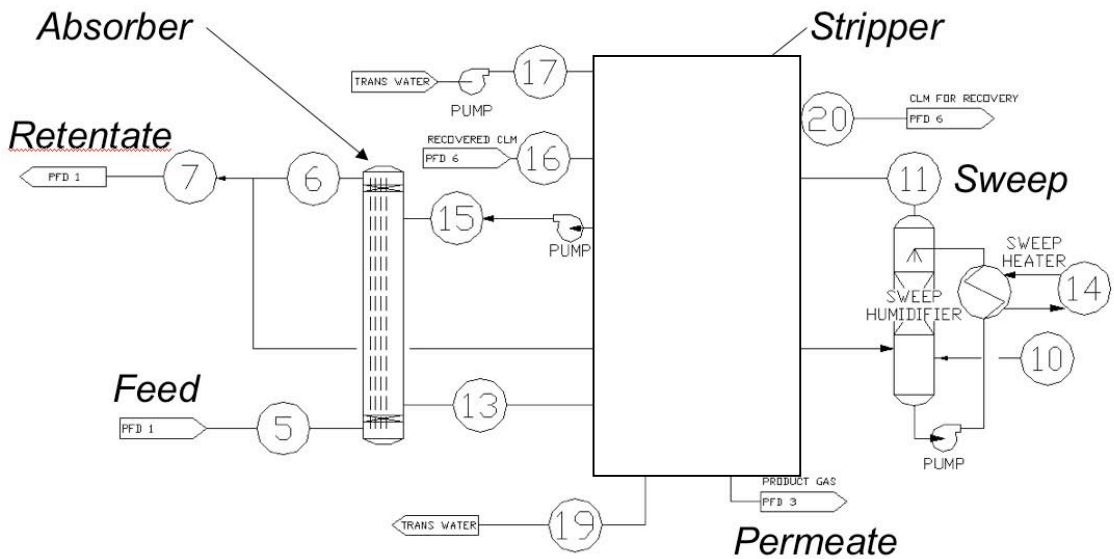


Figure 7-8. PFD Schematic diagram of the Carbozyme absorber/stripper.

The characteristics of the product gas before any cleanup but after drying are:

- CO_2: 99%
- O_2: 128 ppm

Per the mutually agreed to termination the program the task was not furthered.

Results and Discussion

Modeling of Predicted CO_2 Capture Performance

In prior work we constructed a one-dimensional (1-D) model of gas movement across the permeator. In the present work we constructed a 2-D model. Figure 7-9 shows the gas phase partial pressures for CO_2 for the flue gas side (black and blue lines) and the CO_2 product side (green and grey lines) for the 1/10th target enzyme concentration (blue and green lines) and the no-enzyme (black and grey lines) conditions. Flue gas enters at the left and exits at the right. Permeate runs countercurrent and exits at the left. The enzyme condition modeled is the 1/10th the design free enzyme concentration condition.

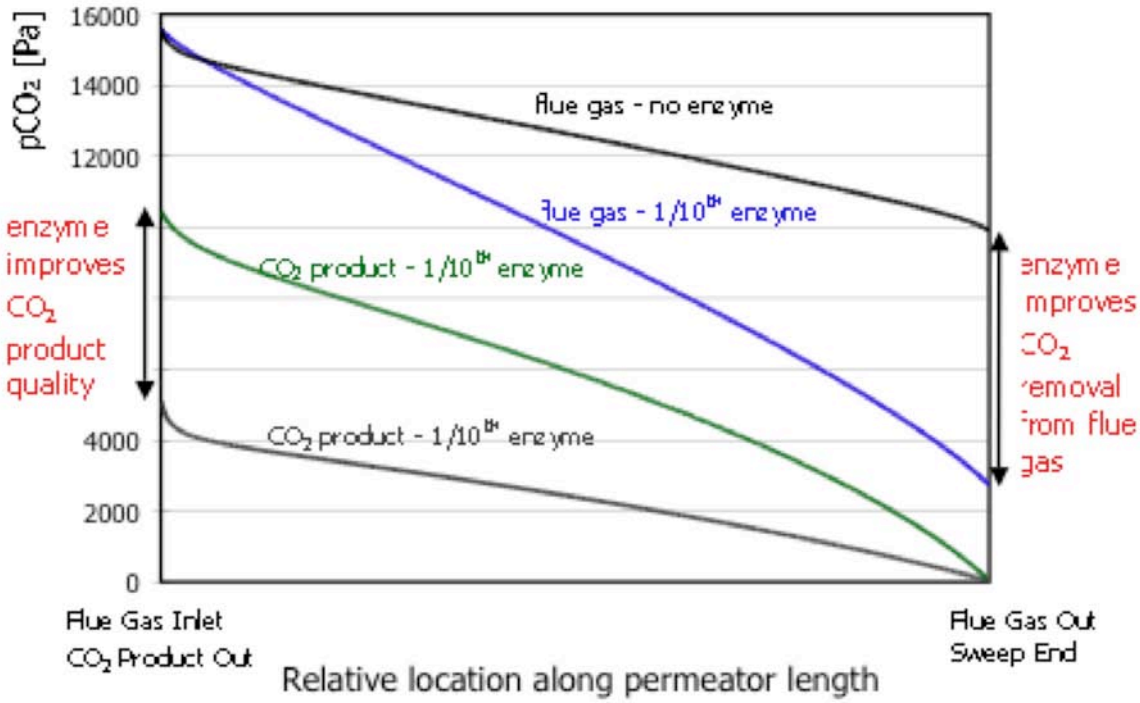


Figure 7-9. Partial pressure of CO_2 in the flue gas and CO_2 product gas sides of a Carbozyme permeator as a function of location within the permeator.

Figure 7-10 shows the enzyme condition simulation results as a CO_2 concentration color surface plot. Flue gas enters at the left and exits at the right. Permeate runs countercurrent and exits at the left. The performance observed for this simulation was 83% CO_2 removal with a dry product gas composition of 95% CO_2.

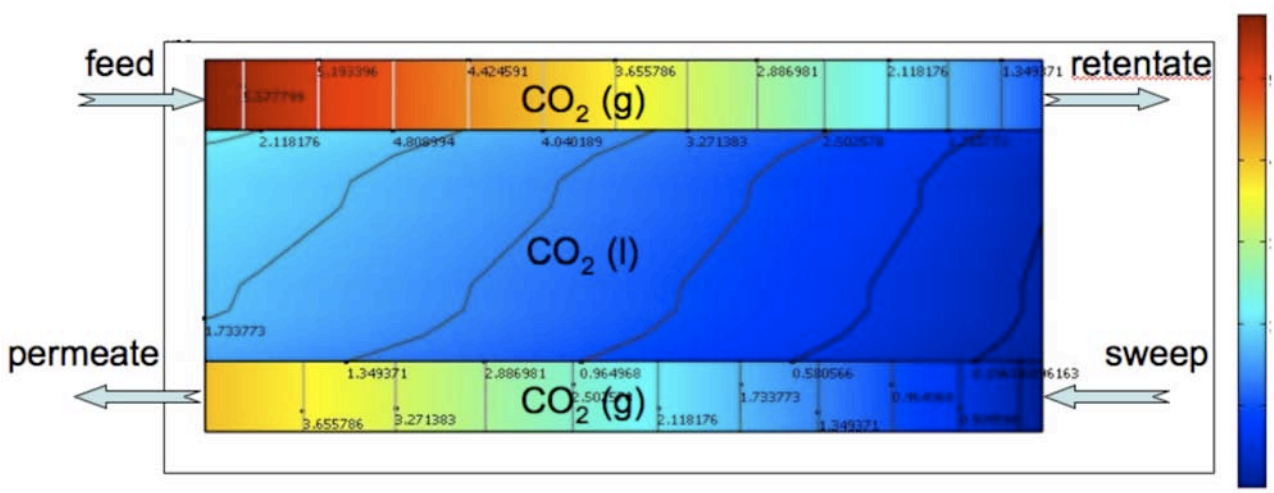


Figure 7-10. CO_2 concentration color surface plot for the flue gas (feed to retentate) and CO_2 product (sweep to permeate) gas sides of a Carbozyme permeator as a function of location within the permeator.

