Department of Energy Office of Energy Efficiency and Renewable Energy

Algae Production CO_2 Absorber with Immobilized Carbonic Anhydrase

FINAL REPORT

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Principal Investigator: Bill Rickman
Owner
TSD Management
wmrickman@aol.com
(615) 374-9879

Project Director: David Hazlebeck, Ph.D.
Chief Executive Officer
Global Algae Innovations
davidhazlebeck@globalgae.com
(619) 884-3206

Name of Submitting Official:
Jesse Traller, Ph.D.
Senior Phycologist
Global Algae Innovations
jessetraller@globalgae.com
(760) 822 – 8277

Signature of submitting official

Global Algae Innovations
PO Box 19623
San Diego, CA 92159-0623
DUNS Number: 0784946

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1 Executive Summary

Low-cost CO2 supply is necessary to achieve algal biofuel cost metrics; and high CO_2 capture and utilization (CCU) efficiency are necessary to achieve algal biofuel cost, life-cycle, and production quantity metrics. The focus of this project is on developing a low cost, high efficiency method for CCU from flue gas for use in production of algae biofuel and commodity bioproducts. A CCU process was developed and demonstrated that met or exceeded all of the project goals:

- 83% CO_2 capture efficiency from flue gas
- 97% utilization efficiency in algae cultivation
- $21/metric ton (mt) projected cost of CO_2 capture and supply at full-scale
- TRL-5 technology maturity

The state-of-the-art approaches to CO_2 supply for algae from industrial sources are (i) to distribute the flue gas directly or (ii) to concentrate and compress the CO_2 prior to distribution[1,2]. Both of these conventional methods require an expensive distribution and control system to provide CO_2 to thousands of acres of algae ponds. The first method has major technical barriers – (i) technology must be invented to prevent ground level release of the flue gas, (ii) maintaining cultivation facilities during utility outages, and (iii) diurnal, daily weather, seasonal variations in CO_2 utilization by the algae limit the capture efficiency to less than 10%. Even without these barriers, the distribution system is expensive, and a large amount of energy is required to compress the flue gas, so the approach is too expensive for producing algal biofuel and commodity co-products. The second method, capturing and compressing carbon dioxide, overcomes the technical barriers noted above because the carbon dioxide is purified to avoid ground level flue gas emissions and it can be stored as liquid carbon dioxide to accommodate variations in supply and use; however, this method is even more expensive because capture and compression costs are added to the cost of the vast distribution and control network.

Global Algae Innovations (Global Algae) new CCU process overcomes all of these obstacles, Table 1. The approach utilizes sodium bicarbonate in the media as a shuttle so that CO_2 is readily captured from flue gas, and no separate gas distribution and control system is required because the CO_2 is distributed to the ponds in the growth media. Figure 1 illustrates the key process blocks and a summary of the key reactions. Figure 2 provides photographs of the key components used to implement this CCU process at the 8-wetted acre open raceway algae farm operated by Global Algae. The CO_2 is recovered 24 hours per day with only 2.5 inches of water pressure drop on the flue gas, and the carbonated media can be stored indefinitely in a covered pond until it is needed for cultivation.

The new process is incorporated into Global Algae's Department of Energy (DOE) funded integrated biorefinery project for scale-up of algae biofuel process as well as eight other DOE projects and one Department of Agriculture (USDA) project. The technology is included in Global

[1] Nagarajan, S., S.K. Chou, S. Cao, C. Wu, and Z. Zhou. 2013. An updated comprehensive techno-economic analysis of algae biodiesel. Bioresource Tech. **145**:150-156.

[2] EERE, National Algae Biofuels Technology Roadmap, May 2010.

Algae's technology package that will be broadly licensed through a franchise model. Additionally, nine new high pH algae strains were isolated that are being used on four other DOE projects.

Table 1. Comparison of Global Algae's CCU process with conventional CCU approaches

Process Attribute	Global Algae bicarbonate shuttle	Conventional bubble in the raceways	Conventional capture & compress
Avoids ground level release	Yes	No	Yes
Capture day and night	Yes	No	Yes
Accommodates variable supply and use of CO_2	Yes	No	Yes
Simple distribution and controls	Yes	No	No
Low energy use CCU	Yes	No	No
Low cost CCU	Yes	No	No

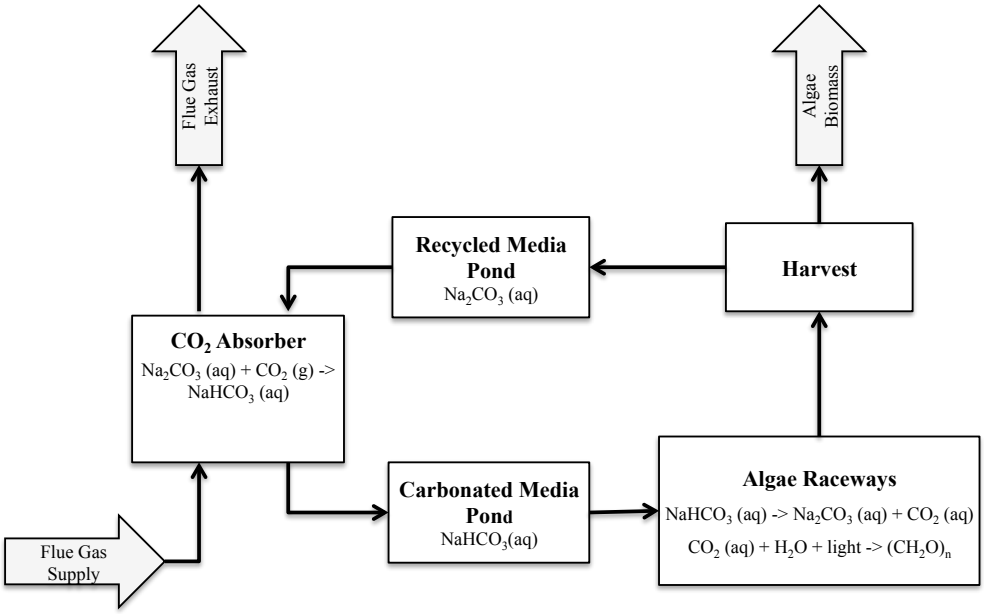


Figure 1. Basic process flow and summary of reactions for Global Algae's CCU process

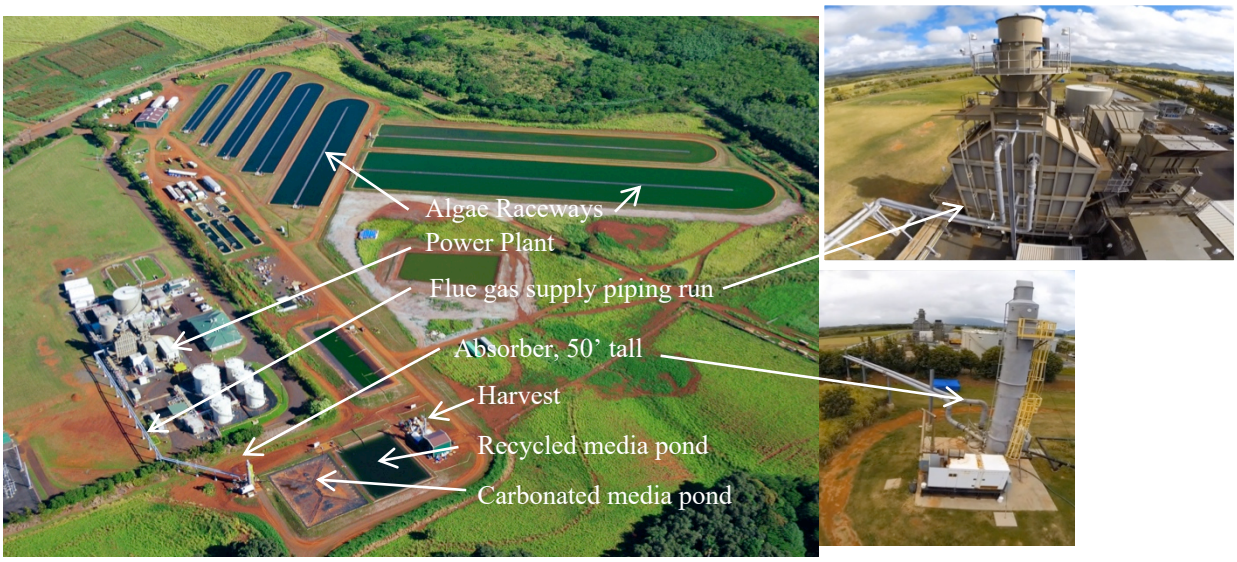


Figure 2. Global Algae CCU process implemented at an 8-wetted acre open raceway facility

2 Project Goals

The project goals were to demonstrate higher algae biomass yield, lower projected model cost of CO_2 supply from industrial stationary flue gas sources, achieve TRL-5, and develop a commercialization plan for implementation of the technology.

The specific objectives for yield were to increase the algal biomass yield from flue gas per MW of power plant production for a low-cost absorber carbonate-based system to 4-8 mt/d per MW from the current 0.6-1.2 mt/d per MW. Performance targets to accomplish the net increase of algae biomass yield from flue gas per MW were:

- increasing the CO_2 capture from 20% to over 80% in single pass column
- increasing the CO_2 utilization from 50% to over 90% in open raceways

The specific objectives for the CO_2 capture and supply cost are to reduce the projected model cost of mature technology from $34/mt to $28/mt. Performance targets to accomplish this cost reduction were:

- increasing the CO_2 capture rate from ~2 kg/m3 hr to ~14 kg/ m3 hr
- increasing the liquid regeneration from 12.5% to 100% in single pass column
- achieving a one-year average catalyst lifetime

The objective for technology maturity of the immobilized carbonic anhydrase absorber system coupled with algae was to increase the TRL-3 to TRL-5. The target was TRL-5 instead of TRL-4 because the utilization of the CO_2 and the effects of recycled media can only be effectively determined in a relevant environment, so demonstration in a laboratory environment would have minimal value.

