

Advanced Manufactured Carbonate Materials for Algal Biomass Production: Joint LLNL-SNL Program

Project Kick-off Meeting

November 7, 2017

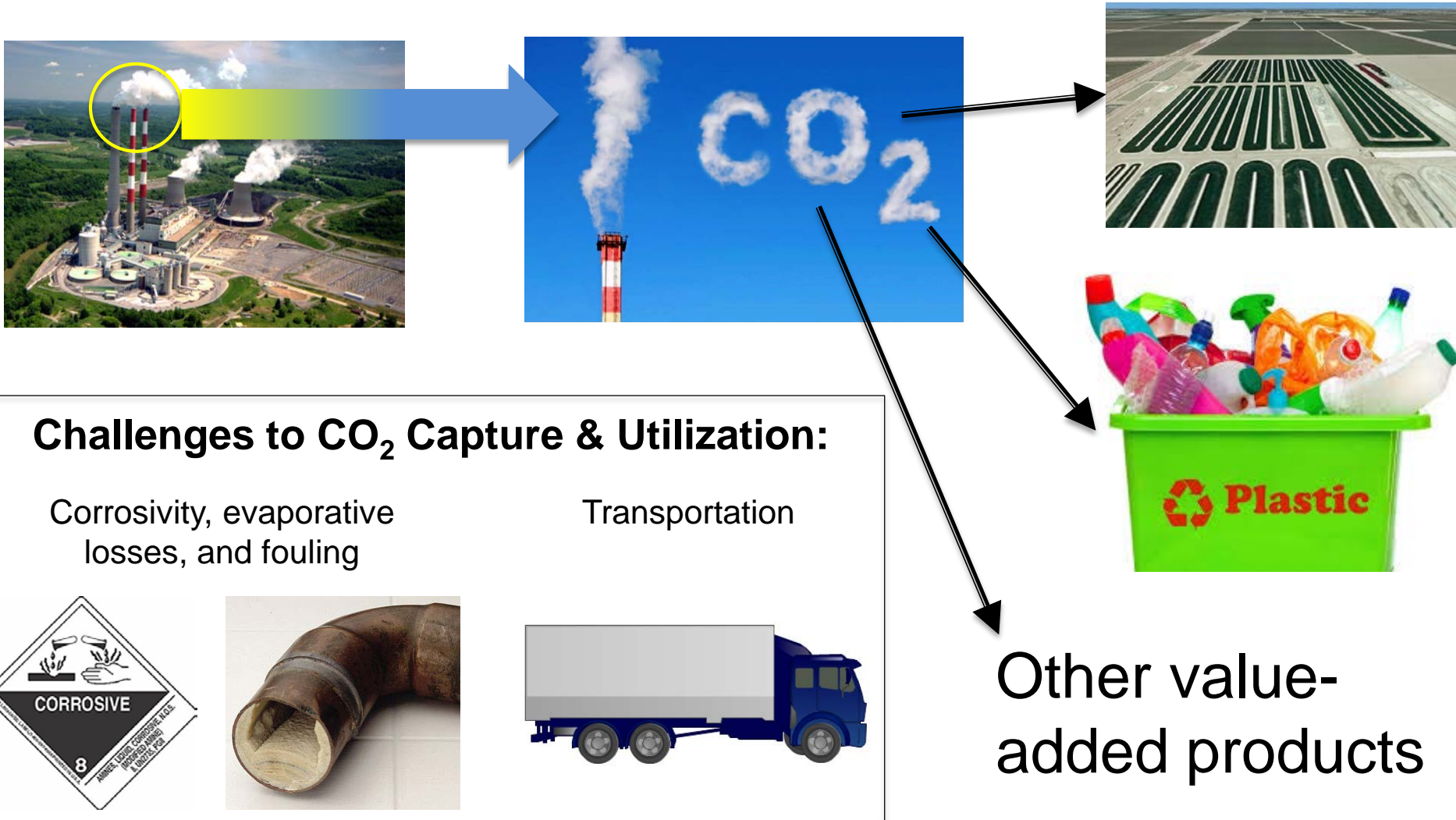
LLNL: Jennifer Knipe, Sarah Baker, Matthew Worthington, Maira Ceron-Hernandez, Sean McCoy
SNL: Todd Lane, Mary Tran-Gyamfi



