FINAL REPORT

pH-Neutral Concrete for Attached Microalgae and Enhanced Carbon Dioxide Fixation - Phase I

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Abstract

The novelty/innovation of the proposed work is as follows. Supercritical carbon dioxide (SC-CO_2)-based extrusion and molding technology can be used to produce significantly improved (in terms of strength/unit weight, durability, hardness and chemical resistance) cement-based products. SC-CO_2 can rapidly convert the calcium hydroxide in cured cement to calcium carbonate, which increases the density and unconfined compressive strength in the treated region. In cured concrete, this treated region is typically a several-mm thick layer (generally <-5mm, unless treatment time is excessive). However, we have found that by treating the entire cement matrix with SC-CO_2 as part of the curing process, we can carbonate it rapidly, regardless of the thickness. By "rapidly" we mean simultaneous carbonation/curing in < 5 ks even for large cement forms, compared to typical carbonation times of several days or even years at low pressures. Carbonation changes the pH in the treated region from -13 to -8, almost exactly compatible with seawater. Therefore the leaching rates from these cements is reduced. These cement improvements are directed to the development of strong but thin artificial reefs, to which can be attached microalgae used for the enhanced fixation of CO_2.

It is shown below that attached microalgae, as algal beds or reefs, are more efficient for CO_2 fixation by a factor of 20, compared to the open ocean on an area basis. We have performed preliminary tests of the pH-neutral cements of our invention for attachment of microalgae populations. We have found pH-neutral materials which attach microalgae readily. These include silica-enriched (pozzolanic) cements, blast-furnace slags and fly ash, which are also silica-rich.

We have already developed technology to simultaneously foam, carbonate and cure the cements; this foaming process further increases cement surface areas for microalgae attachment, in some cases to >10 m^2/g internal surface area.

This project involves a team of researchers with backgrounds in cement technology, supercritical fluid technology, materials science, oceanography, and wetland biogeochemistry.

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APPENDICES

E. EXECUTIVE SUMMARY

The contracted Tasks of Phase I, as spelled out in the original contract, have been completed. A summary of each is as follows:

Task 1. The report providing environmental information required for NEPA was prepared and delivered to DOE in July, 1998. It was also included in the Draft Final Report (January 1999).

Task 2. Monitoring of the carbonation (neutralization) reaction for different cement mix compositions, with concomitant simple strength testing of selected samples.

We prepared samples representative of (a) PC ; (b) blast furnace slags; (c) fly ash; (d) PC/slag mixtures; (e) PC/fly ash mixtures; (f) PC/reactive silica (pozzolan) mixtures. Of these, all but (a) could be carbonated to the maximum extent possible in <5 ks.

Task 3. Measurement of the attachment (mass/area) of microalgae to the pH-neutral cements, and the rates of CO_2 fixation by such microalgae.

Cylindrical specimens molded in Task 2 were tested for saltwater algae attachment in long-term tests at the marine test site of LUMCON (Louisiana Universities Marine Consortium) in Cocodrie, Louisiana, in the Gulf of Mexico. Other samples were also tested in fresh water from a local lake. Material-dependent differences in algae colonization rates were observed. Carbonated cements of type (f), (b) and (c) were especially effective in initial algae colonization in saltwater. Carbonated cements of type (f) and (d) were especially effective in initial algae colonization in fresh water. The rates of CO_2 fixation for the final batch of fresh water samples were successfully measured.

Task 4. Based on results from (2)-(3), development of a preliminary technical and economic assessment of the novel technology for enhanced CO_2 fixation.

The high-pressure CO_2 "one step" molding technology can be adapted to the production of artificial reefs. We anticipate the eventual manufacture of hollow reef balls™ , which are approximately hemispherical in shape, -1 m wide x 1-1.2 m in height x 3 cm thick, with a weight of ~450 kg, and an active surface area for bacteria and microalgae growth of -10^4 m^2.

By our calculations we can produce and install a reef ball for ~$260. Each one can remove ~73 kg CO_2/year indefinitely. If we take a reasonable lifetime of 100 years for the reef ball, this cost becomes ~$36/tonne of CO_2 avoided. One way to put this number in perspective is to consider that one proposed carbon tax is $50/tonne of CO_2 produced. If we use the Reef Ball Development Group estimate of a 500 year lifetime this number is reduced to ~$7.20/tonne.

Task 5. Preparation of a report summarizing results of the assessment, and the preparation of a work plan with costs and schedule to further develop the concept in Phase 2.

Draft Final Report - delivered January 14, 1999 (Volume I); Work Plan for Phase II - Volume II, delivered on same date; Costs and Schedules - Volume III, delivered on same date.

F. TECHNICAL REPORT

i. INTRODUCTION

The permanent removal of a portion of the assimilated carbon dioxide in oceans and wetland systems, coupled with the known enhanced rate of photosynthesis associated with algae beds and reef-associated algae in oceas (Birkeland, 1997), and attached algae (Valiela, 1984), offers the potential for artificial reefs designed to promote algae activity. In this manner substantial amounts of CO_2 could be removed from the oceans and subsequently from the atmosphere.

Mann (1982), citing the data of Whittle, showed a comparison of organic carbon and dry matter produced annually by different marine systems (open ocean, upwelling zones, continental shelf, algal beds and reefs, and estuaries excluding marshes). The open ocean accounted for a total net primary production of organic carbon of 18,900 x 10^6 tons/year while algal beds and reefs accounted for a total production of 700 x 10^6 tons/year. It is important to realize that "net primary production" is the portion of CO_2 absorbed by the ocean which is permanently converted to fixed carbon; in other words, it is not recycled. The discrepancy in favor of open ocean is due to the fact that of the ecosystems described, 91.9% of the total area is open ocean, compared to 0.2% for algal beds and reefs. Put on a square meter basis, net primary production by algal beds and reefs exceeded the next most productive ecosystems by a factor of about 1.7, and exceeded open ocean primary production on a square meter (areal) basis by a factor of 20 to 1. The net production of dry matter for open oceans versus algal beds and reefs is 125 and 2,500 g/m^{2}Cyr, respectively.

This advantage for algal beds and reefs is confirmed in other reports. For example, Carter (1988) presents net production (gross production minus respiratory losses of carbon) of 18 ecosystems associated with coastal waters and subtidal, intertidal, and supratidal systems. The greatest productivity was for coral reefs (1,700-2,500 g of fixed carbon/ m^{2}Cyear) with the next highest values (700-1,300) shown for salt marshes, and a range of 5-50 given for typical ocean waters. In summary, the demonstrated much greater net primary productivity of reef-attached algae compared to other ecosystems, and given that more of this productivity will be "permanently" stored in ocean sediments rather than being remineralized to carbon dioxide, suggest tremendous potential for engineered reef structures to enhance CO_2 removal.

In a typical forest ecosystem, and, in natural and agricultural upland ecosystems, CO_2 removal by photosynthesis is generally balanced by CO_2 released through the utilization of agricultural crops, and by the bacterial decay of residual organic matter returned to upland soils. These decay process produce CO_2 as a by-product. Though these processes are slower than combustion, the fact is that the organic matter content of most upland soils changes little over time, indicating a near equilibrium between accumulation of carbon in residual organic matter and its oxidation and conversion to CO_2.