Table 2 provides a summary of the results for each of the project objectives. As discussed in Section 1 above, all of the overall project goals were met or exceeded. The project included two

approaches for increasing the capture efficiency – carbonic anhydrase catalyst, an alternative absorber design, or a combination of both approaches. The end result was that the ne absorber design without a catalyst provides the lowest cost process, so this approach was selected. A catalyst life of approximately 5-years with 20% replacement per year was estimated by the vendor based on results from the testing; however, the catalyst life is no longer applicable since it is not included in the final process.

Table 2. Summary of results for each of the project objectives

Objective	Start	Target	Achieved	Success?
80% CO_2 capture in a single pass	10%	80%	83%	Yes
90% CO_2 utilization efficiency	60%	90%	97%	Yes
Cost of CCU, \$/mt CO_2	\$47	\$28	\$21	Yes
Integrated CCU process operation	No	Yes	Yes	Yes
Technology maturity	TRL-3	TRL-5	TRL-5	Yes
Volumetric capture rate, kg CO_2/m^3 hr	2	14	17.7	Yes
Catalyst lifetime, year	NA	1	NA	NA

3 Test Results and Analysis

This project focused on two key steps in the new CCU process – (i) re-carbonation of algae media in the absorber and (ii) utilization of the carbonated media for cultivation of algae. In each case, high efficiency and low cost was the target. At the end of the project, the two steps were tested in an integrated fashion over ten cycles to verify that there are no integration issues for the overall CCU process. Testing and Results for each of the steps are presented in Sections 3.1 and 3.2; and the results for the integrated test are presented in Section 3.3.

3.1 Capture results and analysis

The overall goal of this carbon capture portion of this test/design project is to recommend the lowest-cost / lowest-risk flowsheet for commercial-scale re-carbonation of recycled algae harvest media using power plant flue gas. The selected flowsheet is shown in Figure 3. This flowsheet meets all techno-economic goals using an alternative absorber design in a single-pass. Five specific objectives related to the absorber were included in the project proposal – all were successfully completed as illustrated in Table 3. Capital/operating costs for the selected re-carbonation flowsheet are shown in Figure 4, as a function of algae farm acreage. All evaluations used power plant flue gas as defined by NETL in Case 11 of their Baseline Study[3]. Figure provides comparative costs and design parameters for twelve alternatives, all at 160-acre algae farm pilot scale. These design tools can be applied to specific details of any algae farm and CO_2 source.

3.1.1 Absorber Test Systems

Two absorber test systems were used for the project. A 5-foot diameter absorber, Figure 6 and Figure 7, and a 6-inch diameter absorber, Figure 8. The larger absorber contains 30 feet of packing.

[3] 2013 update of DOE/NETL-2010-1397.

The smaller absorber could be operated with 12 feet of packing in a standard configuration, Figure 9, or 12 feet of packing with an alternative absorber design.

This report includes preliminary scale-up of both the conventional and alternative absorber design to commercial size columns (~8-10 ft diameter for 160-acre algae farm) based on results from the 6" column.

The parametric testing performed with the small absorber:

- Column – 5-12 ft deep packing in a vertical 6" PVC pipe, with inlet distributors for gas and liquid feeds in the conventional and alternative absorber designs.
- Flue Gas Supply – 2 KW generator exhaust with supplemental CO_2 to reach 13.5% CO_2
- Media Feed System – in the catalyzed tests, premixed suspended catalyst was added at 1% TSS (per manufacturer's recommendation); the catalyst was carbonic anhydrase coated on 10-15 µm spherical inert particles.
- Catalyst Filtration – removed catalyst from carbonated media after test, using a Zobi ultrafiltration module with 0.04 micron mean pore size, Figure 10.Air sparge was used to control fouling and permeate was withdrawn using a gravity siphon. The permeate rate (at a fixed trans-membrane pressure) did not appear to decrease from test to test as shown in Figure 11. Long-term filtration testing would be required to determine whether any irreversible fouling is occurring with the catalyst filtration.

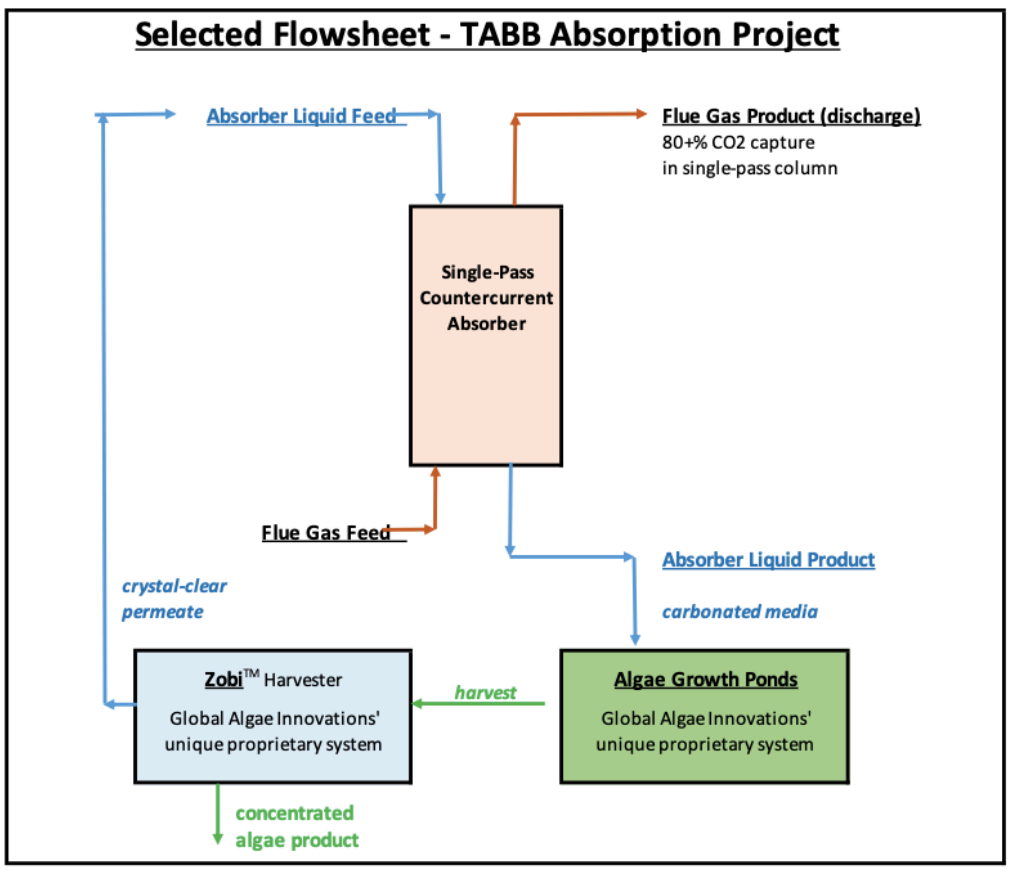


Figure 3. Selected flowsheet based on techno-economic modeling

Table 3. All project objectives met

Project Objectives	Project Results	Success?
80% CO_2 capture in one pass	80% CO_2 capture achieved in one pass	Yes
Integrated operation with algae growth	Integrated operation demonstrated with algae growth	Yes
Increase CO_2 capture rate to 14 kg/m^3 hr	CO_2 capture rate increased to 17.7 kg/m^3 hr	Yes
Reduce projected model cost for capture to \$28/mt CO_2	Reduced projected model cost to \$13/mt CO_2 at 10,000-acre scale	Yes
Move selected flowsheet to TRL-5	Selected flowsheet is now at TRL-5 (validated in relevant environment)	Yes