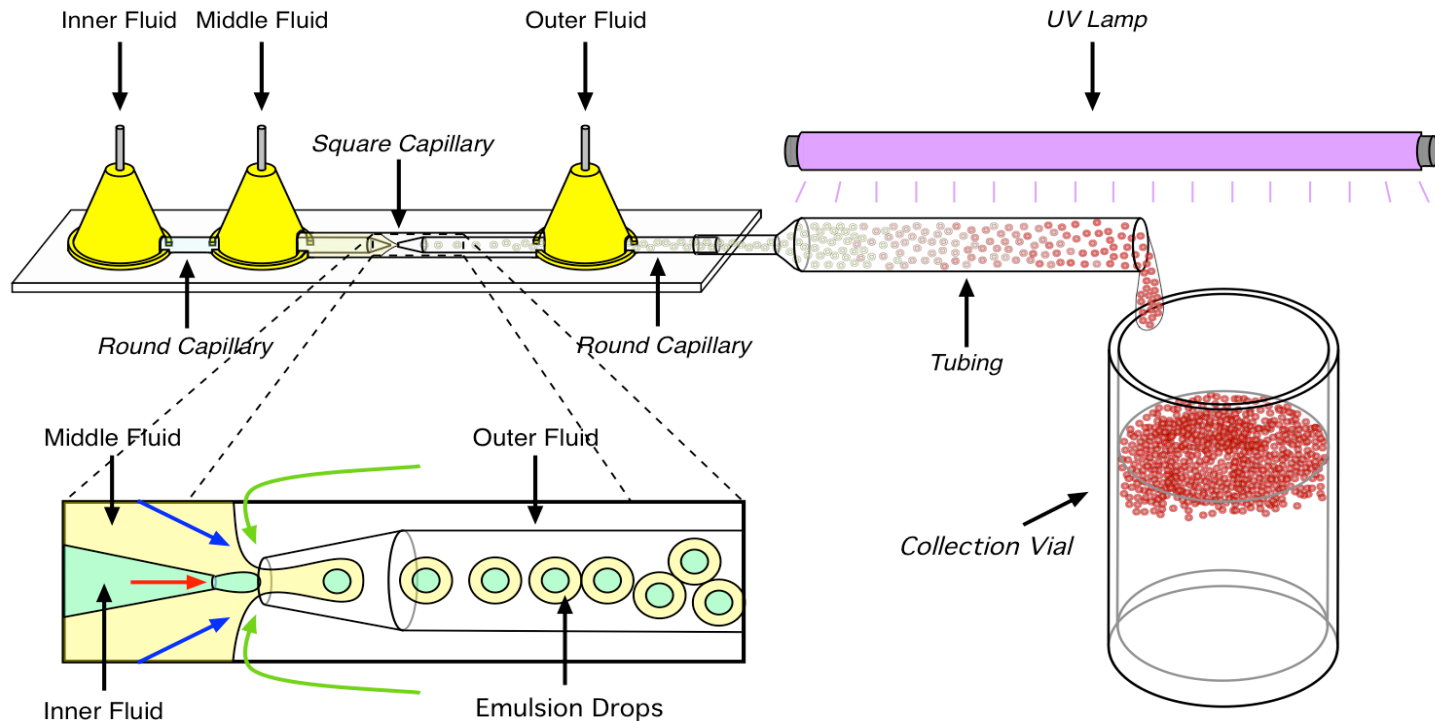
Outline

- Technology Background
- Project Objectives
- Team
- Scope of Work (Tasks)
- Risks
- Schedule
- Milestones
- Success Criteria
- Budget
- Initial results

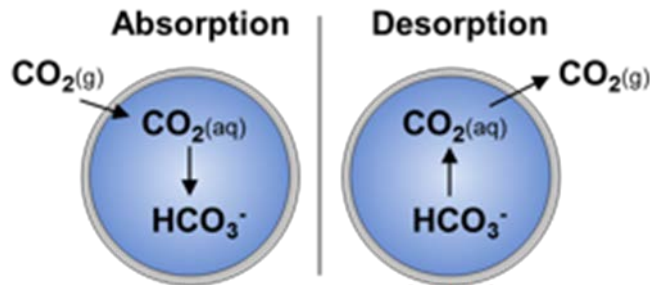
Motivation: CO₂ Capture and Utilization



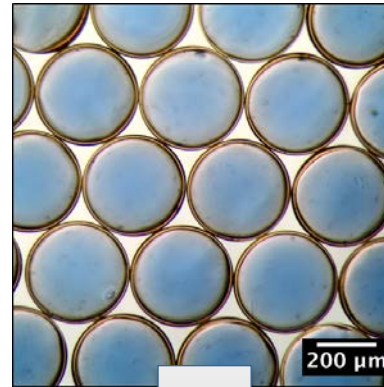
Microencapsulation: an enabling technology for CO₂ solvents



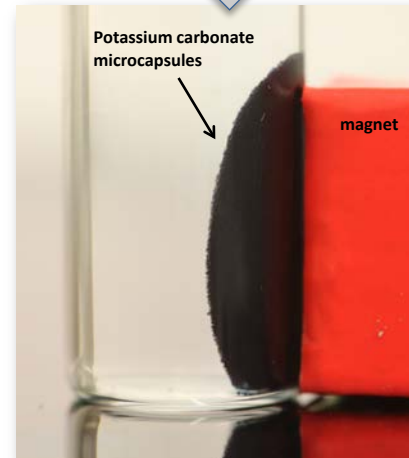
Microcapsules for CO₂ capture and separation



CO₂ loaded capsules are yellow (pH=8) and turn blue (pH= 10.5) as CO₂ is released in marine media