Primary productivity in wetlands, and especially in ocean environments, offers great potential for the long-term removal of CO_2 as organic matter which accumulates in wetland environments. This organic matter is gradually buried by sedimentation processes. The rate of organic matter decomposition is very slow in wetland soils and sediments relative to upland soils, and moreover natural accretion processes result in burial of substantial amounts of organic matter that is thereby removed from the mineralization-photosynthesis cycle that predominates in upland environments. Thus primary productivity in oceans and many coastal and estuarine locals tends to permanently remove the carbon from the cycle as long-term buried organic matter.

It is true that there is a lot of cycling of carbon in ocean environments between mineral (CO_2) and organic forms. Aquatic plants and algae cells producing organic matter by photosynthesis do serve as an energy or food source for animal populations, where much of the carbon is again released to carbon dioxide. However, the portion of residual organic matter (e.g., plant and animal detritus and fecal droppings) that falls to the bottom of water columns and becomes associated with anaerobic sediments tends to permanently accumulate in the bottom sediments. This residual organic matter is gradually being buried by further deposition of sediments and settling organic detritus.

Thus, enhancing photosynthesis in coastal and especially ocean environments offers more potential for permanent CO_2 removal from the atmosphere, both in terms of greater long-term removal rates and in terms of the essentially permanent storage of organic matter derived from carbon dioxide fixation by photosynthesis. Engineered systems to enhance photosynthesis by algae in ocean environments therefore look attractive in terms of lowering atmospheric CO_2 levels.

pH-Neutral Concrete for Artificial Reefs

Given the potential benefits of attached algae, it is reasonable to ask if the task can be accomplished at low cost. Concrete is an ideal solid support, which can be prepared in shapes very similar to existing reefs. Our industrial partner on this project, Reef Ball Development Group Ltd., has already installed 40,000 reef balls in 250 projects worldwide (see available designs at www.reefball.org website). Concrete is also very inexpensive with costs <5 cents/lb. The problem with concrete - whether prepared using portland cement (PC), fly ash, or cement slag - is that the high pH (- 13) of its cementitious component is simply too basic to serve as an artificial reef. Concrete generally needs to age in the ocean for 3-6 months before the pH in the surface region approaches the -8.3 pH of seawater. A major problem is that during this aging process organisms which are more pH resistant (e.g. barnacles) will attach to the concrete and prevent the settlement of other marine life.

We have developed a low-cost process to prepare pH-neutral concrete using any common cement raw material. This process is fully described in a patent application which preceded this project (Knopf and Dooley, 1998). Here wet (uncured) cement or concrete is exposed to high-pressure (usually supercritical or near-critical) CO_2 during a molding process. The CO_2 rapidly reacts with the calcium hydroxide and other calcium-bearing phases, and similar Mg-containing materials in cements to produce Ca(CO_3) and some Mg(CO_3). The final product is both strengthened (compared to untreated cement) and neutralized. Therefore this broad class of new materials represents an ideal candidate for further development as artificial reef materials. Although CO_2 is trapped in the concrete (as carbonates), and this itself means sequestration of some CO_2, we believe the real key to our proposal lies in the continuous sequestration made possible by the algae which will attach to the artificial reef.

It is important to recognize that such pH-neutral concretes can be prepared from a wide range of starting materials - from Portland cement (PC) which is mostly Ca-Si based to fly ash which is more Si-Al based (only -5-10% CaO and MgO) to blast furnace slag (BFS) which is more similar to PC but with a high MgO content. Particular cement compositions have proven more amenable to the attachment of microalgae (Task 3, below). There are no problems associated with using BFS or fly ash in concrete marine applications (Buck et al., 1984). A low-sodium content PC should be used, but this is simply the Type I PC sold throughout the U.S.

It is also important to recognize that almost all past carbonation studies (both high and low pressure) were done on <u>completely cured</u> cement samples. Regardless of the CO_2 pressure or the means of contact only surface carbonation will result unless excessive contacting times are employed. We later discovered that treating cement with CO_2 while it is still uncured or wet allows complete and efficient carbonation of the entire cement matrix. In addition, because somewhat high pressures are involved (~1000-2000 psi) it is possible to conveniently carbonate during a cement molding process, a one-step operation.

ii. PHASE I TASKS RESULTS AND DISCUSSION

<u>Task 1.</u> We prepared a report providing environmental information required for NEPA. It was delivered to Mr. Perry Bergman of DOE-FETC in July 1998, and approved. A copy of the report was also attached to the Draft Final Report (January 1999).

<u>Task 2.</u>

In our initial "one-step" experiments, cements were placed in a simple cylindrical mold operated by a piston (Figure 1). CO_2 (at -900 psi) was introduced below the piston. This pressure could be increased if desired by compression with a diaphragm compressor. The pressure above the piston was rapidly increased using water as a driver fluid. As the piston moved rapidly toward the concrete, the gas pressure above the concrete rose to equalize. Simultaneously the CO_2 reacted with the cement tending to moderate the pressure rise. Typically a 2000 psi water pressure was applied to the piston. This prototype unit allowed us to study various modes of CO_2 addition, without the complexities inherent in mold filling under pressure with cement. Further, it allowed easy control of the amount of CO_2 added to the cement matrix simply by adjusting the initial height of the piston (using spacers) above the cement. The molded cylindrical disks were 39 mm diameter and ~13 mm height in not foamed. We controlled the foaming with the piston to increase the the height by ~50%. Further details on molding procedures can be found in Appendix B.

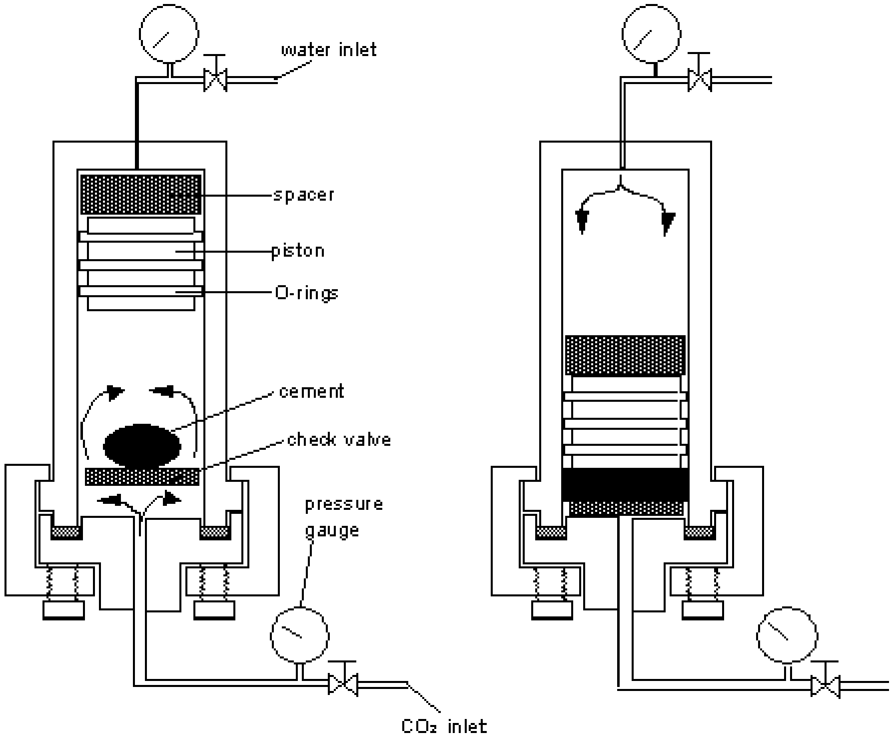

Figure 1. Molding unit for cement disks. Left - CO_2 fill cycle; right - compression by piston.