Short-term Parametric Testing of the 0.5m² SWHF-CLM Module

Acceptance testing of the 0.5m² permeator was performed at 65°C. Insulation was provided sufficient to achieve uniform temperature distribution for this small diameter test rig.

Permeator performance was monitored under progressively elevated temperatures initially under no-enzyme conditions. Permeance values and mass balance calculations were performed. The goal of this experiment was to achieve closure of the system mass balance to detect significant leaks into or out of the permeator and assure high confidence in our pressure, composition, and flow rate (based on differential pressure) measurements.

Successful demonstration of a molar flow rate mass balance was achieved. Table 7-1 shows test data presented in terms of moles/min for gases flowing into the permeator (feed plus sweep), gasses flowing out of the permeator (retentate plus permeate) and the percent difference observed. For CO_2, 18% more CO_2 left the permeator than entered at the time of the measurement. The difference between the CO_2 entering and leaving the system reflects the net loss of the dissolved inorganic carbon from the CLM during the data collection period. For H_2O, the molar flow rate out of the system was 1390% higher than entered into the system. This is consistent with the expected evaporation of water from the CLM. For both N_2 and O_2 there is less than a 1% difference between the flow in and the flow out. For Ar, we found 56% more Ar leaving the permeator than entering. However, this represents a very small number because the molar flow rate of Ar into the permeator was only 2.9% of the total inlet molar flow rate. Overall, we achieved excellent closure on the mass balance of the system with a difference of only 4.3% between the flow of dry gas in to the flow of the dry gas out.

Table 7-1. Mass balance results for multi-tubesheet permeator

	CO_2	H_2O	N_2	O_2	Ar
Input (Feed + Sweep) moles/min	0.0014	0.001	0.0063	0.0017	0.00029
Output (Retentate + Permeate) moles/min	0.0017	0.010	0.0063	0.0017	0.00045
% difference* (output-input/input)	18%	1390%	-0.3%	0.7%	56%

*% differences calculated using more significant digits for molar flow rates than shown in table.

Another test of the quality of the mass balance is comparison of the permeance values calculated on the basis of the change in molar flow rate at each side of the membrane, *i.e.* the difference between molar flow rate of the feed and the retentate. The permeance value on the other side of the membrane is the difference between the sweep and the permeate. Good agreement was achieved between the two separately calculated permeance values for CO_2, N_2, and O_2 (Table **7-2**). The actual permeance is taken as the mean value. The selectivity values for CO_2/N_2 and CO_2/O_2 shown in the table were calculated based on the average permeance values. The observed permeance values are in good agreement with our expectations for the permeator operating in the no enzyme condition.

Table 7-2. Mass balance results for multi-tubesheet permeator

Permeance - (mole/m^2-sec-Pa)	CO_2	N_2	O_2	Ar
Feed-Retentate	6.2E-09	6.1E-11	8.1E-11	7.5E-11
Sweep-Permeate	8.1E-09	4.2E-11	1.2E-10	3.7E-09
Average Permeance	7.2E-09	5.2E-11	1.0E-10	
Selectivity (CO_2/N_2 or CO_2/O_2)		140	70	

*% differences calculated using more significant digits for molar flow rates than shown in table.

The CO_2 permeance of the 0.5m^2 multi-tube sheet permeator with purified enzyme is shown in Figure 7-11. Operating our fully functional multi-tubesheet permeator (countercurrent flow mode with enzyme) resulted in a successful demonstration wherein 87.4% of the CO_2 was removed from a feed containing 15.4% CO_2 in air. The wet permeate gas contained 30.4% CO_2. The calculated composition of the dry product gas was 81.1% when contaminated with argon (used to assist sweep flow), and 93.6% without argon. The results were calculated from a 1-hour performance period collected 35 hours after addition of the enzyme. This performance snapshot was representative of the full operating period from which the performance data were extracted.