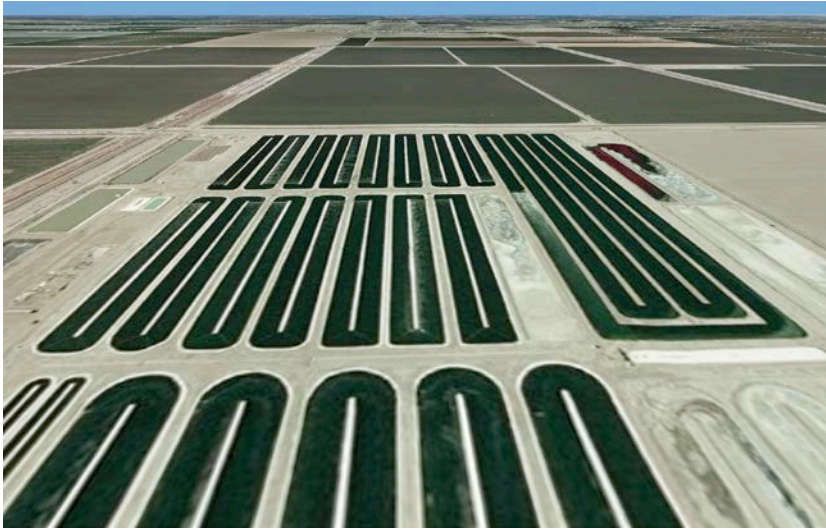


Capsules doped with magnetic nanoparticles

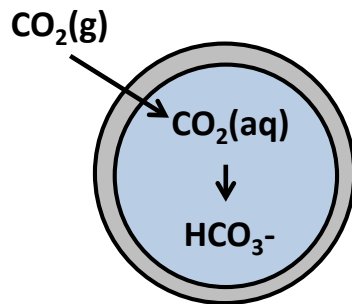


Magnetic separation of capsules from media

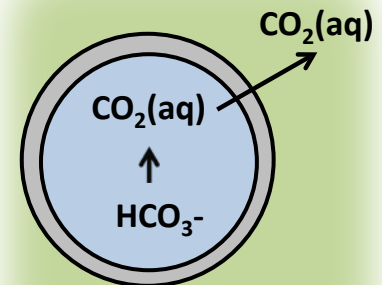
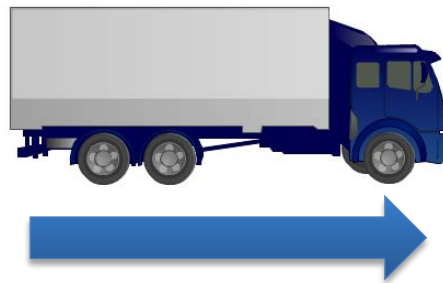
Microcapsules can be used for algae production



- CO_2 is at least 20% of costs of algae cultivation
- CO_2 can be delivered by capsule more efficiently
- Save 75% of cost of capture



Absorption



Release (Algae Pond)

Project Objectives

Task 1

Project
planned and
managed by
Lawrence
Livermore
National
Laboratory

Task 2

Select the
most
promising
material and
geometry

Task 3

Demonstrate
CO₂ storage
in materials
and delivery
to support
algal culture
in an algal
test bed at
pilot scale

Task 4

Evaluate the
economics
and gate-to-
gate GHG
emissions of
the coupled
capture-
transport

Team

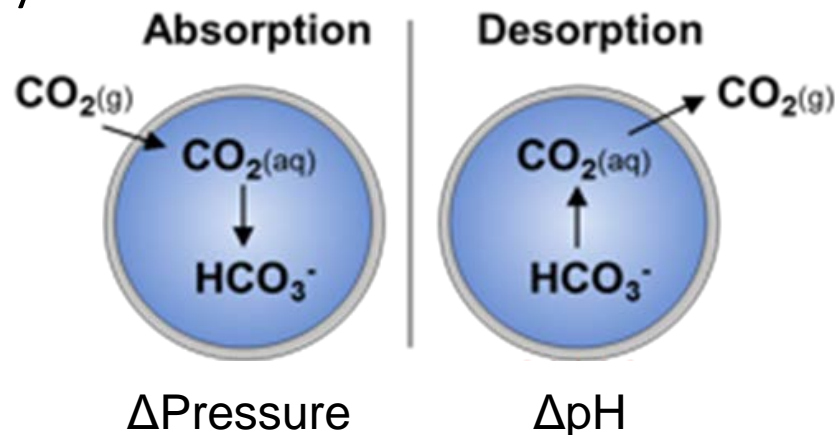
Key Personnel	Institution	Time	Tasks	Title, Roles
J. Knipe	LLNL	30%	Tasks 2,3	Post Doctoral Researcher, Task Lead 2-3.
S. Baker	LLNL	10%	Tasks 1,2,3,4	Staff Scientist, Project PI
M. Worthington	LLNL	30%	Tasks 2,3	Post-Collegiate Appointee, Carbonate Materials Characterization
M. Ceron-Hernandez	LLNL	30%	Tasks 2,3	Staff Scientist, Carbonate Materials Design and Scale-up
S. McCoy	LLNL	20%	Task 4	Energy analyst, Process Design and Economic Analysis
T. Lane	SNL	15%	Tasks 2,3	Sandia PI, Lead Phycologist
M. Tran-Gyamfi	SNL	50 %	Tasks 2,3	Technical Staff, Algae cultivation, characterization of nutrients, biomass, and growth
J. Jaryenneh	SNL	25%	Characterization	Technologist, Support of algae cultivation

Task 1 – Project management and planning

- Monitor and control project scope, cost, schedule and risk
- Maintain and revise the Project Management Plan and Data Management Plan
- Manage and report on activities in accordance with PMP
 - Variances in milestones, cost, schedule, scope, along with the associated mitigation plan
 - Updates on project costs and schedule status and performance against all relevant milestones, schedule and cost variances
 - Conference papers, proceedings, and journal articles