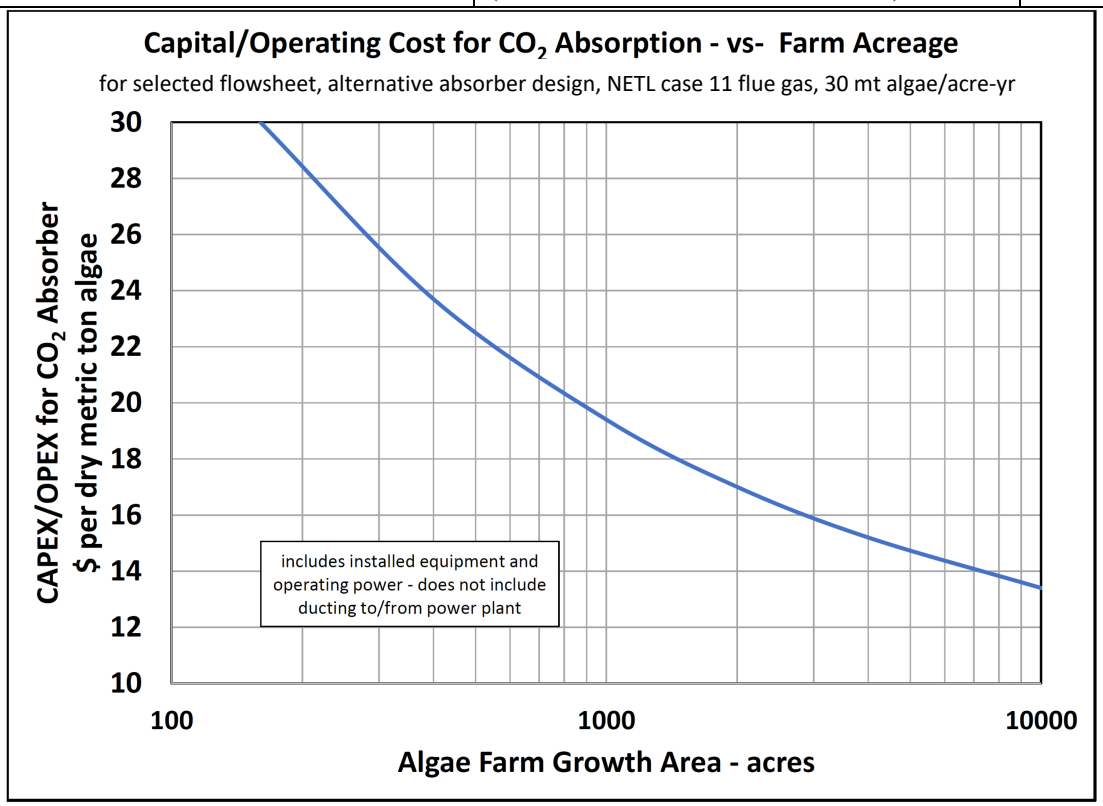


Figure 4. Absorber cost for CO_2 capture from a coal power plant flue gas

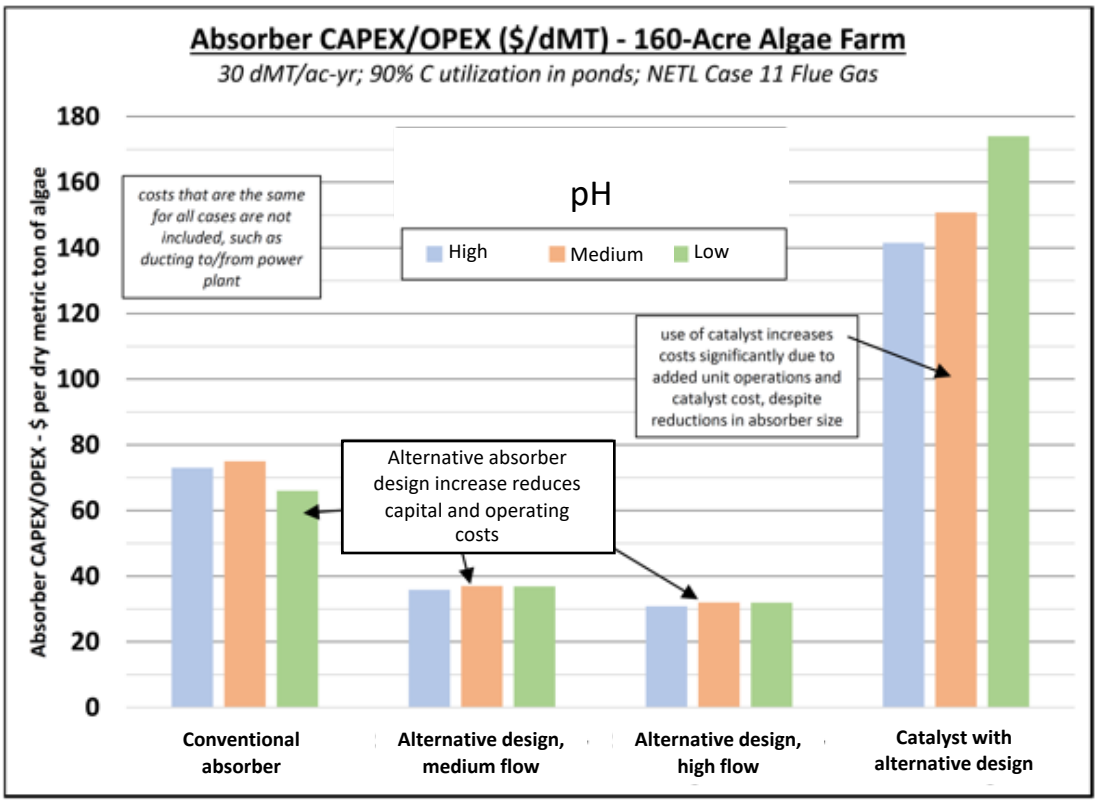
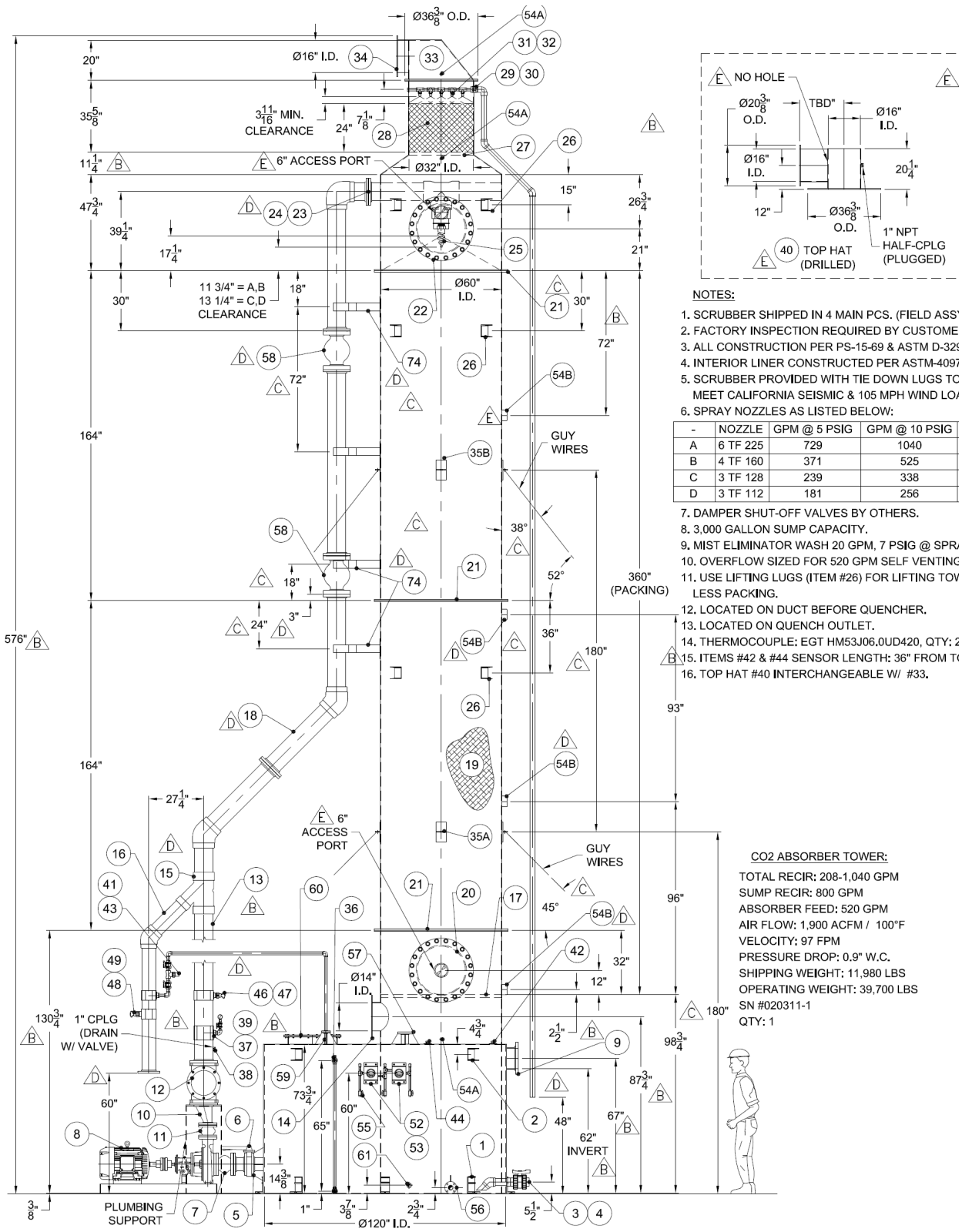


Figure 5. Comparison of absorber capital and operating expense for twelve different options

Figure 6 Packed tower absorber connected to adjacent power plant; 5 feet diameter by 50 feet with packed height of 30 feet of Lanpac XL 3.5" packing



-	NOZZLE	GPM @ 5 PSIG	GPM @ 10 PSIG
A	6 TF 225	729	1040
B	4 TF 160	371	525
C	3 TF 128	239	338
D	3 TF 112	181	256

Figure 7. Engineering drawing of the large absorber

Figure 8. 6-inch absorber column with variable flue gas inputs and 12-foot packing height