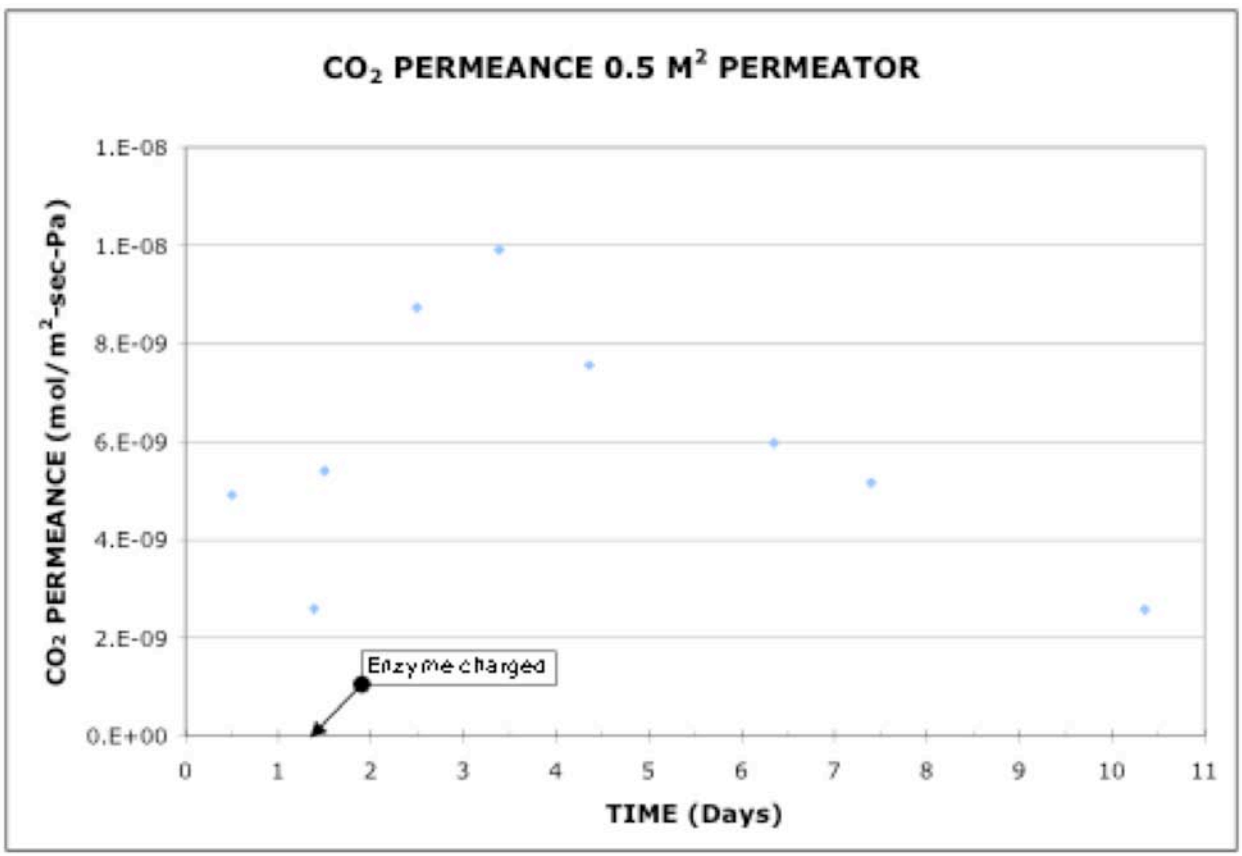


Figure 7-11. CO_2 permeance in the multi-tube sheet permeator over 11 days testing.

The permeator CLM solution Maren assay test results of enzyme activity are shown in Figure 7-12. The permeance data is in line with our expectations for the first run. The isozyme used in this test has a maximal operating temperature of <43°C. A small flow of

argon (sweep gas) was added to the vacuum to supply sufficient sweep flow at the lower temperature

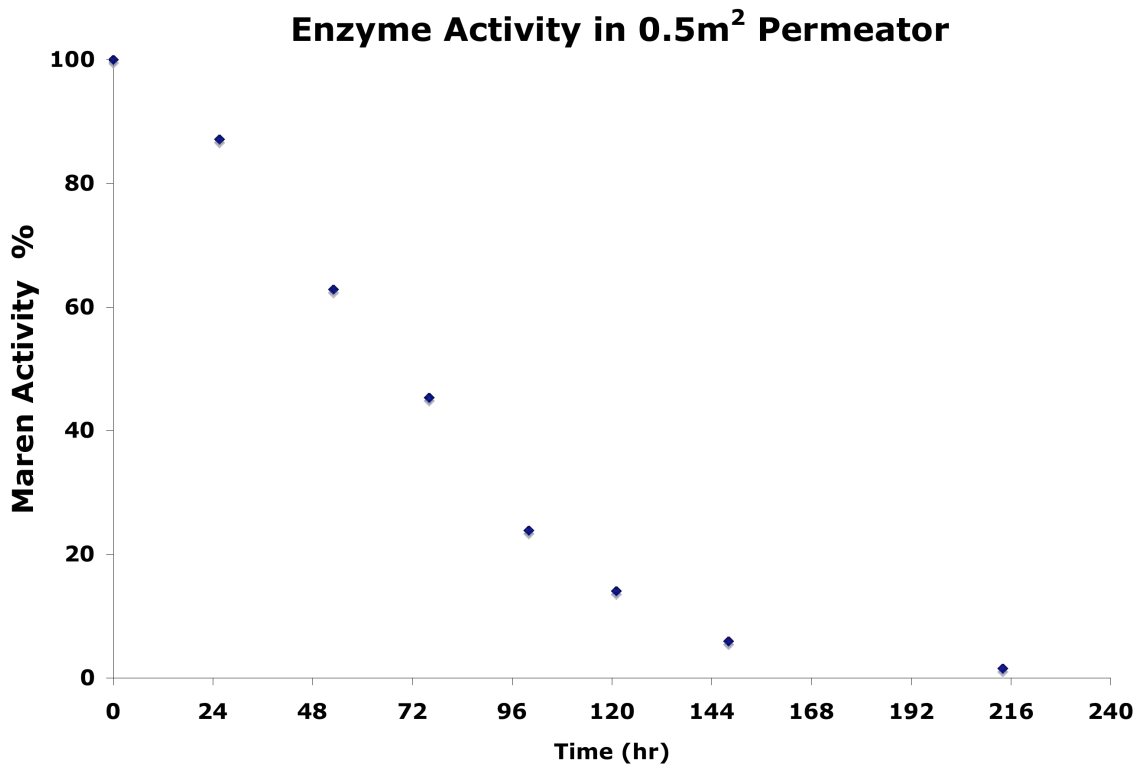


Figure 7-12. Normalized CA Maren activity in the 0.5m2 multi-tube sheet permeator CLM over 11-days of testing.

In sum, analysis of the 0.5m^2 permeator data showed a CO_2 concentration of almost 94% when operating at a temperature below design conditions. The overall performance of the multi-tubesheet permeator is fully in line with expectations.

Short-term Parametric Testing of the 11m^2 System and Comparison with MicroModule Testing

The 0.5m^2 permeator was so constructed that it could also be used as a 1m^2 absorber or desorber. As such it is an ideal test bed for the 11m^2 device; the next scale size (*cf.* Subtask 5.7). A key difference between the permeator and the absorber/desorber is the flow rate of the MTF; slow in the first, rapid in the latter. The surface of the HF was activated using chromic acid. (Plasma activation will not be incorporated until construction of the 11m^2 apparatus). After assembly the apparatus was washed extensively, enzyme added, and later removed using sulfuric acid. These procedures increased the MTF flow rate 4-5-fold.

There were three steps in the test process– water, $KHCO_3$, and $KHCO_3$ + CA. Test variables included gas and liquid flow rates and temperature. Outcome variables included permeance and flux, and percent CO_2 removal. The data were qualified on the basis of the mass balance closure. This introduces some uncertainties due to known difficulties seen in small systems. The mass balance looked at all components - inputs

vs. outputs - for every gas and liquid stream (e.g., N_2, O_2, CO_2 etc.). Closures to within 50% were considered good.

The overall effects of varying gas and liquid flow rates on flux are visible in Figure 7-13. These are connected by black lines to the open symbol, which indicate projected performance at a flux = 0. The black lines are provided to aid the reader in interpreting the plotted data. The length of each black line represents the observed magnitude of the flux for that operating condition. The red filled circles are the flux observed at a lower CO_2 transport liquid flow rate. The green filled circles are the flux observed at a higher CO_2 transport liquid flow rate (2X). These data represent no-enzyme measurements carried out using a 0.5m^2 HF permeator, operating with both gas flow paths for absorption or desorption, thus the effective area was 1m^2.