We monitored the carbonation (neutralization) reaction for different cement mix compositions. We prepared samples representative of: (a) Portland cement (PC) ; (b) blast furnace slag (BFS); (c) Class C fly ash (FAC); (d) PC/slag mixtures; (e) PC/fly ash mixtures; (f) PC/reactive silica (pozzolan) mixtures. The PC was Type I, roughly 60-65% CaO, 20% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and several other components. The fly ash was Class C (FAC), from the Gifford-Hill power plant in Cason, Texas. Its calcium oxide content is >5%, but with SiO_2, Al_2O_3 and Fe_2O_3 as principal components (sum -50-70%). The cement slag was granulated BFS (Lone Star Aucem, Blaine fineness -5900 cm^2/g), roughly 28-38% SiO_2, 8-18% Al_2O_3, 35-45% CaO, and up to 16% MgO

(Czernin, 1980). Reactive silicas include aqueous sols, silica flour, fine quartz sand and fumed silica. The first of these is the most important, because some types are available as waste products. We used sodium metasilicate solution as a sol (~10 wt% silicate in the mix on a dry basis). Mix %'s as high as are 30% silica/70% PC are sometimes used.

Cements (b)-(e) were prepared by alkali activation of BFS or fly ash; this was the subject of a recent patent from LSU (Roy et al., 1996). These compounds react with high-pH solutions (e.g. NaOH) to form a cementitious mass. The rate of reaction and the reaction product are controlled by the strength of the activating solution. For example, at a pH of 14.7, and a solution/solids ratio of 0.4, a high calcium fly ash will react to form a high strength cement within ten min. Reactions with BFS can be similarly rapid. Cement (f) with reactive silica can be hardened and carbonated in <7 ks, and does not require an alkaline activating agent.

Molding Tests of Foaming Methods

Based on analysis of the patent literature for foamed cements, we tested 5 different surfactant mixtures for foaming/molding on PC, PC/silica samples, fly ash, PC/fly ash, BFS, and PC/BFS samples. Details of the molding procedure are in Appendix A. The surfactant mixtures denoted "D" (based on a commercial ethoxyated alcohol and ether) and "E" (based on a mixture of commercial nonionic, cationic and anionic surfactants) were determined most suitable for carbonated cements. Their compositions are as follows.

Surfactant Mixture D (nonionic) --

2 parts Igepal CA-210, 0.5 parts polyoxyethylene-3, methyl ether

Surfactant Mixture E (cationic/nonionic/anionic) --

1 part Aliquat 336, 1 part Igepal CA-210, 10 parts 10% sodium lauryl sulfate solution

The foamed sample recipes and some details on the quality of the resulting materials are given in Appendix C. Carbonation results from characterization tests are given below.

All samples, whether foamed or not, were tested for pH reduction by carbonation. The tests we have found most useful in this regard are a thermogravimetric analysis (TGA) method for $Ca(CO_3)$, quantitative X-ray diffraction (XRD), and an aqueous contact pH measurement using an aqueous bromothymol (BTB) solution. Details of test procedures can be found in Appendix B. In all cases the introduction of SC-CO_2 cuts curing times; in some cases cement disks hardened in <4 ks. Carbonation of the cement also lowers cement surface pH to at least 8 and in some cases to 7.

Pictures of typical disk samples are shown in Figure 2 below. The picture on the right is taken after an algae attachment test.

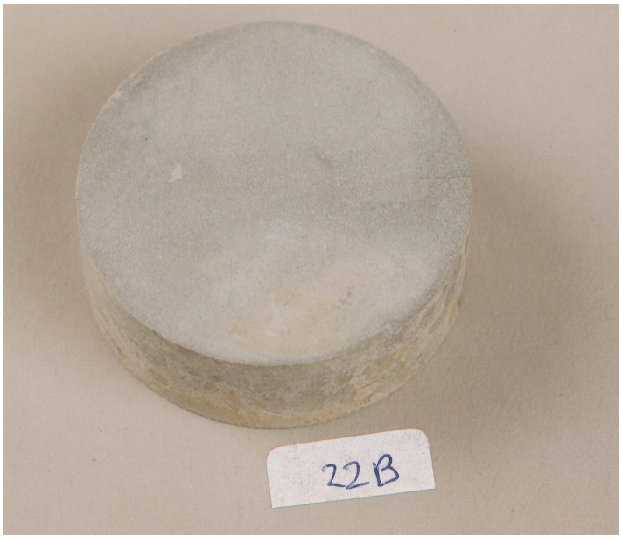

Figure 2A - Carbonated PC/silica, after molding.

Figure 2B - PC/silica, with algae.

(1) Thermogravimetric analysis (TGA) for $Ca(CO_3)$ content, and Contact pH Measurement.

The TGA method used here is standard for $Ca(CO_3)$ but cannot measure $Mg(CO_3)$ (Maycock and Skalny, 1974; Bukowski and Berger, 1979; Ramachandran, 1979; Taylor et al., 1985a; Suzuki et al., 1985). Therefore the actual carbonate content could be slightly higher, but not by more than a factor of 1.05. On all TGA's, if replicates showed >10 % relative error they were run again until duplicates were within the 10% limit. We only had to do this once, so we are confident the TGA method gives a good representation of $CaCO_3$ content. In the Tables below, "core" samples were taken from dead center of the disks, cut in half.

TABLE 1 - TGA Data for Non-Foamed Cement Samples

SAMPLE	wt% hydrate	wt% $Ca(OH)_2$	wt% $CaCO_3$
22B*, Core (PC/silica)	1.8	9.1	2.1
22B*, Surface	1.1	3.7	9.9
22B**, Core	1.6	13.4	1.5
22B**, Surface	1.5	9.9	1.9
22A, Core	2.2	10.6	1.5
22A, Surface	2.1	11.3	1.5
19B, Core (BFS)	0.9	4.2	1.8
19B, Surface	0.8	3.4	2.9
19A, Core	1.3	7.8	0.5
19A, Surface	0.8	6.1	0.6
42B***, Core (PC/silica)	2.0	12.6	1.4
42B***, Surface	1.8	5.1	8.4
24B, Core (PC)	1.1	5.8	6.7
24B, Surface	1.1	6.3	8.6
2A (fly ash)	2.8	9.6	6.5
2B (fly ash)	1.6	3.3	14

*2 h molding time; **0.67 h molding time
***Same recipe as 22B, except 42B molded with 1500 psi CO_2.
A=air set; B=CO_2 set, ~900 psi feed pressure.

Examining Table 1 it is clear that PC itself can be extensively carbonated (7-10 wt% $CaCO_3$) even at ~900 psi CO_2 feed pressure. The PC/silica mixture, from ~8 wt% sodium metasilicate in the mix, could be extensively carbonated only at the surface (surface pH ~8-9). Fly ash can be even better carbonated at these conditions. The BFS surface pH of 10 agrees with the poor carbonation results in Table 1.

For foamed samples, all data reported here were taken using the “D” foamer recipe; the surfactant solutions themselves constituted <1 wt% of the mix. Complete details are in Appendix C. TGA results are in Table 2 below.