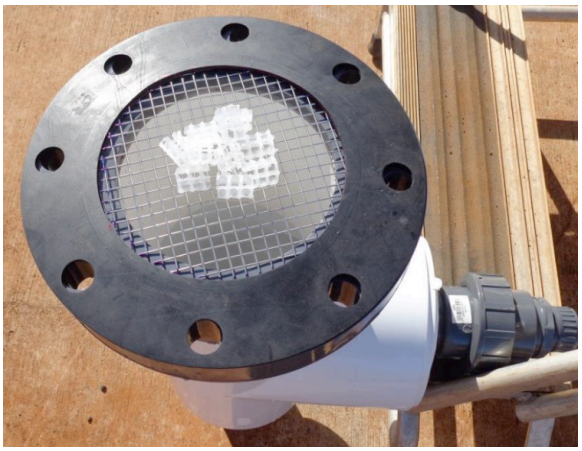


Figure 9. NorPak 5/8" packing for the 6" absorber on the bottom screen

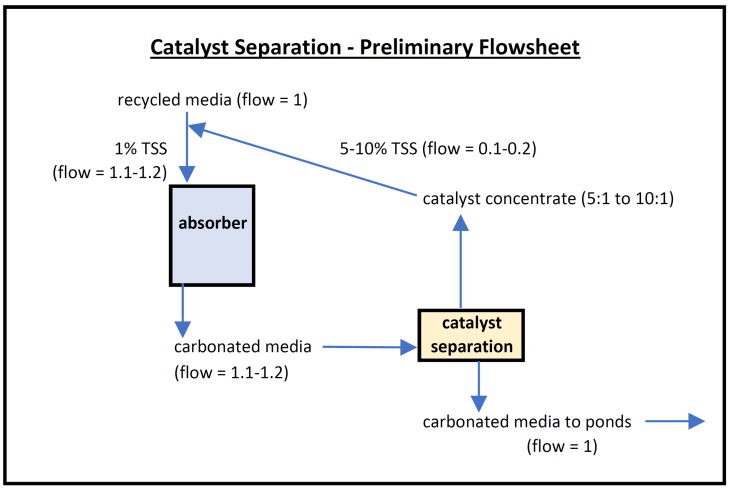


Figure 10. Configuration for carbonic anhydrase catalyzed absorber tests

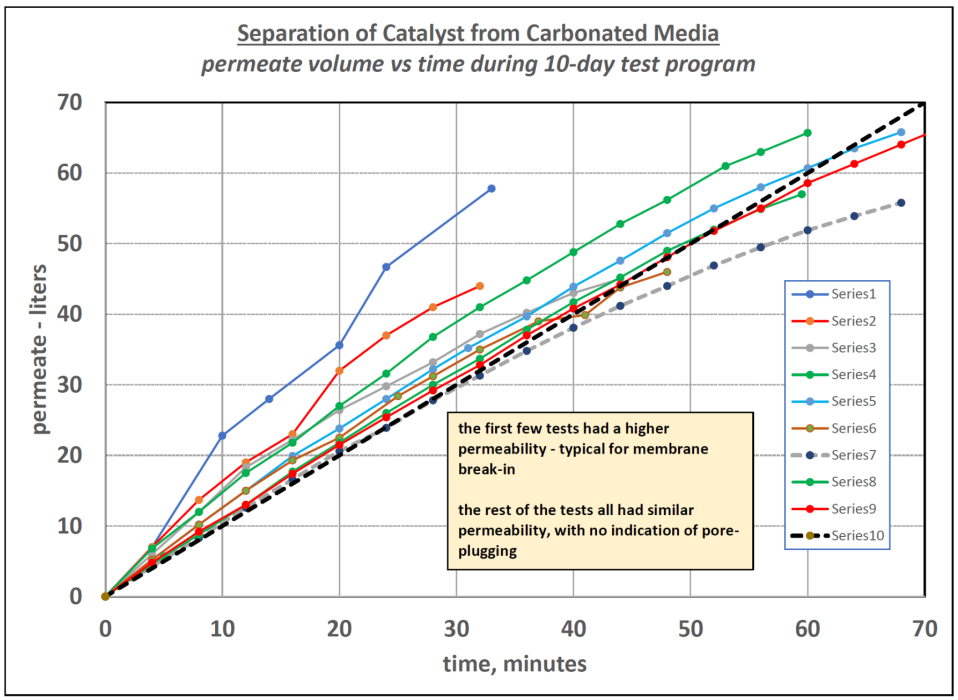


Figure 11. Separation of catalyst from carbonated media showed no indication of long-term fouling

Catalytic absorption of CO_2 is being developed by others for carbon capture applications that produce purified/compressed CO_2 for transport via pipeline to geological sequestration wells. Early testing used catalyst-coated packing to reduce the height of packing. The technology then evolved to catalyst-coated fine particles for recirculation through the absorption column. Current development and demonstration projects are all using soluble catalyst that shuttles back/forth between the absorption column and the desorption column. The first company that we collaborated with, Akermin, went out of business. Catalyst-coated particulates were purchased from CO_2 Solutions, and all of the tests were completed with this material. It should be noted that CO_2 Solutions no longer produces the catalyst-coated particulates, though they provided an

estimate of costs to produce it. Their primary technology is now soluble catalyst that is not exposed to the atmosphere. Even if the catalyst were readily available, the cost of catalyst separation makes this option unattractive, as shown in the cost analysis.

3.1.2 Test data and correlation

The overall reaction in the absorber uses CO_2 from the flue gas to convert Na_2CO_3 (aq) into $NaHCO_3$ (aq):

$$CO_2 + H_2O + Na_2CO_3 \Leftrightarrow 2\ NaHCO_3$$

Data was analyzed using a conventional mass transfer equation in a finite-element model, as follows:

$$Q_{CO2,abs} = k\,V\left(P_{CO2,g} - P_{CO2,LE}\right)$$

where

- $Q_{CO2,abs}$ is the rate of CO_2 absorption, g-moles/hour
- k is the mass transfer coefficient, gram-moles CO_2 absorbed per hour-liter-atmosphere
- V is the volume of packing, liters
- $P_{CO2,g}$ is the partial pressure of CO_2 in the gas
- $P_{CO2,LE}$ is the vapor-liquid equilibrium partial pressure of CO_2 above the liquid

The difference between the partial pressure in the gas and the equilibrium partial pressure is the driving force for the mass transfer.

Two correlations were used to assist in these calculations:

- vapor-liquid equilibrium CO_2 partial pressure as a function of media pH, temperature, and molarity[4]
- sodium bicarbonate content as a function of pH, molarity, and temperature from in-house test data correlation

For each absorber design type and gas/liquid conditions data set, the mass transfer coefficient has been plotted vs the % carbonation ratio (defined as the mole ratio of sodium bicarbonate to total sodium ion). A comparative chart of a family of test curves for k vs carbonation ratio, Figure 12, illustrates the relative mass transfer effects related to absorber design type, liquid loading and catalyst.

The finite element model performs a linked set of mass-balance and absorption calculations for the complete set of 0.1-meter vertical sections of the column. The model was used to calculate mass transfer coefficients as a function of test data. It was then used to calculate large-scale absorber performance with those same mass transfer coefficients.

Energy analyses indicates that the flue gas will only warm the liquid by ~1°C for typical liquid/gas mass flow ratios (L/G ranges from 60-90 for the three cases considered in this report). The

[4] Mai & Babb. Industrial & Engineering Chemistry. Vol 47 No. 9; pp 1749-1757.

absorber temperature is therefore primarily determined by the recycled media temperature and not the flue gas temperature.

CO_2 absorption tests included parametric testing with uncatalyzed and catalyzed operation in the 6" absorber test system to obtain mass transfer data. Additional test data was obtained from the large-scale absorber. A summary of some of this test data is provided in Table 4. The large absorber and small absorber uncatalyzed conventional design results were similar with a mass transfer coefficient of ~2 g-mol CO_2/hr l atm for the lower pH range, Figure 12. For both the conventional and alternative absorber design, the catalyzed tests result in approximately a 4 to 5-fold improvement in the mass transfer coefficient.

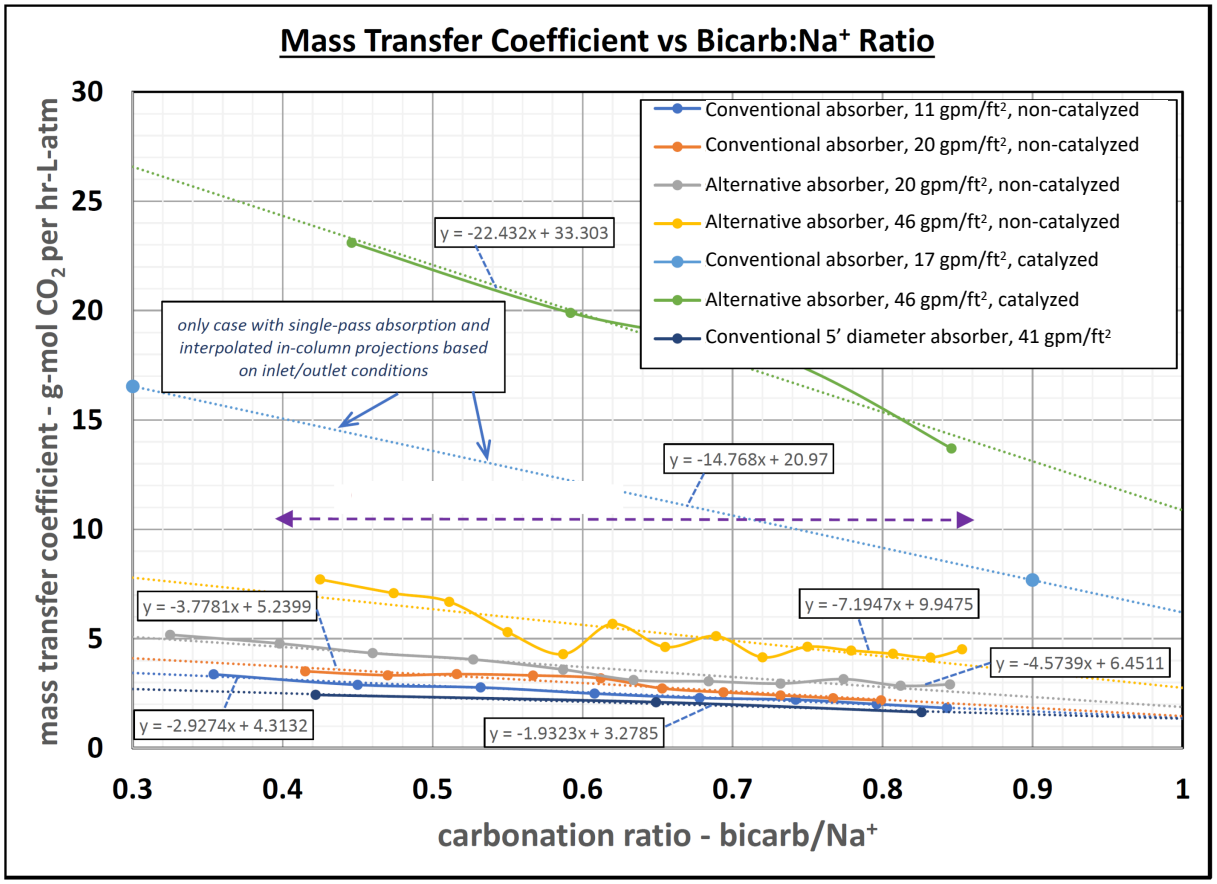


Figure 12. Summary of baseline mass transfer test results and correlations with carbonation ratio