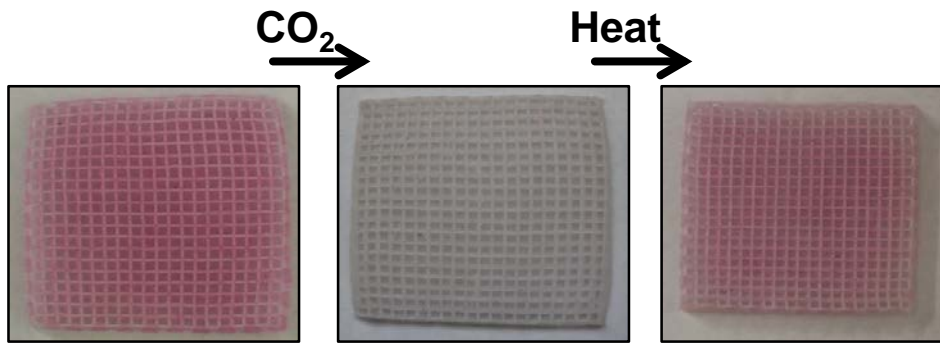
Task 2: Material selection

- Two possible geometries of sodium carbonate-based materials
- Test existing materials set – no optimization
- Choose most promising one or two materials to test in the sub-recipient's (SNL) Algal Testbed
 - highest CO_2 loading
 - matching of CO_2 delivery rates to algal consumption rates
 - biocompatibility



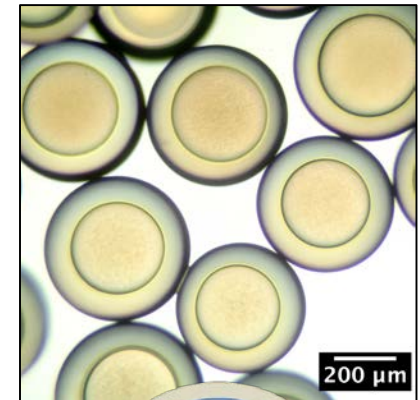
Task 2: Material selection

- **Subtask 2.1 - Synthesize multigram quantities of materials for testing**
 - 20% sodium carbonate solutions or solid sodium bicarbonate
 - Candidate polymers: SiTris, Dow SE1700, and TEGO 2650

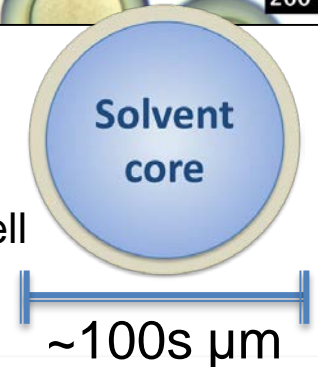


Bicarbonate-polymer composite mesh
printed with Direct Ink Write

Micro-
Encapsulated
CO₂ Sorbents
(MECS)

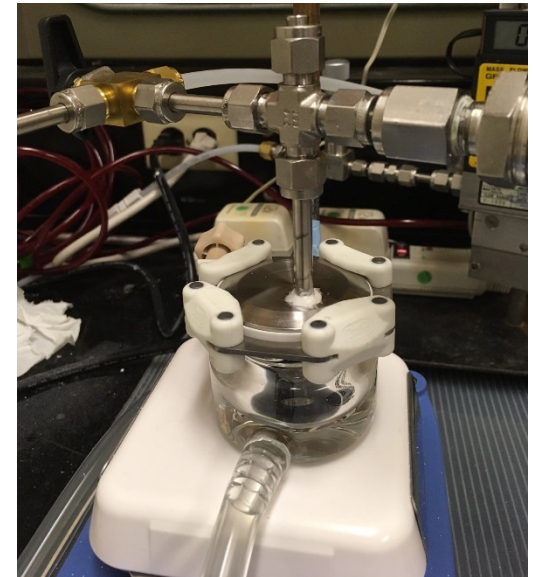
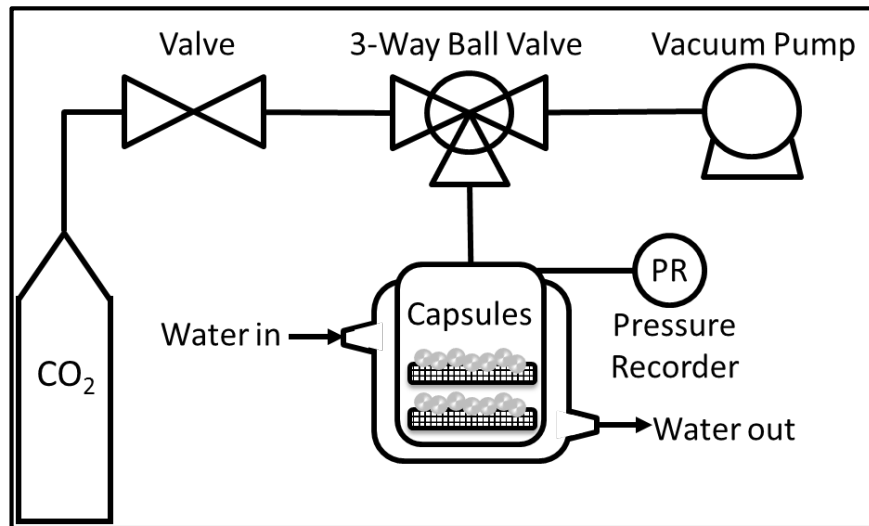


Gas-
permeable
polymer shell



Task 2: Material selection

- **Subtask 2.2 - Measurements of CO₂ absorption and release rates and quantities**
 - Measure CO₂ pressure in the headspace above the material to determine material capacity
 - pH measurements in seawater at a relevant pH and temperature to monitor rates of CO₂ release