TABLE 2 - TGA Data for Foamed Cement Samples

	wt% hydrate	wt% $Ca(OH)_2$	wt% $CaCO_3$
63B*, Core (PC/silica)	1.8	3.1	8.9
63B, Surface	0.7	3.7	16.5
63A, Core	2.0	10.5	2.9
63A, Surface	2.0	4.7	8.8
74B, Core (PC/silica)	0.5	6.0	21.4
74B, Surface	0.5	6.5	22.6
83C, Core (PC/silica)	2.1	8.1	7.5
83C, Surface	2.0	3.3	17.6
83D, Core	1.8	3.6	10.4
83D, Surface	0.5	5.0	20.0
83E, Core	1.1	2.4	13.5
83E, Surface	0.5	4.4	17.0
87A, Core (PC/silica)	0.20	10.2	8.0
87A, Surface	0.20	8.1	6.6
87B, Core	0.33	2.8	16.1
87B, Surface	0.73	9.4	15.1
87D, Core	0.33	8.1	6.7
87D, Surface	0.55	4.6	6.3
77B, Core (PC/BFS)	0.7	3.7	10.9
77B, Surface	0.9	3.3	18.4
88B, Core (PC/BFS)	0.17	7.7	5.9
88B, Surface	0.21	7.1	7.5
64B, Core (fly ash)	2.1	5.5	12.8
64B, Surface	1.7	5.5	12.5

64A, Core	2.3	3.8	2.0
64A, Surface	0.8	0.9	9.0

63B and 63A have w/c=0.55, 64B, etc. have w/c=0.45
A=air set; B=CO_2 set, feed pressure ~900psi.
C=feed pressure 1500psi CO_2
D=feed pressure 2000psi CO_2
E=feed pressure 2500psi CO_2

Molding 63B, which is a foamed PC/silica with the same recipe as 22B (non-foamed), at 1 h air set followed by 2.5 h CO_2 mold time at 900 psi, almost doubled the carbonate content. Time to cure was shorter than the 3.5 h which will be subsequently shown. However, the pH test showed that a core pH>8, so more carbonation was possible.

This problem was solved by using a lower water to cement (w/c) ratio and higher CO_2 feed pressures. Therefore recipe 83 is almost the same as 22 and 63 except for a w/c = 0.45; the mold time could be reduced to 1 h at the higher pressure of 1500 psi, and the carbonate content was unchanged (Table 2). Even higher pressures showed few differences, except the core CO_2 content did increase somewhat. Recipe 87 is the same as 83 except it was allowed to set to a paste in air first. There is a further increase in average carbonate content, and in uniformity of carbonate content. Recipe 74 is the same but set in air for 1 h, then molded for 2.5 h in CO_2. 74B's $CaCO_3$ wt% of 22.6 and core $CaCO_3$ wt% of 21.4, and a core pH~8, proves that the lower w/c ratio allows for complete carbonation. The air setting time (to form the paste) is only ~10 min.

Next we foamed PC/BFS and PC/FAC mixtures. We determined that a 50% BFS-PC mixture (recipe 77) will harden in 1 h with an alkaline/surfactant activating solution of 0.55N NaOH, and is extensively carbonated (Table 1) to core pH~7. However, 77B tended to crack. Cracks become fewer with a decrease in BFS content but mold time takes longer. We can remedy the time factor by using an activating solution of higher normality. In contrast to PC/silica mixtures, PC/BFS was adversely affected by allowing it time to set to a paste (sample 88), probably because curing time is fast and the paste became too hard before it was loaded into the mold.

Fly ash-PC foamed mixtures (recipe 80) with the 0.55N NaOH alkaline/surfactant activating solution take at least 1.5 h to be hard enough to remove from the mold. To harden in 1 h or less, a concentration of at least 1.0N NaOH surfactant would have to be used.

64B is pure fly ash with 5.0N NaOH alkaline/surfactant activating solution with a w/c=0.4. We used a 1 h mold time, but it hardens in only 20 min. The numbers in Table 2 indicate essentially complete carbonation for a fly ash, as does the core pH~7.

In conclusion, foamed samples almost always show increases in extent of carbonation (vs. non-foamed samples), as much as doubling $Ca(CO_3)$ wt%. Going to higher CO_2 feed pressures sometimes further increased the extent of carbonation and decreased mold time for silica- and BFS-

PC mixtures to ~ 1 h.

(2) X-ray Diffraction (XRD) Analysis

XRD results tracked those from the TGA tests well. For example, the surface and core samples for 63B (foamed PC/silica) exhibited no $Ca(OH)_2$ peaks in the core or surface sample. For its non-foamed counterpart (22B), the core sample exhibited a significant $Ca(OH)_2$ peak, but not the surface sample. This agrees with the TGA data showing extensive carbonation at the surface, but not core, of the non-foamed 22B.

For carbonated PC's, enhanced crystallization of calcite was noticeable in all samples to varying extents. The small decreases or even increases in absolute portlandite peak areas sometimes observed in XRD, coupled with large increases in calcite areas, suggest that high-pressure carbonation accelerated the cure of these materials (portlandite is formed upon curing in PC); this is in agreement with previous work (Young et al., 1974; Klemm and Berger, 1972; Simatupang and Habighorst, 1993). The results for fly ash are more dramatic, with extensive calcite formation observed for the molded and carbonated specimens.

(3) Internal Surface Area and Porosity Measurements

The bulk density was measured by simply filling a known volume and weighing. The porosity (void fraction) and particle density were estimated by water displacement (Archimedes' principle). Surface areas were measured by N_2 adsorption at the saturation temperature of liquid N_2 (the BET method). The numbers in the tables below are averages of two independent determinations which agreed to within 10%. Further details of these experiments are in Appendix B.

The data for the non-foamed samples in Table 3 below clearly show porosity (void volume/total volume) reductions upon carbonation. This is in agreement with data from the literature on cement carbonation, and indicates that leaching rates from such samples would be low. The bulk density of the carbonated materials should increase; carbonates are in general more dense than hydroxides. We see that these expectations are completely borne out in Table 3.

The approximation of the void fractions reported in Table 3 to the true void fraction is probably very good for the air-set samples, which absorb water readily and are known to have void fractions in the rang e of 0.2-0.3 for PC and BFS (Taylor et al., 1985a,b; Papadakis et al., 1989). For the carbonated samples the diffusion of water is slower by as much as an order of magnitude; for this reason the samples were hydrated for 1 day.

The nature of the pores of the molded samples was also determined indirectly by measuring the surface areas by N_2 adsorption; at a fixed composition, higher surface areas are often associated with void-filling and therefore decreased total pore volumes, when small pores are created from larger pores in a deposition process. The amount of N_2 adsorbed includes contributions from capillary condensation in small pores. However, as voids are completely filled or sealed off, surface areas decrease significantly. Thus an increase in surface area upon carbonation suggests a small reduction in voidage and an increase in the number of small pores, while a decrease in surface area suggests almost complete closure or sealing off of the pores in a specimen. The samples with reactive silica (e.g., 19B, 22B) lost little or even gained surface area. These results suggest that it is possible to use carbonation to fill large voids or cracks in cements without simultaneously filling all small pores, and that fine pores are present at the surface.