Table 4. Absorber parametric test results

Test Data - 6" Absorber at KAF										Calculated Parameters	
Absorber Type	Packing Depth, in	Catalyst?	L, gpm	gas flow, scfm	vol% CO2	conductivity, mS/cm	inlet pH	outlet pH	media temp, deg C	avg bic/Na+	k, g-mol per hr-atm-L
Conventional	65	no	2.2	12.2	10.3	21	9.97	9.76	26	0.354	3.37
							9.78	9.61	26	0.450	2.89
							9.63	9.47	26	0.532	2.77
							9.49	9.34	26	0.608	2.49
							9.36	9.21	26	0.678	2.29
							9.23	9.07	26	0.742	2.21
							9.10	8.94	27	0.796	2.01
							8.97	8.81	27	0.843	1.83
Conventional	65	no	4	12.2	10.3	21	9.81	9.70	27	0.415	3.51
							9.71	9.61	27	0.470	3.33
							9.68	9.53	27	0.516	3.38
							9.54	9.44	28	0.567	3.32
							9.46	9.36	28	0.612	3.19
							9.38	9.29	28	0.653	2.73
							9.30	9.21	28	0.694	2.55
							9.22	9.13	28	0.732	2.41
							9.14	9.05	28	0.767	2.28
							9.06	8.97	29	0.799	2.18
Alternative Design	65	no	4	12.2	10.3	21	10.00	9.83	28	0.325	5.18
							9.86	9.71	28	0.398	4.78
							9.74	9.61	29	0.460	4.34
							9.62	9.50	29	0.527	4.05
							9.51	9.40	29	0.587	3.59
							9.42	9.32	30	0.634	3.11
							9.325	9.22	30	0.684	3.05
							9.23	9.12	30	0.732	2.95
							9.14	9.015	30	0.774	3.15
							9.04	8.92	30	0.812	2.85
							8.95	8.82	30	0.845	2.91
Alternative Design	65	no	9.15	12.2	10.3	21	9.78	9.69	30	0.425	7.71
							9.69	9.61	30	0.474	7.08
							9.625	9.55	31	0.511	6.69
							9.55	9.49	31	0.550	5.30
							9.48	9.43	31	0.587	4.29
							9.43	9.36	31	0.620	5.68
							9.36	9.30	32	0.655	4.62
							9.30	9.23	32	0.689	5.12
							9.23	9.17	32	0.720	4.15
							9.17	9.10	31	0.750	4.63
							9.10	9.03	31	0.779	4.46
							9.03	8.96	31	0.807	4.31
							8.96	8.89	31	0.832	4.14
							8.90	8.82	31	0.853	4.52
Conventional	144	yes	3.4	12.6	13.5	19	9.78	8.82	24	0.3	16.54
									24	0.4	15.06
									24	0.5	13.59
									24	0.6	12.11
									24	0.7	10.63
									24	0.8	9.16
									24	0.9	7.68
Alternative Design	65	yes	9.15	12.6	13.5	21	9.81	9.28	25	0.446	23.1
							9.55	8.99	25	0.592	19.9
							9.30	8.67	25	0.729	17.9
							9.02	8.80	25	0.846	13.7
Conventional 5 ft diameter	360	no	700	1070	6.7% avg	20.7	pH range of 9.8 to 8.8		25	0.422	2.43
									25	0.649	2.10
									25	0.826	1.64

In order to gather a wide range of data, testing was conducted at a wide range of single pass absorber efficiencies. Figure 13 illustrates a summary of the single pass efficiency results. A maximum of 83% capture efficiency was demonstrated.

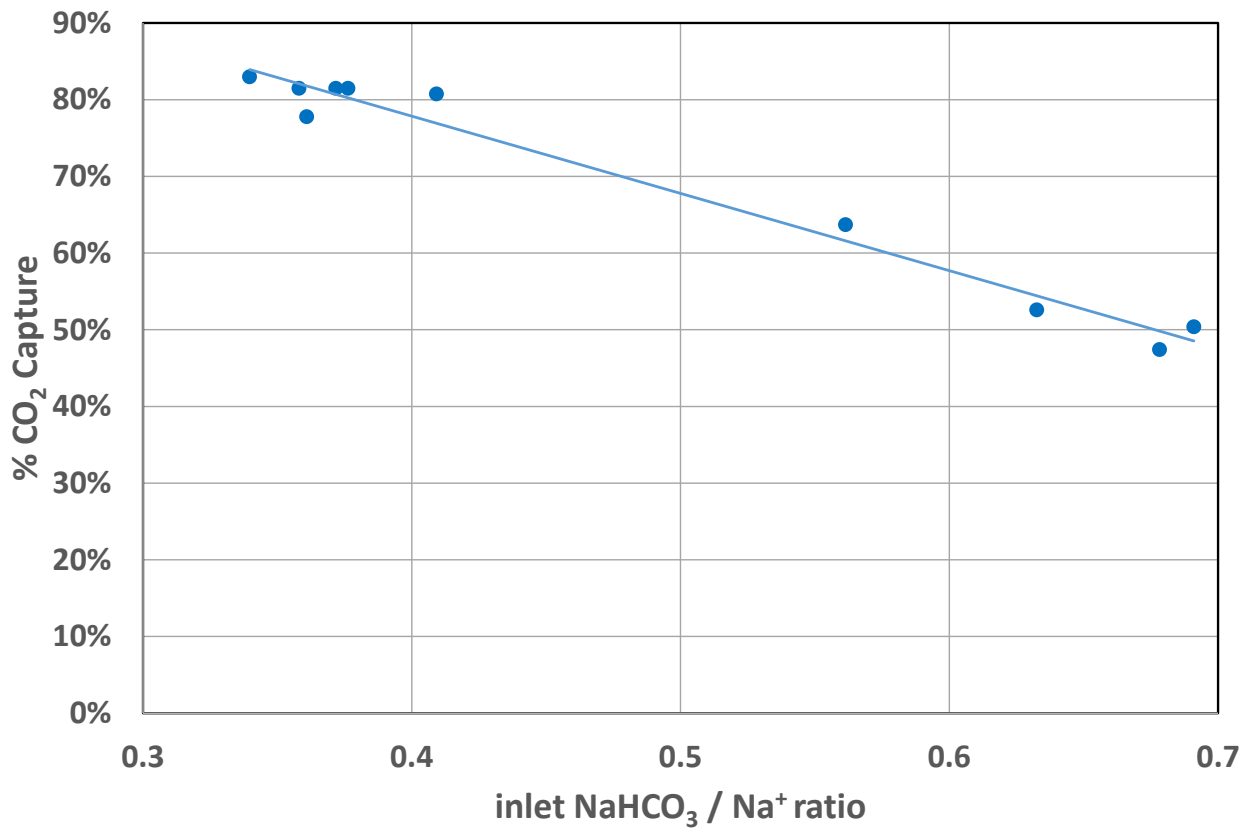


Figure 13. Single pass absorber capture efficiency as function of carbonation ratio

3.1.3 Scale-up calculations and techno-economic modeling

As discussed above, a finite-element model is used to size the absorber for scale-up. Global Algae's current farm contains ~8 acres of open raceways; the current scale-up plan is a 20x scale-up to a pilot facility with approximately 160 acres of open raceways and then another 20x scale-up to 3200 acres of open raceways.

Economic calculations used the actual installed cost of a 5 ft diameter x 30 ft packed height absorption system as a basis for determining costs of a larger-scale system.

The cost of systems utilizing a catalyst always come out higher than the non-catalyzed cases. For catalyzed operation, as shown in Figure 10, the 5-10% TSS catalyst suspension will be added to the media upstream of the absorber to form a 1% TSS catalyst suspension. The media will pass through the absorber at 1% TSS catalyst suspension. The catalyst particles will be separated from the carbonated media downstream of the absorber outlet. The recovered 5-10% TSS catalyst

suspension will be recycled back to the absorber inlet. The facility will have 30 minutes of catalyst surge capacity. For the 160-acre facility, the absorber flow averages 2163 gpm for Cases 1, 2 & 3. At 1% TSS, that equates to ~82 kg/min of catalyst, or ~2500 kg of catalyst for a 30-min surge supply. Assuming a make-up rate of 20% per year, an additional ~500 kg of catalyst will be purchased each year of operation. The catalyst supplier, CO_2 Solutions, has provided a budgetary estimate of catalyst cost of $420/kg (dry basis). The catalyst cost for a 160-acre facility is therefore $1,050,000 plus an additional $210,000 each year.

These design tools can be applied to specific details of any algae farm and CO_2 source. A summary of 12 cases for a 160-acre pilot-scale algae farm was presented in Figure 5.