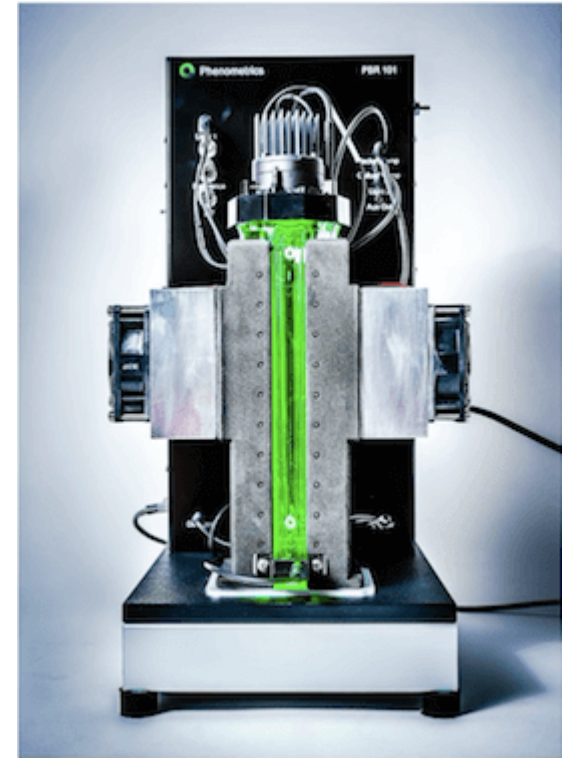
Task 2: Material selection

■ Subtask 2.3 - Materials biocompatibility evaluation

- Introduce unloaded materials at lab-scale (500 mL) using Phenometrics Photobioreactors and introduce CO₂ in the standard way (sparging)
- Monitor relevant growth parameters including pH, dissolved O₂, growth rate, productivity and yield
- Buoyancy of the materials in the algal culture and any shading effects will be noted

■ Subtask 2.4 - Materials selection for scale-up and TEA

- Down-select up to two carbonate materials on the basis of highest CO₂ loading, matching of CO₂ delivery rates to algal consumption rates, and biocompatibility



<http://www.phenometricsinc.com/all-products-2/pbr101/>

Task 3: Testing selected materials to support algal growth and CO₂ cycling

- Test the ability of the carbonate materials to supply CO₂ in lab-scale cultures at the sub-recipient's Algal Testbed
- Demonstrate that:
 1. Algae can live on captured and stored carbon in the form of encapsulated carbonate solutions or carbonate composites at pilot-scale
 2. Materials are biocompatible and can be delivered to the algae at a rate concomitant with the algal growth rate
 3. Materials can be retrieved and reused with little to no loss in function

Task 3: Testing selected materials to support algal growth and CO₂ cycling

■ Subtask 3.1 - Material delivery method

- Use lab-scale Phenometrics Photobioreactors to approximate open algae pond conditions while tracking the dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and particulate organic carbon (POC)
- Compare the total carbon budget of the algal culture to the inorganic carbon load of the carbonate materials to determine the optimal feed rate and method of delivery

■ Subtask 3.2 – Scale up materials synthesis

- Synthesis of selected carbonate material(s) at kilogram scale
- The scale-up method employed may require different manufacturing techniques such as using a vibrating coaxial tip rather than microfluidics to produce encapsulated carbonate solutions

Task 3: Testing selected materials to support algal growth and CO₂ cycling

■ Subtask 3.3 – Pilot-scale testing

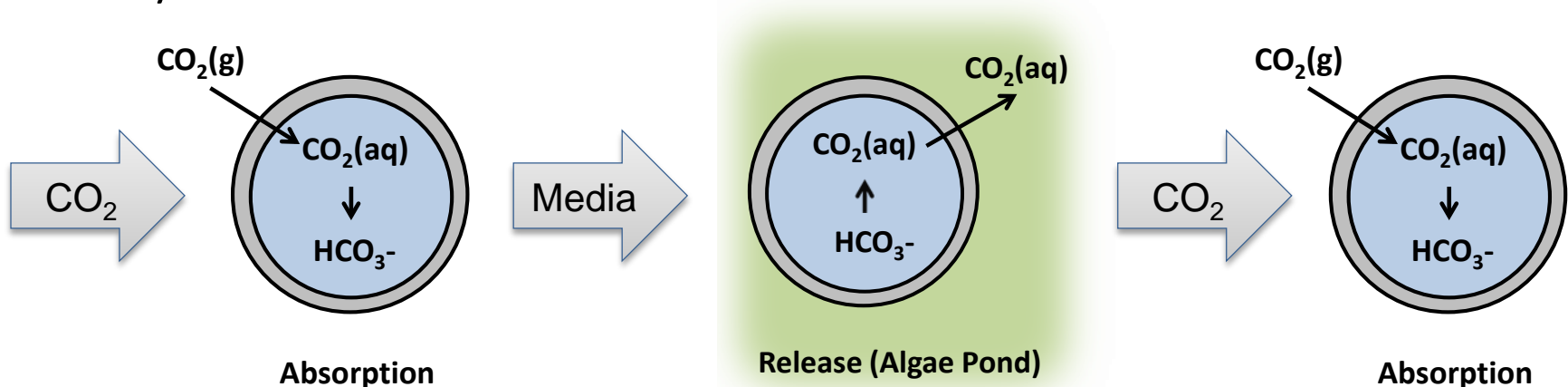
- Use 1000-Liter Algal Testbed to show that the carbonate materials can support the growth of algae at 80% productivity for one day-night cycle (16 hours)
- Monitor all relevant growth parameters, including pH, dissolved O₂, growth rate, productivity and yield
- Determine whether there is any shading effect from the presence of the CO₂-loaded carbonate materials; devise operational strategies
- Compare culture performance and biochemical make-up of the final biomass to cultures grown under standard CO₂ production systems