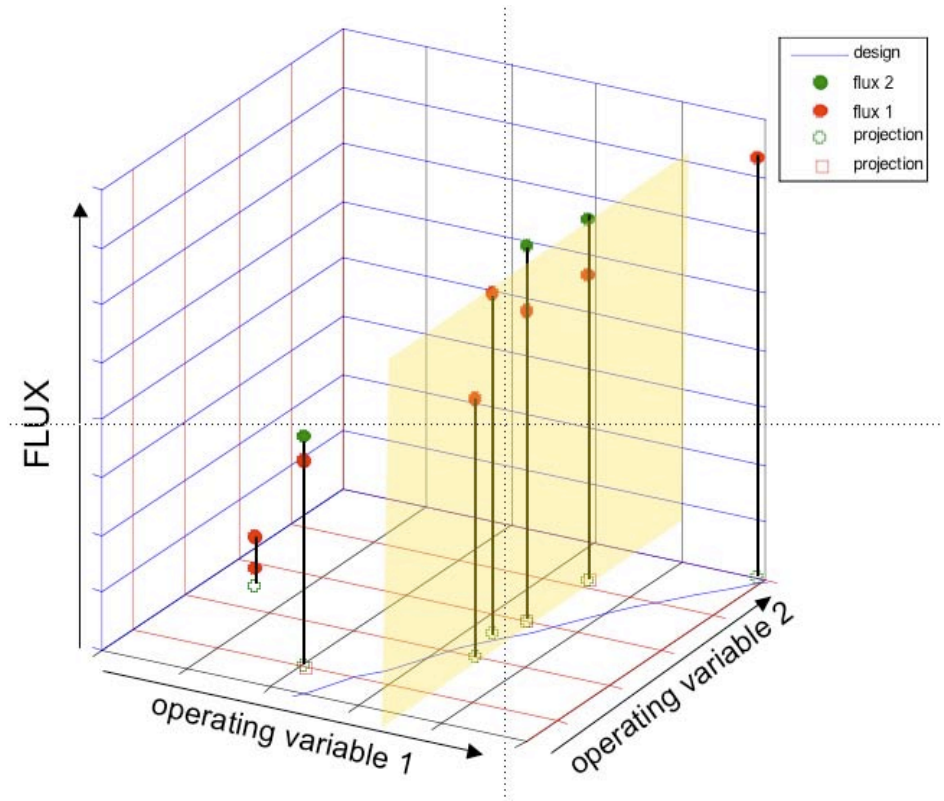


Figure 7-13. Stripping flux (flux of CO_2) under no-enzyme conditions as a function of changes in gas and liquid flow rates.

When used in the absorber mode with enzyme, immobilized *in situ*, the module exhibited a 38% CO_2 removal, for the conditions used (fairly high gas flow and gas to liquid flow volumetric rate ratio). Under desorption mode with the product gas composition was 98% CO_2 dry gas (77% CO_2 wet gas).

Conclusion

We designed an extensive regimen for pre-pilot testing, initially using ersatz gas mixtures, at the Carbozyme facility. At EERC the testing would be expanded to use three ranks of coal. The planned scaling progression was 0.5m^2, 1m^2, and 11m^2 permeators.

The infrastructure accomplishments of Tasks 1, 2, and 3 provided the basis for the design and construction of the permeators and absorber/desorbers developed in this

task. There were two components to the work. The first was modeling the system to try to predict appropriate flow rates for gas and liquid and to determine the minimal amount of enzyme needed. The results visualized the counter-current distribution of CO_2 along the fibers and allowed minimization of the number of test conditions that would have to be examined. This modeling was done under the no enzyme and with enzyme conditions to appreciate the benefit of adding enzyme to the system.

Modeling was followed by actual testing under projected operating conditions of temperature, gas mixtures and flow rates for gas and liquid. Despite the small size of the equipment we carried out mass balance studies. Initial studies showed the dry CO_2 concentration to be 93.6% from a 15.4% feed using the 0.5m^2 permeator. These same permeators could be arranged to operate as a 1m^2 absorber or desorber given that the liquid flow rate was increased 4-5 fold. Now the final dry CO_2 concentration achieved 98%. This is important as the permeator product would have required secondary cleanup to achieve pipeline acceptance standards.

Control studies with the 11m^2 permeator supported the scale-up expectations and calculations, *i.e.* that scale-up continued on a linear basis, a key assumption in going forward.

8. TASK 6 - ENGINEERING AND ECONOMIC ANALYSIS

Goal

Task 6 - Engineering and Economic Analysis addressed the performance of engineering and economic analyses toward achievement of the Sequestration Program 2012 cost target. Specifically, the cost target is a maximum ceiling of 35% increase in the cost of electricity due to the addition of post-combustion capture and separation technologies. This task was focused on the following items:

- Development of an MEA Base Case Engineering and Economic Analysis – this analysis would develop a baseline analysis for a monoethanolamine (MEA) system, based on Cases 11 and 12 of the NETL Baseline Study and literature data. Base case designs for a Greenfield 500-MW (net) supercritical PC plant without CO_2 controls and one with amine-based CO_2 control will be performed.
- Development of a Carbozyme System Capital Cost Analysis – this analysis would include an order-of-magnitude capital cost analysis of the components of Carbozyme's System as well as a comparative capital cost analysis between a commercial membrane system and the Carbozyme System.
- Development of a Carbozyme System Engineering and Economic Analysis – this analysis will be developed for the baseline power plant (same characteristics as the MEA Base Case) as if were retrofitted with a Carbozyme System. A Greenfield application of the Carbozyme technology when designed into a supercritical PC plant will also be developed. The advantages and disadvantages of the Carbozyme System will be identified relative to the baseline MEA capture plant.
- Development of an EDI Engineering and Economic Analysis – this analysis will be developed for the baseline power plant (same characteristics as the MEA Base Case) as if were retrofitted with a Carbozyme EDI system. A Greenfield application of the Carbozyme EDI technology when designed into a supercritical PC plant will also be developed. The advantages and disadvantages of the Carbozyme System will be identified relative to the baseline MEA capture plant.
- Development of a Case Studies for Carbozyme's Systems – this analysis will looks at the engineering and economic impact of making existing plants "capture-ready" (i.e. technically compatible with a CO_2capture process).

Approach

The first element in this task was the development of a process by which we could evaluate, in a consistent and broad based manner, a variety of CO_2 capture systems in terms of their cost and performance as applied to standardized power plant configurations and operation. The strategy was to use established base cases for the power plants and MEA for the capture process to establish the baseline metric. The Carbozyme process could then be compared to monoethanolamine (MEA) using this metric.

Upon completion of the MEA model and the development of an initial prototype of Carbozyme's module, Siemens developed a preliminary capital cost analysis of the Carbozyme System. After the development of the initial prototype, Carbozyme redesigned it system. Further work on a capital cost analysis of the Carbozyme systems was placed on hold until the new module design was built and tested

Upon completion of Task 4 - Electrodialytic (EDI) Test Cell Design, Construction and Testing, Carbozyme communicated to the COR that the cost profile of the EDI system as completed in Task 4 was too expensive to meet the DOE goals. Carbozyme suggested that an economic analysis of that system would not be a fruitful of use of the projects resources and funding. It is Carbozyme's belief that with the information learned in that task and additional developmental funding, an improved design can be built that would meet the DOE goals.

Inasmuch as Carbozyme and the DOE mutually terminated the program (July 31, 2009), as a result, the remainder of this task was not accomplished.

MEA Base Case Engineering and Economic Analysis

As part of an ongoing effort to develop fair methods of system evaluation, NETL (2007) commissioned a comprehensive comparison of 12 plants representing combinations of fuel type and fuel conversion approach, with and without carbon capture. Two of those plants are supercritical pulverized-coal (SCPC) steam plants – one without carbon capture and the other with MEA carbon capture. Those two plants provide the bridge between that 2007 study and the current study of biomimetic carbon capture.