3.2 Utilization results and analysis

The goal of the utilization tests was to increase the utilization efficiency from 60% in prior testing to over 90% using 2m^2 raceways at shallow depth. A series of tests were conducted to identify a simple operational control method to increase the utilization efficiency. By controlling the addition rate of carbonated media based on pH in the culture media, the utilization efficiency was increased to 97%.

3.2.1 Calculation methods

The key calculated quantities are the productivity and utilization efficiency. The measurements used to determine this are ash-free dry weight of algae in the media in the morning, the volume in the raceway in the morning, the carbon content in the algae, the quantity of media harvested each day, the quantity of carbonated media added each day, and the concentration of sodium bicarbonate in the media in the morning and in the carbonated media added each day. The concentration of sodium bicarbonate is determined from the pH, conductivity, and temperature using calibration curves. The volume in the raceway is determined from the depth of the raceway and calibration curves for the volume versus depth for the raceways. Each morning, the concentration, pH, temperature, conductivity, and depth of the raceway are measured. Then a portion of the raceway is harvested, and carbonated media is added throughout the day.

Daily productivity is calculated by change in algae biomass divided by the area:

$$P = \frac{\{C_{A,1}V_1 - C_{A,0}V_0\}}{A}$$

where

P is the productivity of algae growth, g/m^{2}d

$C_{a,1}$ is the concentration of algae in the raceway in the morning, g/l

$C_{a,0}$ is the concentration of algae in the raceway in the morning on the previous day, g/l

V_1 is the volume in the raceway in the morning prior to harvesting, l

V_0 is the volume in the raceway in the morning on the previous day after harvesting, l

A is the area of the raceway, m^2

The carbon dioxide is supplied in the carbonated media as bicarbonate as illustrated in Figure 1. The stoichiometric equation for bicarbonate is:

$$2\ NaHCO_3\ \rightarrow CO_2 + Na_2CO_3 +\ H_2O$$

The utilization efficiency is calculated by change of carbon in algae divided by the carbon supplied from $NaHCO_3$:

$$U_{eff} = \frac{\{C_{a,1}V_1x_1 - C_{a,0}V_0x_0\}}{\{C_{B,0}V_0 + C_{B,CM}V_{CM} - C_{B,1}V_1\}\frac{Mw_C}{2\ Mw_{NaHCO3}}}$$

where

U_{eff} is the utilization efficiency, %

x_1 is the fraction of carbon in the algae biomass in the raceway in the morning, g carbon / g algae

x_0 is the fraction of carbon in the algae biomass in the raceway in the morning on the previous day, g carbon / g algae

$C_{B,1}$ is the concentration of $NaHCO_3$ in the raceway in the morning, g/l

$C_{B,0}$ is the concentration of $NaHCO_3$ in the raceway after harvesting the previous morning, g/l

$C_{B,CM}$ is the concentration of $NaHCO_3$ in the carbonated media added during the day, g/l

V_{CM} is the volume of carbonated media added during the day, l

Mw_C is the molecular weight of carbon, 12.01 g/mole

Mw_{NaHCO3} is the molecular weight of sodium bicarbonate, 84.01 g/mole

3.2.2 Test results

The baseline utilization efficiency was based on long-term testing in sloped raceways with carbonated media addition at a fixed rate over about 4 hours each day. The $2m^2$ raceways used for this testing do not have automated carbonated media feed controls, so the standard approach is to add carbonated media twice a day. The first test series was conducted to measure the baseline in $2m^2$ raceways with the standard approach. Table 5 provides a summary of the data. Surprisingly, the average utilization efficiency with two additions of carbonated media compared to a slow addition over four hours was 59% vs 60%. An interesting observation is that the utilization efficiency is high during high productivity periods and low during low productivity periods. Figure 14 provides a plot of the utilization efficiency versus productivity. The red points have a productivity below the average, i.e. < 15.1 g/m^2d, and the blue points have a productivity above the average. The average utilization efficiency at the lower productivity is 30% while the average at higher productivity is 88%. This relationship shows that controlling the addition rate with respect to growth rate may be a possible method of attaining 90% utilization efficiency.

The key reactions in the capture of CO_2 are:

(1) $CO_2(g) \leftrightarrow CO_2(aq)$
(2) $CO_2(aq) + H_2O \leftrightarrow H_2CO_3$
(3) $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$
(4) $H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$

The kinetics of the first, third, and fourth reactions are very fast relative to the second reaction[5]. Thus, during growth when CO_2 is utilized by the algae, the reaction rate for reaction two may be too slow to keep up with the utilization rate, so the concentration of aqueous CO2 in the media will be below the equilibrium level. If this occurs, then CO_2 will be absorbed from the atmosphere even though at equilibrium, CO_2 would be off-gassed to the atmosphere; thus, likely factor in the observed higher utilization efficiency for higher productivity is that the rate of utilization of CO_2 by the algae may be faster than the rate at which CO_2 is released from the bicarbonate reaction, so CO_2 is being absorbed from the atmosphere.

Table 5. Baseline utilization efficiency test for 2m² raceways

Date	C_{algae} (g/l)	V_1 (liter)	V_0 (liter)	V_{CM} (liter)	P (g/m²d)	U_{eff} (%)
8/17/16	0.74	127.4	127.4	45.8	10.7	24
8/18/16	0.65	174.7	127.4	45.8	25.9	121
8/19/16	0.67	193.3	127.4	22.9	17.9	42
8/20/16	0.78	150.7	127.4	45.8	18.6	28
8/21/16	0.76	174.7	127.4	45.8	8.4	23
8/22/16	0.63	177.6	127.4	45.8	18.7	94
8/23/16	0.63	180.7	127.4	45.8	16.6	116
8/24/16	0.63	174.7	127.4	45.8	21.4	66
8/25/16	0.68	174.7	127.4	45.8	15.0	36
8/26/16	0.64	177.6	127.4	45.8	20.7	107
8/27/16	0.68	174.7	127.4	45.8	18.5	126
8/28/16	0.62	193.3	127.4	21.0	12.1	23
8/29/16	0.58	174.7	104.7	21.8	11.7	67
8/30/16	0.64	127.4	104.7	30.5	3.6	6
8/31/16	0.54	136.2	127.4	45.7	10.5	25
9/1/16	0.50	174.7	127.4	47.2	11.5	37
9/2/16	0.48	174.7	127.4			
Average	**0.64**	**168.3**	**124.7**	**40.4**	**15.1**	**59**

[5] Mitchell, M.J., O. E. Jensen, K.A. Cliffe and M. M. Maroto-Valer. 2010. A model of carbon dioxide dissolution and mineral carbonation kinetics. *Proc. R. Soc.* A **466**:1265–1290.

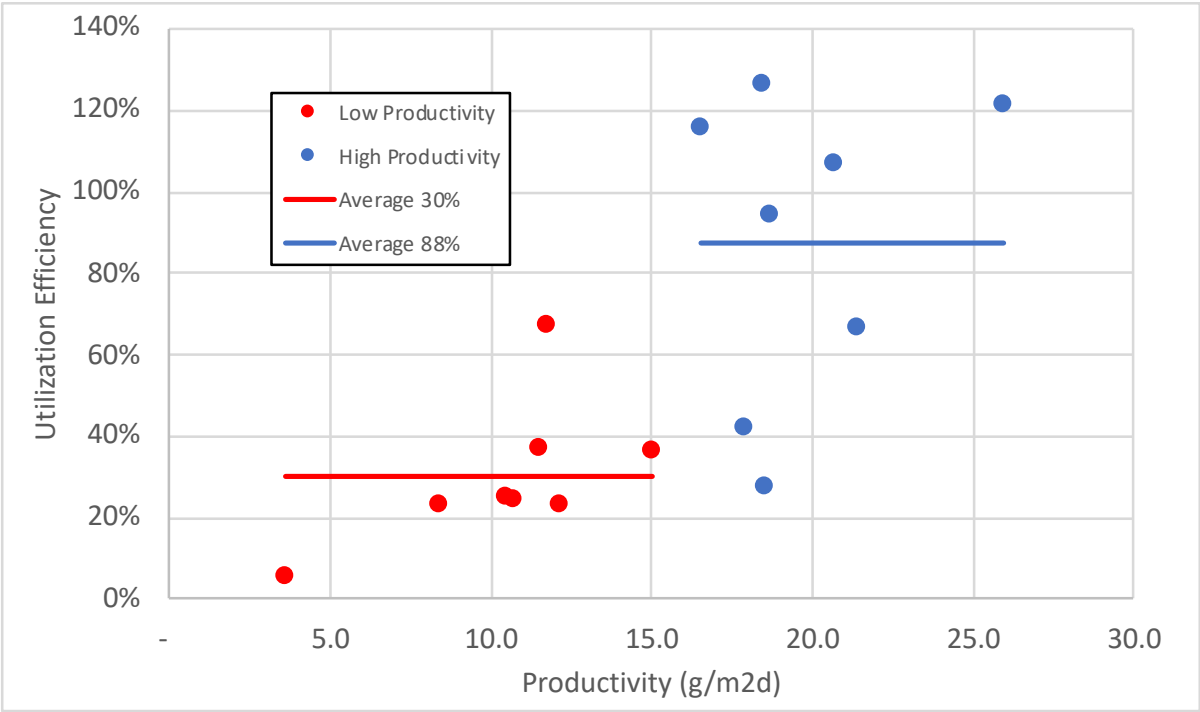


Figure 14. Utilization efficiency dependence on productivity, baseline test

In the second test series, the total amount of carbonated media to be added was fixed, but the addition rate was controlled to keep the pH at a fixed level until the maximum amount of media had been added. It rained throughout most of the testing, so the productivity was lower during this test than the prior run. Two different raceways were operated, and Table 6 provides the results based on an average of the two raceways. The average utilization efficiency increased to 77% with pH-controlled addition.