Task 3: Testing selected materials to support algal growth and CO₂ cycling

■ Subtask 3.4 - Measure material capacity during cycling

- Show that the carbonate materials can be re-used effectively at <1L scale using pH measurements and pressure measurements of the carbonate materials
- Re-load materials with CO₂ as part of the pressure-based measurements of CO₂ uptake rates and capacity
- Show that the carbonate materials can be loaded with CO₂ and unloaded in seawater 10 times with less than 10% loss of CO₂ capacity over 10 cycles



Task 4. Process synthesis and Techno-economic analysis

- **Subtask 4.1 - Identify process configurations for capture, transport and delivery**
 - Identify an integrated process to capture, transport, and deliver CO₂ using carbonate materials
 - Include details of transport of carbonate materials to algal farms, on-site delivery of CO₂ to algal ponds or bioreactors, and recovery and recycling of the carbonate materials
- **Subtask 4.2 - Refine process configuration and cost model**
 - Estimate the capital and operating costs of the process for several different CO₂ supply scenarios to provide a per ton estimate of the cost of CO₂ supply and profitability of the system
 - GHG emissions will also be estimated and reported
- **Subtask 4.3 - Finalize results of techno-economic and lifecycle assessments**
 - Complete an initial TEA and LCA
 - Compare the results of the TEA and gate-to-gate LCA to an equivalent system that delivers liquefied CO₂

Technical Risks

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Osmotic rupture or mechanical instability of carbonate materials	Moderate	High	Reduce starting concentration of carbonate, use high elasticity polymer, and/or increase polymer thickness.
Poor biocompatibility of materials	Low	High	Determine whether poor biocompatibility is due to direct contact with materials or elution of toxic molecules from cured polymers. In direct contact scenario, CO ₂ can be introduced in marine media and pumped into pond, or coating can be applied to polymers. Toxic molecules can be eluted from polymers prior to introduction to algae.
Difficulty with scale-up, or performance variations at larger-scale	Low	Moderate	We can reach kg scale if necessary by synthesizing smaller batches on the multi-gram scale.

Resource & Management Risks

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Costs exceed budget due to unforeseen experimental challenges or changes in institutional rates	Low	Moderate	Carefully monitor spending and technical progress as part of quarterly progress reporting process.
Workforce scheduling challenges due to conflicting project timelines or unexpected loss of staff	Moderate	Moderate	Discuss timelines and staff availability during regular workgroup meetings; create overlap on critical components of the project
Hiring delays at start of project delay work	Low	Low	Make LLNL management aware of timeline; shift back start date of one or more tasks if necessary.

Schedule, Tasks 1-2

Task	Milestone Description*	Project Duration				Planned Start Date	Planned End Date
		Start : October 1, 2017 End: September 30, 2018					
		Project Year (PY) 1					
		Q1	Q2	Q3	Q4		
1.0	Project Management and Planning					1-Oct-17	30-Sept-18
2.1	Synthesize multigram quantities of carbonate materials	x				1-Oct-17	15-Nov-17
2.2	Measurements of CO ₂ release rates and quantities	x				1-Oct-17	31-Dec-17
2.3	Materials Biocompatibility Evaluation		x			1-Oct-17	30-Jan-18
2.4	Materials Selection for scale-up and TEA		x			1-Feb-18	31-Mar-18

Schedule, Tasks 3-4

Task	Milestone Description*	Project Duration				Planned Start Date	Planned End Date
		Start : October 1, 2017 End: September 30, 2018					
		Project Year (PY) 1					
		Q1	Q2	Q3	Q4		
3.1	Material delivery method determined			x		1-Apr-18	30-Jun-18
3.2	Scaleup materials synthesis to kg scale				x	1-Apr-18	30-Sep-18
3.3	Pilot scale testing				x	1-Apr-18	30-Sep-18
3.4	Measure material capacity during cycling				x	1-Aug-18	30-Sep-18
4.1	Identify Process Configurations for capture, transport, delivery		x			1-Oct-17	30-Mar-18
4.2	Refine Process Configuration and cost model				x	1-Apr-18	30-Aug-18
4.3	Finalize results of technoeconomic and lifecycle assessments				x	30-Aug-18	30-Sep-18

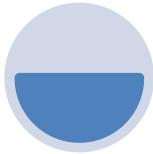
Milestones, Tasks 1-2

ID	Task	Description	Planned Completion Date	Verification Method
a	1	Updated Project Management Plan	December 31, 2017	Project Management Plan file
b	1	Kickoff Meeting	December 31, 2017	Presentation file
c	2.1	Synthesize multigram quantities of carbonate materials	November 15, 2017	Report completion in 1st Quarterly Report to FE
d	2.2	Measurements of CO ₂ release rates and quantities	December 31, 2017	Report completion in 1st Quarterly Report to FE
e	2.3	Materials Compatibility Evaluation	January 30, 2018	Report completion in 2nd Quarterly Report to FE
f	2.4	Materials Selection for Scale-up and TEA	March 31, 2018	Report completion in 3rd Quarterly Report to FE

Milestones, Tasks 3-4

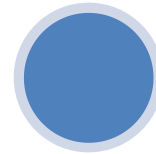
ID	Task	Description	Planned Completion Date	Verification Method
g	3.1	Determine carbonate material delivery method	June 30, 2018	Report completion in Final Report to FE
h	3.2	Scaleup materials synthesis	September 30, 2018	Report completion in Final Report to FE
i	3.3	Pilot scale testing of materials at SNL algal test bed	September 30, 2018	Report completion in Final Report to FE
j	3.4	Carbonate material cycling and capacity measurements	September 30, 2018	Report completion in Final Report to FE
k	4.1	Identify process configurations for capture, transport, delivery	March 1, 2018	Report completion in 3rd Quarterly Report to FE
l	4.2	Refine process and cost model, develop lifecycle assessment model	August 30, 2018	Report completion in Final Report to FE
m	4.3	Finalize technoeconomic and lifecycle assessments	September 30, 2018	Report completion in Final Report to FE

Success Criteria



June 30, 2018
(FY18)

Carbonate materials can support algal growth at laboratory scale.