We quantified the "baseline" affect of MEA CO_2 removal by comparing its parameters to a corresponding set of parameters for a similar SCPC steam plant without CO_2 removal. The selected reference plant is a 545MW SCPC steam power plant with MEA CO_2 removal. This plant is Case 12 in a published a set of cost and performance baselines for fossil energy plants (NETL, 2007).

This process involves identifying the areas that are affected by the introduction of CO_2 removal equipment, then developing relatively simple models to estimate the effect of that equipment on power production, capital cost, and operating cost.

CO_2 removal systems affect the rest of the power plant by consuming portions of process streams, adding pressure drops that require additional fan power in the flue gas stream, using additional power for compressors and other CO_2 removal components, and increasing the total plant cooling load. The interface points through which the CO_2 removal systems interact with the rest of the power plant are listed in Table 8-1, along with brief descriptions of their effects.

Table 8-1. CO_2 Removal System Interface Points

Interface Point	Effect on Plant
CO_2 Removal System	Addition of new equipment increases the capital, maintenance, and operating costs of the plant.
FGD hot gas exit	Removal system pressure loss downstream from the ID fan increases ID fan exit pressure and ID fan power.
IP or LP steam flow	Steam used by removal system is taken from the Rankine bottoming cycle and reduces steam turbine power.
CO_2 separation auxiliary power	Additional auxiliary power requirement reduces net plant power.
CO_2 compressor power	Additional power requirement reduces net plant power.
CO_2 compressor cooling	Heat rejected from compressor intercoolers adds to plant heat rejection and cooling tower requirements.

NETL Cases 11 and 12 are fundamentally the same power plant except for the addition of CO_2 removal equipment in Case 12. These two cases provide parallel sets of readily comparable performance parameters in which only flow rates, power generation, and power consumption vary. For the purposes of this study, the relationships between the flow and power parameters are assumed to be linear, so that plant-wide performance effects can be determined with a set of linear equations in a small number of variables.

All models follow the same four steps:

1. Determine the ratio of power requirements for each component, dividing the power for Case 12 by the power for Case 11. (For CO_2-related equipment, the comparison is between Cases 10 and 12).
2. Determine the flow ratios for several associated process streams for both comparison cases.
3. Compare the flow ratios with the power ratio of each component. The process stream with the ratio that was closest to the power ratio is normally selected as the driving parameter for that component.
4. Calculate the slope and intercept values of the linear equation correlating the flow rate of the selected stream with the power output (or requirement) of the selected component.

The comparison cases also provide parallel sets of readily comparable equipment systems that are amenable to capital cost modeling using capacity-ratio-exponent equations.

Operating costs, such as consumable feedstocks, are estimated to be proportional to selected feedstock flow rates. Maintenance materials and labor costs are proportional to total plant cost, and operating labor costs depend only on whether the plant has CO_2 removal equipment. .

Comparisons in this subtask are presented as flowsheets and performance and cost tables that facilitate the comparison of alternate carbon capture technologies.

Reference Cases

Key performance parameters for the Case 11 and 12 data are listed in Table 8-2.

Table 8-2. Reference Plant Thermal Performance

NETL Case	Case 11	Case 12
HP Steam Conditions	24.1 MPa / 593°C (3515 psia / 1100°F)	24.1 MPa / 593°C (3515 psia / 1100°F)
Reheat Steam Conditions	4.5 MPa / 593°C (654 psia / 1100°F)	4.5 MPa / 593°C (654 psia / 1100°F)
Condenser Conditions	69 mbar (1.0 psia)	69 mbar (1.0 psia)
CO_2 Capture	No	Yes
CO_2 Product	-0-	568,000 kg/h (1,252,440 lb/h)
Gross Power [1]	589,480 kW	673,350 kW
Generator Loss [1]	9,215 kW	9,905 kW
Gross Power at Generator [1]	580,265 kW	663,445 kW
Auxiliary Power	30,110 kW	117,450 kW
Net Power	550,150 kW	545,995 kW
Coal feed [1]	186,547 kg/h (411,259 lb/h)	266,117 kg/h (586,677 lb/h)
Net HHV Efficiency	39.1%	27.2%

[1] Values taken from process flow sheets in NETL Report, which are slightly different than the values in Exhibits 4-28 and 4-38 in the same report.

All cases in the NETL study follow a consistent set of thermal and financial assumptions and methods, so comparisons of other cases to these cases are valid if they follow the same assumptions and methods. In regard to costs, the absolute values of the costs might become outdated, but comparisons of relative costs between the various plant types will remain viable.

Performance Models

Steam turbine and auxiliary performance models were developed as functions of key stream parameters to provide a way to estimate power requirements for turbines and auxiliaries without the need for detailed equipment calculations. This was possible to do using NETL Cases 11 and 12 because these two cases were similar but not identical in size and scope. Performance models for the CO_2 removal equipment in Case 12 were based on comparisons of the same equipment in Case 10, which also had CO_2 removal.

The LP steam requirement for the MEA-based CO_2 removal system was estimated by comparing the ratio of CO_2 compressor exit flow rates for Cases 10 and 12 with the ratio of LP steam requirements in Cases 10 and 12. Finally, the calculation progression for steam turbine power is defined by a set of linear equations based on coal feed rate.

For coal-steam plants in this general size range, the power requirements of plant auxiliaries are represented by linear functions of selected plant operating parameters. The general form of the auxiliary power equation is:

$$Pa = B + M*Qe$$

Where:

B	= Base (zero-capacity) power requirement, kW
M	= Capacity power multiplier, kW per unit
Pa	= Auxiliary power requirement, kW
Qe	= Equipment capacity, units

For auxiliary system not related to CO_2 removal, key stream parameters were selected for each component by comparing the ratio of parameter values for Case 11 and Case 12 with the ratio of power requirements in Case 11 and Case 12.

Power algorithms for CO_2-related auxiliary components, such as Carbon Dioxide Recovery (CDR) system (the MEA unit) and CO_2 compressors, were developed using key stream parameters from Cases 10 and 12, which are subcritical and supercritical steam plants, respectively, that have CO_2 removal.

Cost Models

Capacity-based cost models were used to estimate capital costs of all major power plant systems, so that the costs of other power plants with CO_2 removal systems can be compared to the costs of the plants in Cases 11 and 12. To accomplish this purpose, the cost of each major plant system in Case 11 was compared with its counterpart in Case 12, and the two costs were fitted into a capacity-ratio-exponent cost equation of the form:

$$C = Cref*(Q/Qref)^e$$

Where:

C	= Capital cost, $k
Cref	= Reference capital cost = $k
Q	= Equipment capacity, (units)
Qref	= Reference Equipment capacity, (units)
e	= Capacity ratio exponent (an "economy-of-scale" parameter between 0 and 1, normally around 0.6 - 0.8)

Indirect costs such as engineering, construction management, home office charges, fees process contingency, or project contingency are estimated as percentages of estimated equipment cost and are added to equipment costs, resulting in the total plant cost.

Estimates of four types of operating costs -- consumables unrelated to CO_2 capture, consumables related to CO_2 capture, maintenance, and operating labor -- are based on comparisons of Cases 10, 11, and 12. The cost of each consumable feedstock is the product of its quantity and unit cost.