Table 6. Utilization efficiency with carbonated media addition a fixed pH

Date	C_{algae} (g/l)	V_1 (liter)	V_0 (liter)	V_{CM} (liter)	P (g/m^{2}d)	U_{eff} (%)
9/20/16	0.82	139.1	127.4	28.1	14.2	85
9/21/16	0.82	159.8	120.8	34.0	12.9	63
9/22/16	0.79	155.2	127.4	34.0	11.3	79
9/23/16	0.74	162.6	127.4	34.0	15.0	72
9/24/16	0.72	168.6	127.4	34.0	20.9	114
9/25/16	0.77	168.6	162.7	34.0	14.0	46
Average	**0.78**	**159.0**	**132.2**	**33.0**	**14.7**	**77**

The next series of tests were operated using a lower molarity. As in the second test series, carbonated media was only added if the pH was above a minimum range. The tests were conducted over 7 days, October 13-20, and the total utilization efficiency was calculated based on total carbon supplied from sodium bicarbonate and total carbon fixed in the algae. For the low, medium, and high pH ranges, the utilization efficiencies were 79%, 87%, and 95%, respectively, Table 7.

Table 7. Utilization efficiency at lower molarity with variable carbonated media addition pH set points

pH set point	Productivity (g/m^2d)	CO_2 from $NaHCO_3$ (gC)	CO_2 fixed in algae (gC)	CO_2 off-gas (gC)	Utilization Efficiency
Low	10.1	87.2	68.5	18.6	79 %
Medium	8.1	63.2	55.0	8.2	87 %
High	8.6	61.6	58.4	3.2	95 %

Because of the lower molarity and limited volume available for addition, the growth was limited by carbon dioxide availability in all three cases, so the final pH was typically above the target range at the end of each day. The main effect of the different pH range set points is that carbonated media was added faster in the morning to reach a lower pH, but the afternoon pH was similar as all of the carbonated media was added in the morning. The utilization efficiency results were further complicated by the competing effects of higher ending pH resulting in higher efficiency and lower productivity resulting in lower efficiency. A confirmatory 11-day test was conducted November 1-11 with a larger carbonated media reservoir to enable higher productivity and lower ending pH. The results of this test are presented in Table 8. As expected, the productivity was higher at 14.2 g/m^2d vs. 10.1 g/m^2d; however, the utilization efficiency was lower at 68% vs. 79%, so the lower pH was more important than the higher productivity in driving the utilization efficiency.

Table 8. Utilization efficiency at lower molarity, low pH set point with higher carbonated media volume

pH set point	Productivity (g/m^2d)	CO_2 from $NaHCO_3$ (gC)	CO_2 fixed in algae (gC)	CO_2 off-gas (gC)	Utilization Efficiency
Low	14.2	142.2	96.8	45.4	68 %

Based on these tests, the sodium molarity was increased to the standard level, and a high pH set point was selected for a final test series to verify that greater than 90% utilization efficiency is obtained. The test was conducted in mid-November with three raceways operating under the same conditions. Table 9 presents the results for each raceway. The average utilization efficiency was 97%, and the lowest raceways had a utilization efficiency of 96%, This test confirmed that the overall objective of greater than 90% utilization efficiency with a simple operational control method was achieved.

Table 9. Greater than 90% Utilization efficiency demonstration test

Raceway	Productivity (g/m^2d)	CO_2 from $NaHCO_3$ (gC)	CO_2 fixed in algae (gC)	CO_2 off-gas (gC)	Utilization Efficiency
1	14.2	72.2	69.2	3.0	96 %
2	15.4	75.2	74.6	0.6	99 %
3	12.8	64.9	62.2	2.7	96 %
Average	14.1	70.8	68.7	2.1	97 %

3.3 Integrated test and analysis

An integrated test of absorption and cultivation was conducted with ten cycles of harvesting, carbonating, and cultivation using the same media as illustrated in Figure 1. A fixed amount was harvested, re-carbonated, and added each day during test. A summary of the results is provided in Table 10; a high utilization efficiency, 91%, and high productivity, 22.8 g/m^{2}d, was attained.

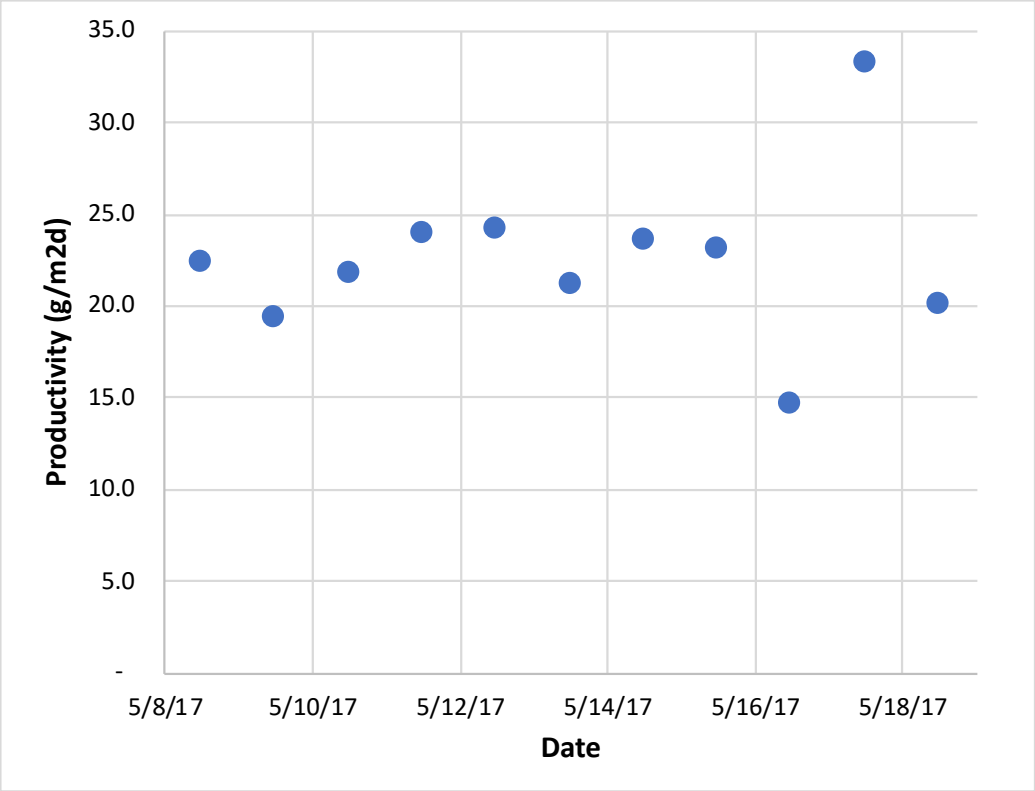


Figure 15 provides a plot of the productivity during the test.

Table 10. Summary of integrated test utilization efficiency and productivity

Test Date	Productivity (g/m^{2}d)	CO_2 from $NaHCO_3$ (gC)	CO_2 fixed in algae (gC)	CO_2 off-gas (gC)	Utilization Efficiency
5/9/17 to 5/19/17	22.8	244.3	221.4	22.9	91 %

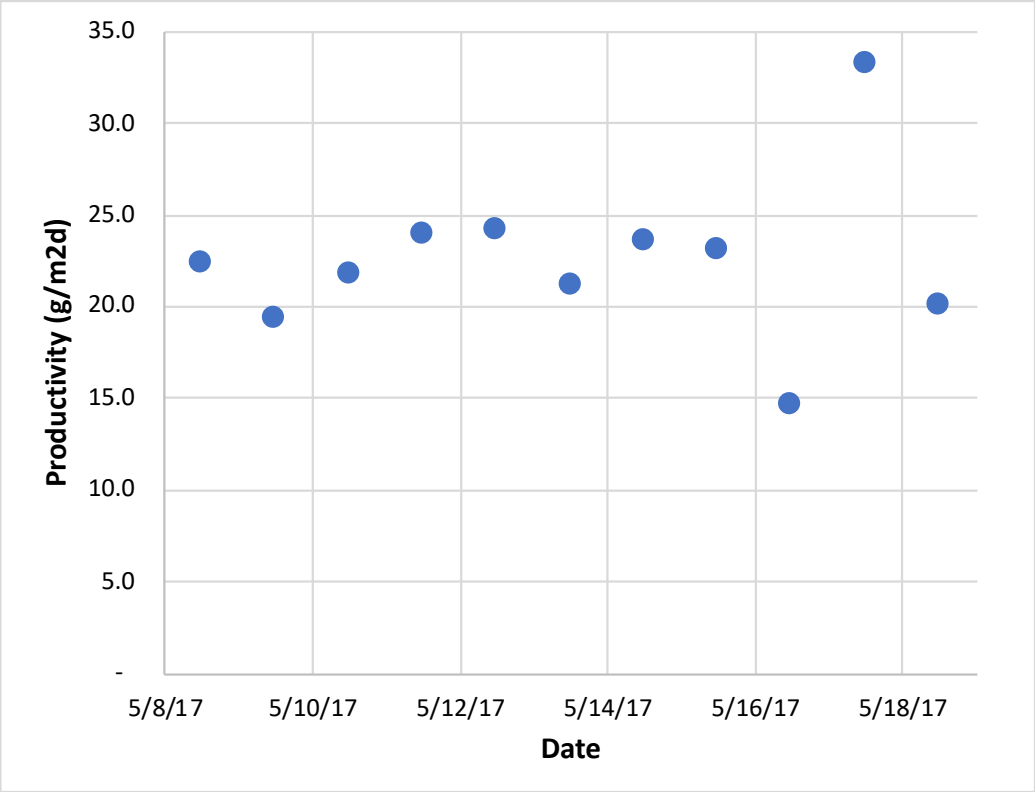


Figure 15. High productivity achieved during integrated test

The integrated test was conducted using carbonic anhydrase coated beads in the absorber to determine whether using the recycled media caused in any change in the mass transfer coefficient. Figure 16 illustrates the measured mass transfer coefficient data points versus the predicted mass transfer coefficient. There was no observable change in mass transfer relative to the predicted over the ten cycles, so there was nothing in the recycled media that interferes with the carbonic anhydrase activity.