TABLE 3 - Surface Area (m^2/g) and Porosity Data for Non-Foamed Cement Samples

SAMPLE	19A(BFS)	19B	22B* (PC/silica)	22B**	22A	42B*** (PC/silica)
"Core" Surface Area	1.6	7.0	4.8	4.4	6.4	5.5
"Surface" Surface Area	2.2	7.2	10.3	3.6	4.2	3.6
Porosity (void fraction)	0.07	0.04	0.039	0.13	0.13	0.02
Bulk Density, g/cm^3	1.96	2.00	2.10		1.73	
SAMPLE	2A (fly ash)	2B	3A (PC)	3B	24A (PC)	
"Core" Surface Area	8.5	5.4	6.0	5.1		
"Surface" Surface Area						
Porosity (void fraction)	0.085	0.065		0.27	0.28	
Bulk Density, g/cm^3	1.87	1.94		1.81	1.48	

* 22B with 2 h molding time.
** 22B with 0.67 h molding time.
*** 42B same recipe as 22B but molded with 1500 psi CO_2.
A=air dried
B=CO_2 vapor pressure approximately 900psi.

TABLE 4 - Surface Area (m^2/g) and Porosity Data for Foamed Cement Samples

SAMPLE	64B (fly ash)	64A	72B (fly ash)	72A	73B (fly ash)	73A
“Core” Surface Area	13.3					
“Surface” Surface Area	8.4					
Porosity (void fraction)	0.26	0.35	0.25	0.25	0.42	0.39
Bulk ?, g/cm^3	1.37	1.26	1.33	1.33	1.30	1.25
SAMPLE	74B (PC/silica)	83C (PC/silica)	83D	83E	63B (PC/silica)	63A
“Core” Surface Area	4.7				13.1	4.0
“Surface” Surface Area	7.5				21.0	2.9
Porosity	0.27	0.29	0.30	0.29	0.28	0.32
Bulk ?, g/cm^3	1.40	1.37	1.43	1.39	1.38	1.28
SAMPLE	84C (PC/silica)	84D	77B (PC/BFS)	75B (PC/BFS)	75A (PC/BFS)	80B (PC/FAC)
“Core” Surface Area			6.0			
“Surface” Surface Area			6.2			
Porosity	0.26	0.22	0.40	0.24	0.36	0.34
Bulk ?, g/cm^3	1.49	1.40	1.37	1.52	1.33	1.39
SAMPLE	87B (PC/silica)	87A	88B (PC/BFS)			
Porosity	0.046	0.072	0.12			
Bulk ?, g/cm^3	1.99	1.76	2.06			

63B - w/c = 0.55; 64B, etc. - w/c = 0.45
A=air set; B=CO_2 set, feed pressure ~900psi.
C=feed pressure 1500psi CO_2
D=feed pressure 2000psi CO_2
E=feed pressure 2500psi CO_2

Comparing Tables 3 and 4, it is easy to see that both surface areas and porosities (void fractions) are usually increased by foaming, so both small and large pores are formed. This suggests more area for possible microalgae attachment. There is a compromise here; if leaching rates in seawater for these samples are high, non-foamed samples would be preferred. If not, foamed samples would definitely be preferable.

As was the case for non-foamed samples, the porosities (void fractions) generally decreased and the densities generally increased when going from air-set ("A") to carbonated ("B", "C", etc.) samples. This was expected because carbonates are in general denser than oxides. As the CO_2 feed pressure was increased, the same phenomenon was not always observed (samples 83 and 84), because as seen previously this step did not always increase the carbonate content.

(4) Cement Strengths

The earliest saltwater Organic Matter Attachment tests (Months 3-4) indicated that PC/silica, PC/BFS, fly ash and BFS cement materials were suitable for rapid microalgae colonization. Therefore replicates (3) of these materials, both carbonated and non-carbonated, were molded in month 6 in order to conduct tests of compressive strength. The recipes (2, 19, 22, 87, 88) are given in Appendix C.

We measured the 7-day unconfined compressive strength of these select samples by a relevant ASTM test (ASTM, 1986). The repeated load test facility was that of the Louisiana Transportation Research Center, and is therefore re-calibrated on a prescribed schedule. The test dies were machined in our shop. The results are given in the graph below (Figure 3).

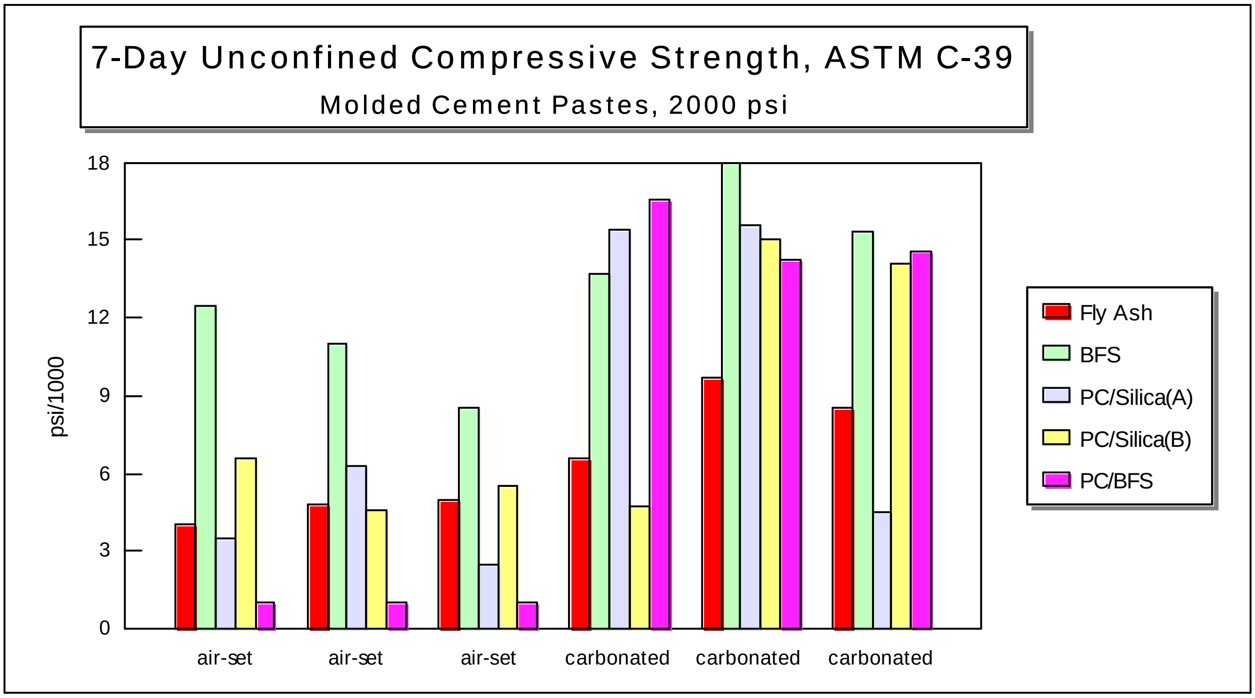

Figure 3 - Comparison of Strengths, Air-Set vs. Carbonated Samples

Based on previous work we anticipated no drastic reductions in flexural or compressive strength for non-foamed samples; in fact, carbonation usually increases compressive and flexural strengths of concretes (Young et al., 1974; Bukowski and Berger, 1979; Simatupang and Habighorst, 1993). This proved to be the case here also. For all recipes the strengths of the carbonated samples exceeded those of non-carbonated samples, sometimes by a large margin. In fact, the PC/BFS samples (88) did not even harden in the mold unless they were carbonated. This result might be important in construction of reefs for shallow waters which can withstand large waves. The inability to harden 88A in the mold in 2 h is not a problem. All this proves is that carbonated samples are cured faster so molding times can sometimes be shortened significantly. This is a positive result.