Sept. 30, 2018
(FY18)

Carbonate materials can be loaded with CO₂ and unloaded in marine media with <10 % loss in capacity over 10 cycles.

Budget- Fiscal Year 1 (FY2018)

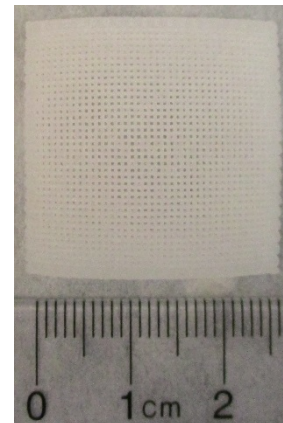
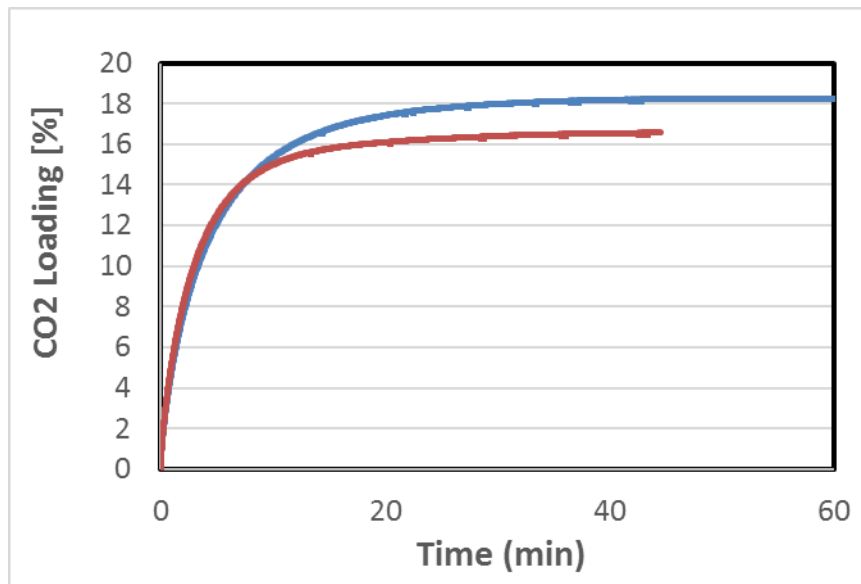
	Government Share
Lawrence Livermore National Laboratory	\$390,000
Sandia National Laboratory	\$360,000
Total	\$750,000

Lawrence Livermore National Laboratory - Fiscal Year 1								
	10/01/2017 - 12/31/2017		1/1/2018 – 3/31/2018		4/1/2018 – 6/30/2018		7/1/2018 – 9/30/2018	
	Q1	Total Project	Q2	Total Project	Q3	Total Project	Q4	Total Project
Federal Share	\$112,500	\$112,500	\$92,500	\$205,000	\$92,500	\$297,500	\$92,500	\$390,000
Total Planned	\$112,500	\$112,500	\$92,500	\$205,500	\$92,500	\$297,500	\$92,500	\$390,000

Sandia National Laboratory - Fiscal Year 1								
	10/01/2017 - 12/31/2017		1/1/2018 – 3/31/2018		4/1/2018 – 6/30/2018		7/1/2018 – 9/30/2018	
	Q1	Total Project	Q2	Total Project	Q3	Total Project	Q4	Total Project
Federal Share	\$90,000	\$90,000	\$90,000	\$180,000	\$90,000	\$270,000	\$90,000	\$360,000
Total Planned	\$90,000	\$90,000	\$90,000	\$180,000	\$90,000	\$270,000	\$90,000	\$360,000

Initial Results

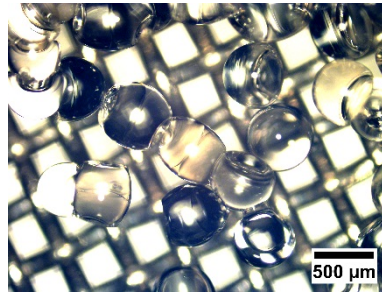
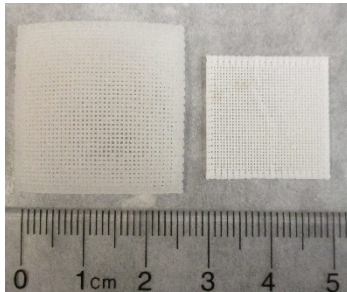
- Soaked polymer-carbonate composite mesh material in ESAW overnight
- Measured pH before and after soaking
- Measured CO₂ absorption capacity following soaking