Results and Discussion

MEA Base Case Engineering and Economic Analysis

Table 8-3 shows the levelized cost of electricity, the cost of CO_2 removal, and the cost of CO_2 avoided, for the reference (MEA) case.

Table 8-3. CO_2 Removal and Avoidance Costs

Cost	Units	Levelized	First-year
CO2 Removal	$/tonne	$45.00	$41.37
CO2 Removal	$/ton	$40.82	$37.53
CO2 Avoided	$/tonne	$67.46	$62.02
CO2 Avoided	$/ton	$61.20	$56.26

The flows, power production, and power consumption needed to estimate performance and cost are determined by sets of linear equations in which all of the variables are functions, either directly or indirectly, of coal feed rate and CO_2 removal rate. Since all of these thermal performance equations are linear, any desired plant size can be obtained with no more than two iterations.

Capital costs of major plant areas were estimated using exponential equations based on ratios of equipment capacities, which are also functions, either directly or indirectly, on coal feed rate and CO_2 removal rate.

The results of this study can be used to assess the effects of other CO_2 removal systems on supercritical coal-steam plants using the following procedure.

1. Determine algebraic coefficients and constants for the candidate CO_2 removal system to be used in the linear equations below, based on one or two baseline cases.
2. Pick a coal feed rate, Wcf, from which all other values will be derived.
3. Estimate key steam flow rates and steam turbine gross power
4. Estimate plant auxiliary power consumption and plant net power
5. Calculate plant net power by subtracting all auxiliary power loads from steam turbine gross power.
6. Adjust coal flow as needed and repeat Steps 3, 4, and 5 to achieve desired plant net power.
7. Estimate process equipment costs
8. Estimate total plant costs (TPC)
9. Estimate plant operating costs
10. Estimate levelized cost of electricity
11. Estimate CO_2 removal and avoided costs

The thermal and economic impacts of various other CO_2-removal technologies can also be estimated by applying these same equations to the changes at those interfaces in a supercritical coal-steam power plant.

Upon completion of the base case analysis, Siemens undertook the task of assessing whether their model could be extended from 400MW-600MW plants to larger or smaller plants. Siemens checked their model results against published information on PC plants and concluded that the model is valid for bituminous coal-steam plants

ranging from 200MW to 800MW. Figure 8-1 illustrates the normalized total plant cost for plants between 200 MW and 800 MW.

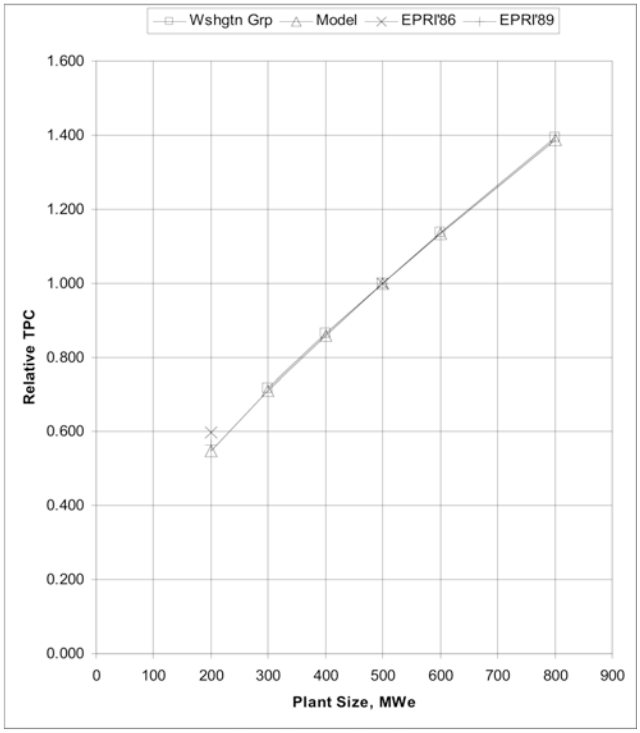


Figure 8-1. Normalized Total Plant Cost (TPC) Comparison

SWHF-CLM Membrane Capital Cost Analysis

Siemens performed a preliminary capital cost analysis of the Carbozyme module, using information about the design provided to them by Carbozyme. Table 8-4 contains the preliminary analysis of the SWHF-CLM system based upon the MEA Base Case Engineering and Economic Analysis methodology.

Table 8-4. Preliminary SWHF-CLM base case capital analysis

		Today	Pre-pilot	Field Pilot	Field Demo
Module CO2 capacity	g/day	144	17,300	170,000	170,000
Module CO2 capacity	Mg/day	0.00014	0.02	0.17	0.17
Modules per skid	mod/skid		3	18	18
Skid CO2 capacity	Mg/day		0.05	3.06	3.06
Skids			1	1	4,471
Modules			3	18	80,471
Total CO2 capacity	Mg/day	0.00014	0.052	3.06	13,680
Equiv. Power Plant	kW	0.005	1.9	111.8	500,000

Conclusion

This study identified the process interfaces between the CO_2 removal system and the rest of the power plant, and quantified the plant-wide effects of changes at those interfaces as sets of linear and exponential equations.

The thermal and economic impacts of various other CO_2-removal technologies can also be estimated by applying these same equations to the changes at those interfaces in a supercritical coal-steam power plant.

9. TASK 7 – DEVELOPMENT OF A COMMERCIALIZATION STUDY

Goal

Task 7 – Development of a Commercialization Study addressed the commercialization of the Carbozyme technology. This task was focused on the following items:

- Development of a Market Analysis and an assessment of the strengths and weaknesses of the Carbozyme's technology as compared to its competitors, in particular focus on utility market requirements.
- Identification and documentation of the requirements and issues associated with financing an emerging CO_2 capture technology for retrofit and Greenfield application as well as those associated with CO_2 transportation and its possible end uses, e.g., EOR/EGR.
- Development of a Commercialization Pathway Schedule to illustrate the various maturation stages that the technology has undergone and those that remain to be completed.
- Development of feasible approaches for the commercialization of the technology within the markets and sectors in Market Analysis.
- Evaluation of the technology transfer opportunities associated with the technology (e.g., Licensing Model, Joint Venture).
- Development of a commercialization plan to include the financial and insurance aspects associated with the successful progression through the remaining maturation R &D stages of the technology.

Approach

The initial subtask performed on this project were:

- Developing a Market Analysis of Technology
- Developing a Commercialization Pathway Schedule

The SOPO was re-scoped and this task was put on hold until year 3 of the program. In view of the mutually agreed to termination of the program additional elements of this task were initiated.

Developing a Market Analysis of Technology

The first part of this task was to identify the relevant players in the sphere and then to characterize their roles, authority and criticality in promoting the acceptance and utilization of CCS technologies. Visage Energy personnel engaged in discussions with numerous candidate customers to determine market requirements of CCS technologies.

Developing a Commercialization Pathway Schedule

SRI International, an independent research and development organization with the mission of creating and delivering innovations, has gathered its best practices for turning ideas into high-impact customer value and organized them into a training program. The program it developed to help businesses grow is known as SRI Innovation Partnership Programs. These programs are designed to help accelerate innovation, reduce time to market, and reduce costs for new products and services through the use of SRI's Disciplines of Innovation (DOI) approach.