However, highly foamed samples are not nearly as strong as non-foamed samples. Of the highly foamed samples, the PC/silicas (63, 74, and 83) are the hardest. Sample 77 (foamed PC/BFS) is just as hard, but it can form cracks during molding. Using less BFS in the PC/BFS mixtures decreases cracking, but it increases mold times.

The variability in the ASTM compressive strength testing for the PC/silicas and the BFS samples was high, although the trend was clear. This suggests that some of these samples developed cracks during molding or demolding. In all cases at least 2 of the 3 samples showed similar strength. More careful initial mixing and demolding procedures can be followed in the future to try to prevent crack formation.

Task 3. Measurement of the attachment (mass/area) of microalgae to the pH-neutral cements, and the rates of CO_2 fixation by such microalgae.

We have measured the attachment (mass/area) of organic matter to both uncarbonated and pH-neutral cements. Test procedures are given in Appendix B. The test was designed to eliminate contributions from attached sediment, but there was some contribution from the organic matter in barnacles, especially for uncarbonated samples. This is discussed in more detail below. Cylindrical specimens molded in Task 2 were tested for saltwater algae attachment in long-term (it takes at least 28 days to run an entire attachment test including the attachment phase and the analytical phase) tests at the marine test site of LUMCON (Louisiana Universities Marine Consortium) in Cocodrie, Louisiana, in the Gulf of Mexico. Other samples were also tested in fresh water from a local lake (University Lake), added to an aquarium. Material-dependent differences in algae colonization rates were observed. PC/silica was generally the most effective in initial colonization (~0.009 mg/cm^{2}Cday for saltwater algae attachment). CO_2 utilization rates were also measured in the last 2 months of this project, on freshwater samples.

Saltwater Algae Attachment

For all samples of the same type, the relative precision was 30 wt%, and in most cases within 10%. Such differences can be attributed to the depth difference in the water, with an increase in depth also increasing algae attachment.

The second and third saltwater runs (each run consisting of a batch of several sample disks) were the most successful. Disks of the same type were located at different depths, to 30 inches, and the results averaged. We have have not included data from the 4th and 5th batches because there was so much mud on them data have no meaning. There was a minimum of one Gulf hurricane in all runs after Run 2, which caused many problems, including severe weather variations, inconsistent tides which stirred up mud in the basin, more than normal boat traffic seeking shelter from hurricanes (which stirred up more mud), etc. We removed as much as possible with water rinsing, but could not get all of it and in doing so removed some algae. The results from run 3 generally agreed with run 2; sample 42B (PC/silica) performed best. Test conditions for these runs are shown below.

Top level=4-22 inches
Middle level=8-26 inches
Bottom level= 9-27 inches

Run 2, Sept. 4-18, 1998
On Sept. 4, 1998, pH=7.8; Salinity=8000 ppm; O_2=5.2mg/l

Run 3, Sept. 18-Oct. 7, 1998
On Oct. 7, 1998, pH=7.8; Salinity=13000 ppm; O_2=5.4mg/l

Runs 1 & 2 both had good weather, with run 2 having sunshine almost every day all day. Unfortunately for Run 1 the sample holders were poor and we lost the samples. These were replaced with polypropylene vise clamps which preformed well in all subsequent tests. Saltwater tests were then suspended due to the onset of winter weather. Foamed samples had to be tested using freshwater only, because it was the only water readily available for laboratory studies using artificial sunlight (fluorescent lamps).

Data Run 2 - See Figure 4 Below

The PC/silica (22B, 42B) and fly ash cements (2A, 2B) did considerably better than BFS (19A, B) in this run. 42B, molded at 1500 psi CO_2 pressure, seems to have done slightly better as would be expected from its greater extent of carbonation. 42B's average collection of organic matter is 0.87mg/(cm^2 day), the highest average in this run. 24B (PC) collected less than half of this amount; the BFS was even worse.

The result for 19A4 (non-carbonated BFS) may seem puzzling, but the extra weight here was contributed by many barnacles on the surface, which was true of the non-carbonated samples. This is discussed in more detail below. Initial visual observation revealed that 19A4 had very little algae on it, just like 19B5 and 19B6.

Level is also an important factor in algae attachment. The lower into the water our samples were, the more algae attachment, with only a couple of exceptions. For example, 42B1 collected 0.78 mg/(cm^{2}Cday) being 4-22 inches under water (depending on tide). 42B2 collected 0.96 mg/(cm^2 day) being 8-26 inches under water (depending on tide). Therefore there is an improvement in algae attachment from a small increase in depth (4-8 inches). This increase in algae growth with depth agrees with the literature. However, such an increase only applies to the photic zone; at greater depths, significant decreases take place.