15-20%
stoichiometric
loading capacity in
DIW printed 30
wt% bicarbonate
meshes

Soaking capsules and mesh in ESAW overnight

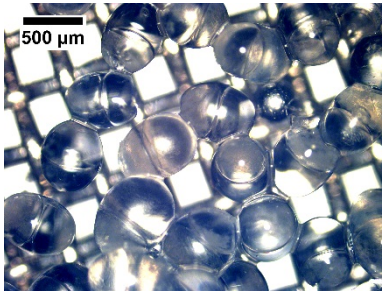
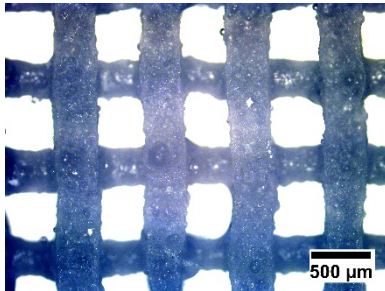
ESAW, left
Dry, right



Capsules
before

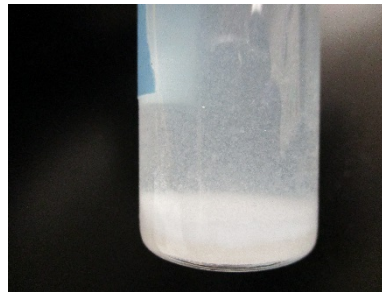
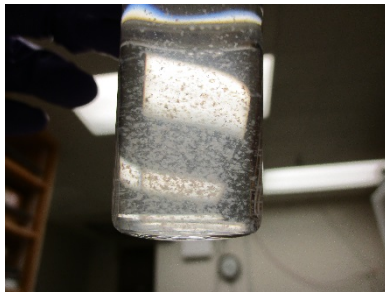
Both
materials
swell in
marine
media

Mesh in
ESAW



Capsules
in ESAW

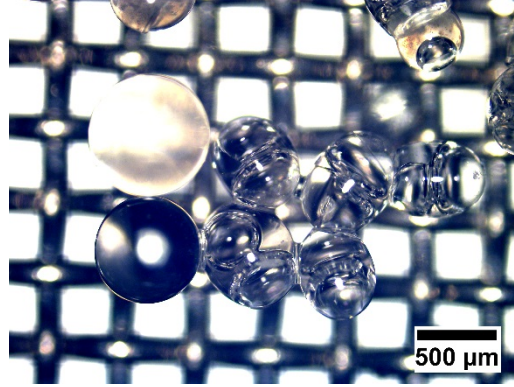
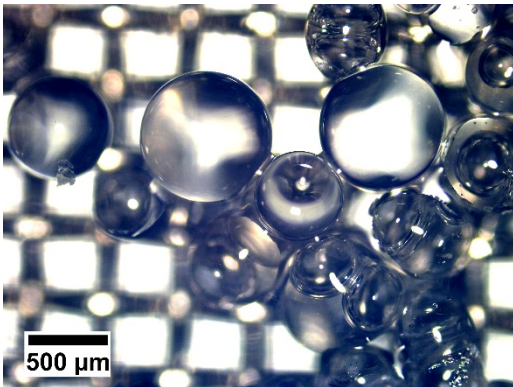
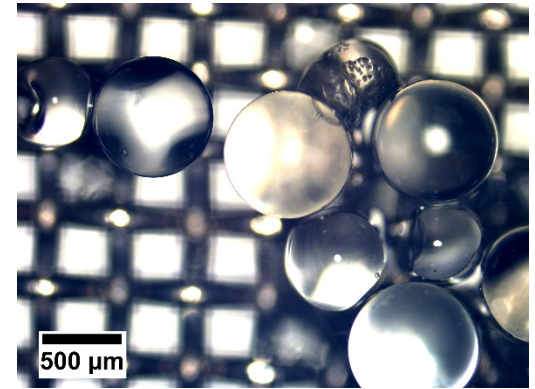
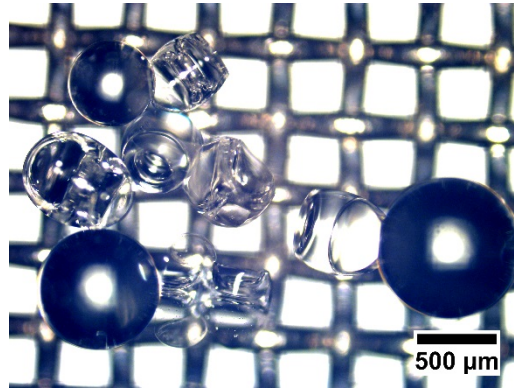
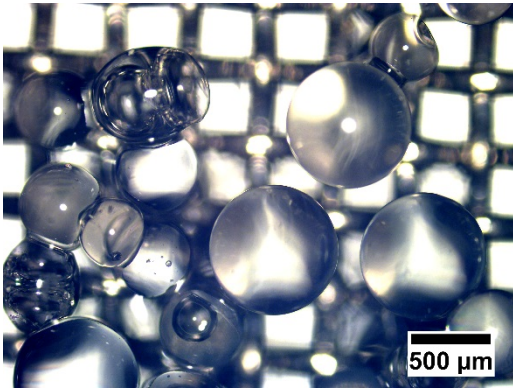
Precipitant in
ESAW
pH increased
from 7.92 to
9.43



Precipitant in
ESAW
pH increased
from 7.92 to
9.44

pH
increased?

Soaking capsules and mesh in ESAW for a week



Single-core swelled
from ~550 μm to ~700
μm
Multi-core didn't swell
at all!

Capsules did NOT burst with osmotic difference!

Next steps

- Improve CO₂ capacity of materials
 - Fresh capsules with single cores
 - Meshes prepare with carbonate instead of bicarbonate
- Identify cause of pH increase
- Cycle CO₂ absorption/desorption with pH measurement
- Biocompatibility of materials
- December 31, 2017: First quarterly report