A component of this approach is the development of a Commercialization Pathway Schedule that combines technical, market, and commercialization domain expertise to avoid the traditional "valley of death" for many technologies, i.e. the condition where an invention has been created but dies through lack of funds before there is enough interest in the technology for it to be picked up by companies interested in commercializing the idea. The Commercialization Pathway Schedule aligns multi-organizational teams to focus on end-user needs within the context of the project's Statement of Project Objectives (SOPO), thereby, substantially reducing the technology development timeline and ensuring seamless deployment of technology by the end user. Specifically, the Commercialization Pathway Schedule process intends to:

- Infuse business perspective and acumen into technology development processes
- Expedite development of the technical and commercial potential of the technology
- Expose business community to the technology and highlight its functional and cost benefits over state-of-the-art
- Incorporate feedback from potential customers, financial, and insurance communities

To start the Commercialization Pathway Schedule process, a meeting was held January 8-9, 2008 at SRI International's headquarters in Menlo Park, California. Twenty attendees from nearly every organization involved in the project including technology developers, OEMs, utilities, government labs, and private sector funding sources.

The DOI method is an important step in aligning team members in a very complex project. It is important for the team members, developing the technology, to be aware of not only the science, but also how the science will be translated into a product that will impact the following parties:

- The rate payer;
- Utility plant operator;
- Engineering firms that will install the technology into the plant;
- OEMs supplying components for the final system.

The objectives of this element are a) to define technical progress, and b) to identify the Needs Assessment for the major parties involved in the program. This is a critical step in the SRI DOI process; it uses the acronym - NABC (Need, Approach, Benefit, Competition). This process entails the following:

- Compiling the Needs of the utility industry
- Examining the technical Approach of the project and identifying technical and business risks and methods to mitigate these risks;
- Ensuring the Benefits expected by the utilities will be achieved during the commercialization of the HFCLM and EDI technologies;
- Comparing the benefits of the HFCLM and EDI technology to the utilities relative to Competitive technologies

The NABC methodology enabled the team to become better aligned to meet the needs of utilities. This improved alignment was especially evident as risks were identified and mitigation strategies developed. Multi-organizational "tiger teams" spontaneously formed to address technical concerns. For example, risks were identified in the scale-up of the membrane fabrication. Prior to this meeting this risk was being analyzed only by the enzyme supplier and membrane designer. Another team member from an OEM for downstream processes immediately recognized that a subsidiary of his company possessed expertise that could assist in mitigating the risk. Representatives

from the enzyme supplier, membrane designer, and OEM formed a "tiger team" and an action plan to address these scale-up risks.

The preliminary specifications, process diagrams, and risk mitigation analysis started the process of motivating team members to go beyond just the science. They were able to begin to appreciate how their technology and expertise impact end users and others within the ecosystem.

The DOI approach was used to align the team by focusing on end user's needs, present current status of the technology development, identify ways to mitigate technical and business risks, and outline future requirements for the project to meet the demands of the marketplace and satisfy the aforementioned NETL objectives. One of the key benefits of aligning the team was to improve communication amongst the organizations and to more fully focus their efforts to only those stipulated in the SOPO to minimize any cost or schedule excursions. The following were the outcome of the DOI:

- Clear lines of communication were developed to identify roles and responsibilities for each of the technology's multi-corporate teams.
- Aligned both technologies (HFCLM and EDI) with the market needs through identification of the flue gas composition of various coal ranks used by the power generation sector. This alignment would help to ensure that the design, scale-up and performance of the HFCLM and EDI capture technologies could operate under actual flue gas compositions.
- A risk management analysis was performed, uncovering several system-level questions pertaining to the HFCLM and EDI technologies. Mitigation strategies were developed and refined using an iterative process. Preliminary specifications were established for both the HFCLM and EDI technologies.
- Identified accomplishments and progress to date.
- Reviewed the SOPO and compared the planned against the actual cost and schedule to develop a mitigation approach for getting back on schedule and budget.
- Modified the Project Management Plan to incorporate the outcome of the DOI.
- Confirmed the adoption of the commercialization efforts by the project team to reduce project risk and expedite the deployment of the technologies under development in this project.

Results and Discussion

Developing a Market Analysis of Technology

The first part of this task was to identify the relevant players in the sphere and then to characterize their roles, authority and criticality in promoting the acceptance and utilization of CCS technologies. Visage Energy personnel engaged in discussions with numerous candidate customers to determine market requirements of CCS technologies. These included utility companies, power generators, PUCs, industrial providers, etc. in order to determine the level of interest that utility companies might have in investing in new CCS technologies. Figure 9-1 is a star representation of the various players whose interests must be considered.

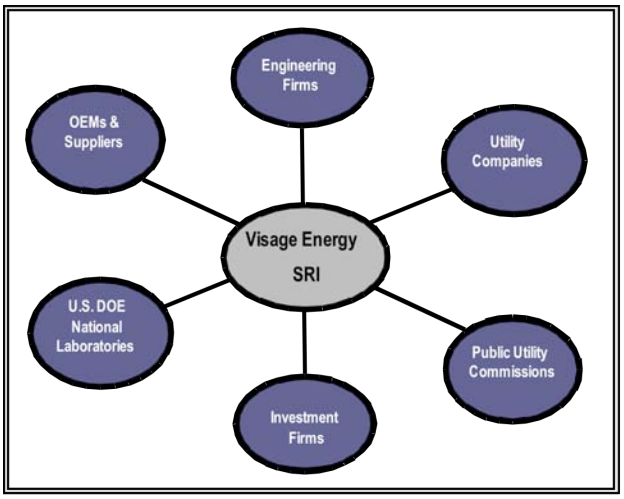


Figure 9-1. Relevant players associated with the promotion, acceptance and utilization of CCS technologies

Introductory discussions and follow-up meetings were held with numerous potential customers (utility companies/power generators) to assess their interest in deploying CCS technology as well as their technology requirements. The research revealed that the level of interest that utility companies have in investing in new CCS technologies is a function of the utility company's ability to receive rate base treatment from the state Public Utility Commission for funds invested in new technologies. Consequently unregulated markets provided no ability to support such work. This discovery led to meetings with Commissioners from California, Indiana, Pennsylvania and Texas, which have strong PUC presence. The discussions focused on RD&E funding for utility companies to invest in CCS technologies, as had been the case in many instances for Renewable technologies.

A second finding was that the range of players (stakeholders) was larger than originally thought. Figure 9-2 lists many of these stakeholders and defines the issues that are important to them.

To develop the concept shown in Figure 9-2, numerous discussions were held with representatives of key financial and insurance institutions wherein the insurance agency personnel were provided with information about CCS technologies in general as well as to highlight the cost and functional benefits of the technologies Carbozyme is developing.

Frame Setters

1. **Federal Stakeholders** – to provide federal policy commitments and funding vehicles to acceleration deployment of CCS projects.
2. **NETL/Other Technology Sources** – critical to CCS technology development.
3. **State Stakeholders** – to develop the regulatory framework and provide ratepayer funding to create necessary incentives.
4. **End users/Utility Companies** – to collaborate with PUCs in the R,D&E process.
5. **Environmental Groups** – critical to gaining public acceptance of CCS as a safe climate change mitigation tool.