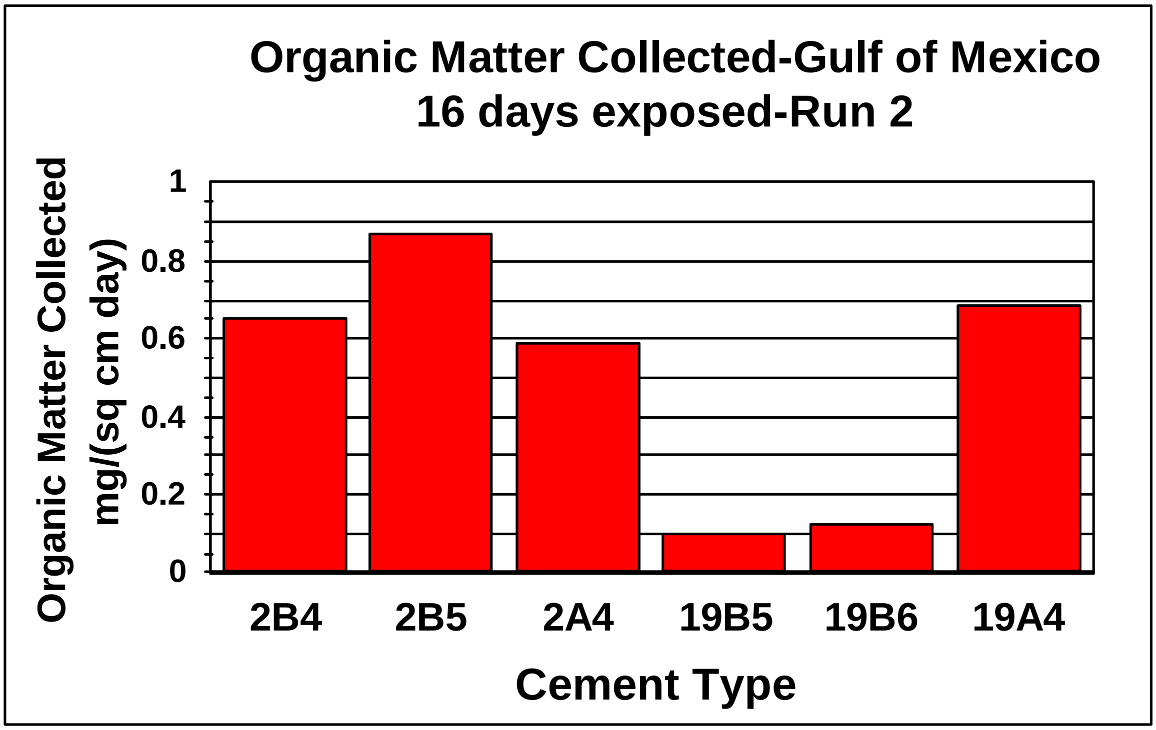

Figure 4A

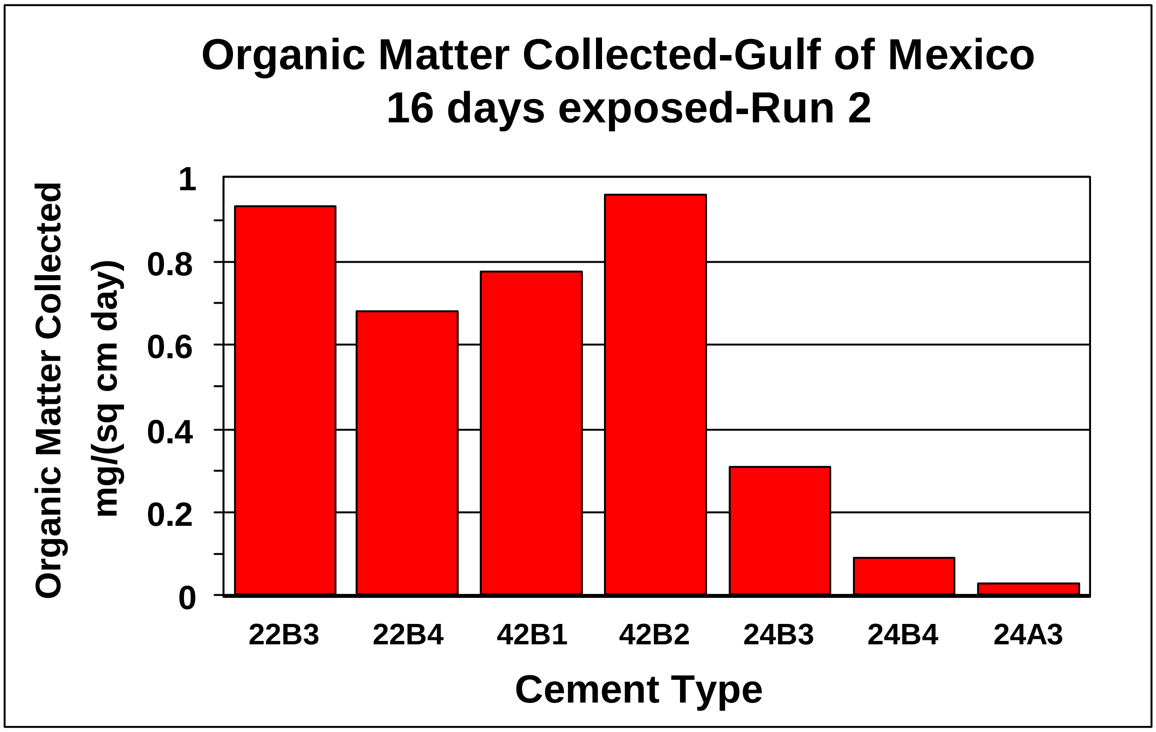

Figure 4B

Data Run 3 - See Figure 5 Below

For the most part Run 3 repeated the results of Run 2. 42B’s algae attachment improved from 0.62 mg/(cm^{2}Cday) to 1.3 mg/(cm^{2}Cday) with an increase in depth of 4-6 inches. 19B’s (BFS) algae attachment rates also increased from 0.40 mg/(cm^2 day) to 0.63 mg/(cm^2 day) with an increase in depth of 4-6 inches. However, 2B’s (fly ash) algae attachment did not increase with increasing depth - this was the only anomalous depth result observed.

Comparing 2A to 2B at the same level there is good indication that carbonation increases algae attachment. Comparing 22B to 22A at the same level also shows that carbonation increases algae attachment. For Run 3 on the whole the PC/silicas again did best followed by BFS followed by the fly ash.

The results for the non-carbonated samples are again skewed in that a large portion of their total organic matter was from inside barnacles rather than as algae. A wet oxidation /oven organic matter attachment test such as that used here cannot eliminate this contribution. The barnacles are attracted by the high surface pH of the non-carbonated samples. From visual observation, the non-carbonated sample surfaces were at a minimum 50% covered by barnacles, some as large as 3/4". The carbonated samples had a maximum of 10% barnacle coverage, with much smaller barnacles. Therefore even a few barnacles significantly reduce actual microalgae colony counts on the small sample disks. We can estimate the oxidizable mass of barnacles by visual observation of barnacle size; on non-carbonated surfaces barnacles this would account for at least 50% of the mass determined from the test. When this is considered, the great advantage of carbonation in initial colonization is clear. A picture of barnacles removed is shown below, Fig. 6.