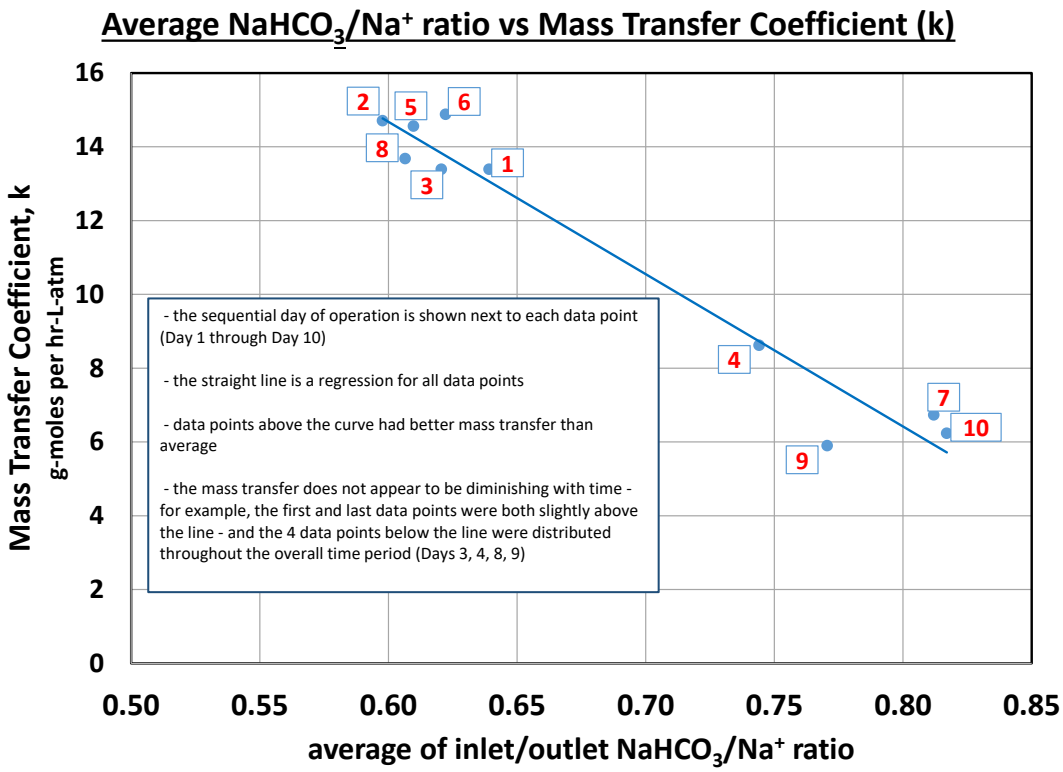


Figure 16. Absorber CO_2 mass transfer coefficient for 10-cycles during the integrated test

3.4 New isolates and carbonic anhydrase tests for direct air CO_2 capture

With the goals of the project achieved, additional work was focused on achieving even higher carbon and capture utilization efficiency. The focus was on two areas – higher pH strains to push the absorption efficiency to 90% and utilization efficiency above 100%, and direct air capture to eliminate the need for a concentrated CO_2 source.

3.4.1 Very high pH strain library

It is clear from Figure 12 and Figure 16 that the lower bicarbonate levels, i.e. higher pH, results in much greater mass transfer coefficients. If the pH is high enough, then capture efficiencies of 90% or greater could be attained with a relatively short column. The key is achieving high productivity at higher pH.

Also, it is clear from the utilization testing that operation at higher pH results in greater utilization efficiency. The key is that the driving force loss of the CO_2 to the atmosphere diminishes as the pH is increased. If the pH is high enough CO_2 will be absorbed from the atmosphere rather than lost, so the utilization efficiency would be greater than 100%.

Because of the need for higher pH operation, a library of new algal strains that grow at much higher pH in bicarbonate/carbonate media was recently created through environmental sampling and

selection from Soap Lake, WA and surrounding alkaline environments, Figure 17. Soap Lake is a meromictic, haloalkaline (pH 9.8-9.9) that can exhibit carbonate concentrations of 8,500 mgL-1 in the mixolimnion and 24,000 mgL^{-1} in the monimolimnion[6]. Collections were made from fifteen different sample site locations with environmental pH ranging from 7.99-9.92. Nine strains were isolated and are currently grown in bicarbonate/carbonate media at elevated pH,

Table 11. Three strains are diatoms, different species of Nitzschia, three are cyanobacterial strains, including a filamentous Spirulina, and three are chlorophytes. These strains have exhibited pH tolerance as high as 10.54. The diatoms appear to be similar to our current biofuel production diatom strain, so they are good candidates for outdoor cultivation.

Figure 17. Alkaline environments in the Soap Lake, WA and surrounding area

Table 11. Nine new strains collected from Soap Lake area

Strain	**Class**	***Species***	**pH**
GAI-326	Diatom	*Nitzschia communis*	9.92
GAI-327	Diatom	*Nitzschia communis*	9.92
GAI-328	Diatom	*Nitzschia communis*	9.94
GAI-324	Chlorophyte	*Chlorella sp*	10.02
GAI-325	Chlorophyte	*Nannochloris sp.*	10.20
GAI-329	Chlorophyte	*Monoraphidium sp.*	10.40
GAI-332	Cyanobacteria	Synechocystis	10.07
GAI-331	Cyanobacteria	*Spirulina subsalsa*	9.86
GAI-330	Cyanobacteria	*Synechocystis*	9.92

[6] Anderson GC. 1958. Seasonal characteristics of two saline lakes in Washington. *Limnol. Oceanogr.* 3, 51–68. doi: 10.4319/lo.1958.3.1.0051

3.4.2 Atmospheric CO_2 absorption

As discussed previously, the key reactions in CO_2 absorption are:

(1) $CO_2(g) \leftrightarrow CO_2(aq)$
(2) $CO_2(aq) + H_2O \leftrightarrow H_2CO_3$
(3) $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$
(4) $H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$

Reaction 2 is the rate limiting reaction that is accelerated by adding carbonic anhydrase, so adding carbonic anhydrase to the media could increase the rate of atmospheric CO_2 absorption in an open raceway. Additionally, there are literature results showing that increasing the pH above 10 will accelerate the reaction enough to enable support of high productivity with atmospheric CO_2 absorption[7]. To test the potential of these options, the rate of CO_2 absorption in a raceway without algae was measured as a function of pH with and without carbonic anhydrase. Figure 18 illustrates the results of these tests. These results do not support a major change in absorption rate at high pH; however, adding algae would increase the absorption rate by lowering the CO_2 concentration during the day as described in Section 3.2.2. A standard open raceway was used for these rather than a system where the area of paddlewheel was similar to the area of the raceway as described in the literature on high productivity with direct air capture[7]. In a system dominated by the paddlewheel, there is much greater surface area and air/media mixing than in a standard raceway, so this may explain the discrepancy between the results illustrated in Figure 26 and the prior literature. The direct air capture rate with carbonic anhydrase is reasonable for support of high productivity, so this is a potential route to direct air CO_2 capture.

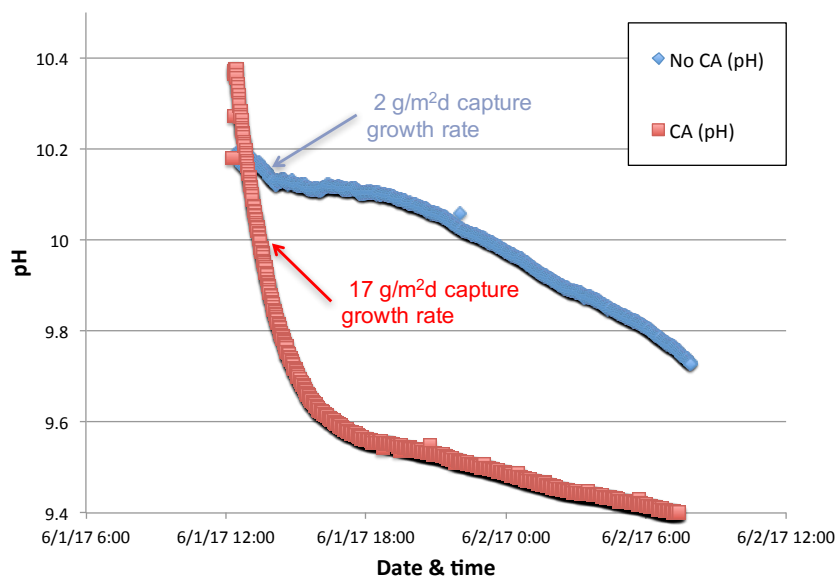


Figure 18. Rate of CO_2 capture in an open raceway without algae using carbonic anhydrase

[7] Vadlamani A. 2016. Enhanced biomass and lipid productivities of outdoor alkaliphilic microalgae cultures through increased media alkalinity. Dissertation. The University of Toledo.