Enablers

6. **Insurance Companies** – to be engaged in the process to begin to model the risk associated with sequestration.
7. **Financial Institutions** – with the alignment of groups I - VI, this group should be willing to provide funding to CCS projects that have Federal and State policies & funding support.

Figure 9-2. Additional Players that need to be considered in the promotion, acceptance and utilization of CCS technologies

Among the commercialization risks identified at this time (2007), the principal risk was that Federal and State regulatory issues had not been resolved to date. Since CO_2 capture will be regulatory-driven, the extent to which utilities will be required to remove CO_2 from their exhaust stream will likely dictate the technology used to do so. There may also be liability risk associated with sequestered CO_2.

The issues above hamper the financing of projects. Insurance risks can also add to this issue in the form of uncertainty around risk ownership. Financial institutes need to be educated early in the process. Financial risk of the project participants will be reduced by State incentives and backing from larger companies.

One potential end-user, Ottertail Energy, not only confirmed these conclusions but emphasized that any control technology must be able to handle various coal types and quality as some power companies blend coals within individual units or at specific times. Control technologies should also minimize cost impact, which is passed on to users through higher electricity rates and eventually flow through the economy to consumers. Ottertail also emphasized the importance of space constraints, i.e. footprint, as some utility sites are space-limited.

Ottertail Energy also indicated that the amount of power provided to the grid is more important to them that the amount of CO_2 removal. They will naturally meet any regulations that are passed, but emphasized the need to minimize parasitic losses as well as reagent costs. It is also important to them to minimize required changes in skill sets for their engineering staff.

Conclusion

This element served to underline the idea that there were many stakeholders and that the concerns of each stakeholder was changing over time. Thus, for any demonstration or implementation it was crucial to select the stakeholder grouping

carefully and to align carefully the performance elements to the stakeholder requirements.

10. SUMMARY

In this work we succeeded in building and demonstrating a 0.5m^2 permeator, a 1m^2 absorber and a 1m^2 desorber that effectively and rapidly removed 90% of CO_2 from an ersatz post-combustion coal flue gas containing 13-16% CO_2. Using the permeator design (a dual hollow fiber spiral wound array enclosing a contained liquid membrane) we demonstrated a final, dry CO_2 concentration of 95%. Using the absorber/desorber design (a single hollow fiber spiral wound array in each apparatus) we demonstrated a final, dry CO_2 concentration of 98-99%.

To achieved this performance activated the polypropylene membrane surface by means of a plasma and then immobilized CAM (a thermophilic carbonic anhydrase) onto this surface by means of a layer-by-layer (LBL) approach. The CAM immobilized in this manner showed as much as 80% retained activity over a 60 day period. The LBL enzyme layer could be removed and replaced as needed and we demonstrated this 5 times to illustrate repeatability.

We also built and tested an enzyme facilitated, resin wafer, electrodialytic process for CO_2 capture. Whereas the permeator or the absorber/desorbed used a combination of vacuum, water vapor sweep and vacuum to effect release of the CO_2 the RE-EDI process used a pH swing method. This method demonstrated 90% CO_2 extraction.

The chemical complexity and diversity of post-combustion flue gas streams presented a possible issue with respect to inactivation of the enzyme or compromise of the CLM/MTF. To address this concern we examined the effects of various flue gas stream components on the operation of the enzyme and on the CLM/MTF. We carried out sensitivity analyses to establish acceptance criteria for each relevant component. The data showed that the only component that might adversely affect enzyme performance was ionized mercury. Assuming the use of mercury capture then any excess concentration in the CLM/MTF could be managed by use of EDTA. The second flue gas component of issue was the level of SO_2 (SOx) as over time it would acidify the CLM/MTF. Inasmuch as CO_2 capture, using our approach or using amines, is an acid-base process wherein CO_2 or CO_2 equivalents are absorbed into an alkaline solution SOx-based acidification compromises the process. Our data showed that the desired SO2 level should be <10ppmv. SOx clean up would be necessary.

To determine the magnitude of the cleanup that would be needed we evaluated a large fraction of the flue gas streams released by coal burning power plants in the U.S. This investigation revealed a wide range of SOx levels. It indicated that even after traditional FGD scrubbing thee would be need for a polisher. The FGD at the EERC commonly put out SOx at 50ppmv. A calcium carbonate-based polisher was developed, tested and successfully demonstrated the ability to reduce SOx levels to 5ppmv, more than sufficient for our requirements.

A key step to determine the efficacy of this approach vs. that of existing amines to construct a metric by which these could be compared on equal footing. This work was done and successfully demonstrated the ability to linearly correlate the relative TPC (total plant cost) and plant size for power plants ranging from 200 to 800MW output.

An initial evaluation of the barriers to entry revealed a multitude of stakeholders that had interests in the capture of CO_2. The important role of PUCs in promoting demonstrations was emphasized.

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12. Abbreviations And Acronyms

accm	Actual cubic centimeters per minute
ANL	Argonne National Laboratories
APC	Air pollution control
bd	Bubble diameter
BTU	British thermal units
CA	Carbonic anhydrase
CAM	A thermophilc CA isoform
CCS	Carbon capture and storage
CDR	Carbon dioxide recovery
Ce	CO_2-equivalents
CEPS	Conversion and Environmental Process Simulator
CLM	Contained Liquid Membrane
CMM	Continuous mercury monitor
DIC	Dissolved Inorganic Carbonate
DOI	Disciplines Of Innovation
ED	Electrodialysis
EDI	Electrodialytic
EDTA	Ethylenediaminetetraacetic acid
EERC	Energy and Environmental Research Center

EIA	Energy Information Adminiatration
EPA	Environmental Protection Agency
FGD	Flue gas desulfurization
FS	Flat sheet
HF	Hollow fiber
HFCLM	Hollow fiber contained liquid membrane
ICR	Information collection request
IECM	Integrated Environmental Control Model
LBL	Layer-by-Layer
MEA	monoethanoloamine
MIMS	Membrane inlet mass spectrometer
MTF	Mass transfer fluid
n-NPA	Para-nitrophenyl acetate
NABC	Need, approach, benefit, competition
Ni-NTA	Nickel nitrilotriacetic acid
PAA	Poly-amino acid
PEI	Polyethyleneimine
PG	Purified grade
pHSA	pH swing absorption
Poly-His	Multiple histidine residues
PRB	Powder River Basin
PSA	Pressure swing absorption
PSU	Pennsylvania State University
PTFE	Poly==========
PVDF	Polyvinyl========
R&R	Remove and replace
RGA	Residual gas analyzing mass spectrometer
RW-EDI	Resin wafer electrodialytic
SCPS	Supercritical pulverized coal
SCR	Selective catalytic reduction
Se	Gas-liquid interface area
SOP	Statement of project objectives
tc	Contact time
TG	Technical grade
TOC	Total organic carbon
TPC	Total plant cost
TSA	Temperature swing absorption
USGS	U.S. Geological Survey
VSA	Vacuum swing absorption
VSP	Very Small Permeator
W-A	Wilbur-Anderson assay (for CA activity)
μMOD	Micro-module