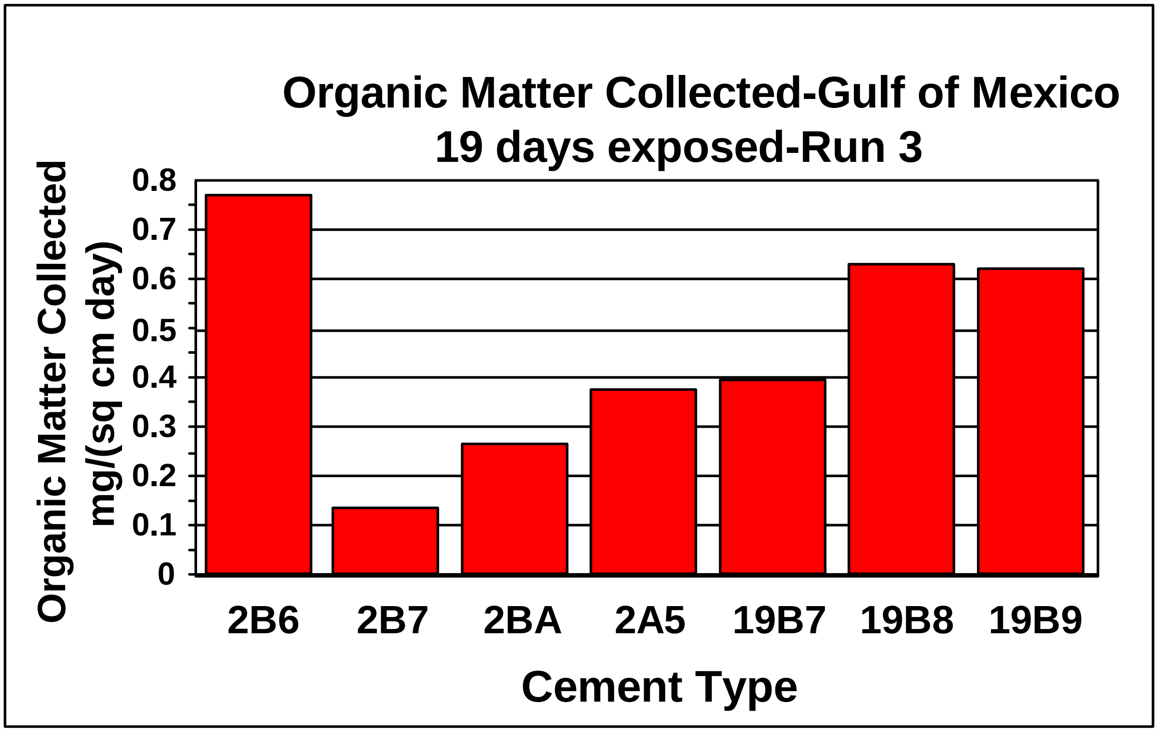

Figure 5A

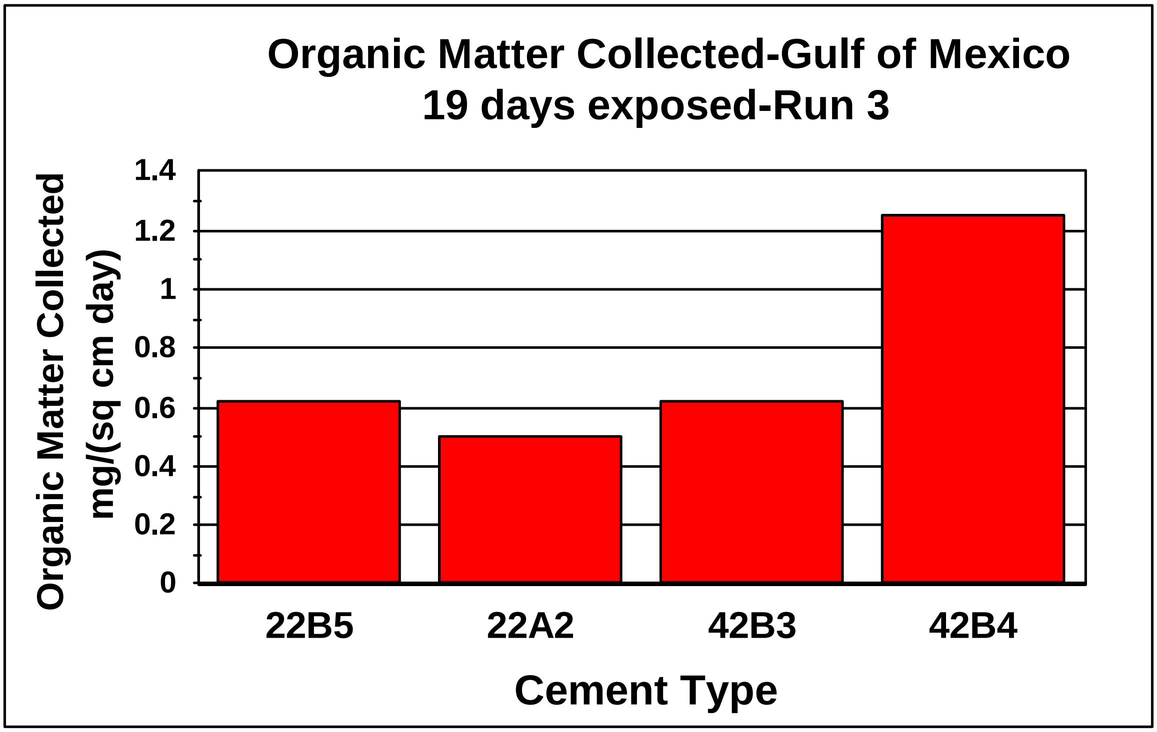

Figure 5B

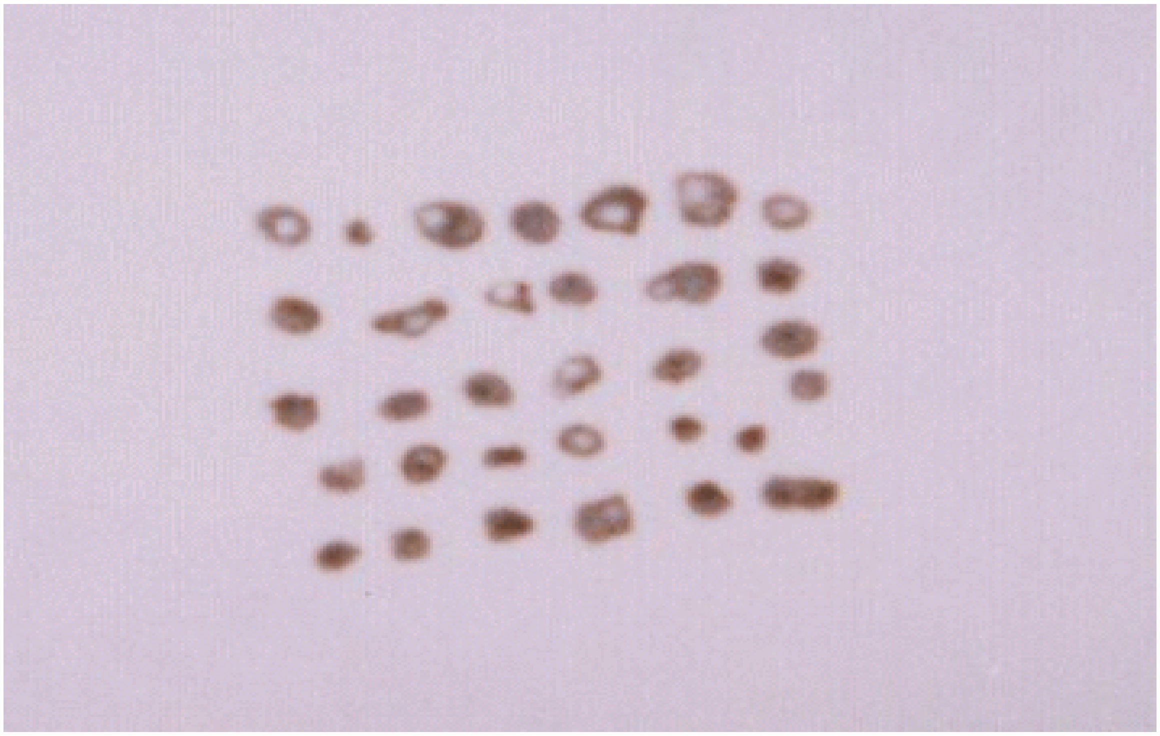

Figure 6 - Barnacles, ~1.5 x actual size

We will revise the test in future work in order to eliminate all "barnacle" contributions to the results. This was extensively discussed in Vol. II of the Phase II proposal on pages 12-13.

Freshwater Algae Attachment

In the first freshwater attachment test, aquarium water was changed every day with water drawn from University Lake on the LSU campus. The water is changed to simulate lake turnover conditions. The pH of the lake water varies during the day, ~10 after a day of good sunlight and ~7 overnight. The decrease at night is caused by bacteria consuming dead algae (which releases CO_2) at a rate exceeding CO_2 fixation. These first tests were done in the summer and so under ideal algae growth conditions.

Six types of cement were used in the first freshwater study. These samples were from initial moldings, and so not as good in terms of carbonation and pH reduction as those used in the saltwater studies. Type I PC (3A, air set), w/c = 0.32 and surface pH ~9, collected 0.73 mg/(cm^2·day) for 24 days. Type I PC (3B, CO_2 treated), w/c = 0.32, surface pH ~ 8, collected 0.75 mg/(cm^2·day) and 0.51 mg/(cm^2·day) (2 samples). The relatively low surface pH for 3A accounts for the small deviation in results, carbonated vs. non-carbonated. A Class C fly ash, treated with CO_2 but pH still >10, collected 0.19 and 0.19 mg/(cm^2·day) (2 samples). The air-set fly ash collected 0.20 mg/(cm^2·day), because its surface pH was also ~10. For a BFS, the surface pH of CO_2-treated slag was ~10, but this was low enough for fresh water, as the samples collected ~0.49 mg/(cm^{2}Cday). Algae removal tests were run on two blank samples (never exposed to algae) and both showed less than a 0.35 wt% weight loss. The difference in these and the saltwater tests is the result that carbonation in these initial freshwater tests did not improve algae attachment. Our initial assessment was that the combination of the higher average lake pH and the poorly carbonated samples used in these early tests contributed to this result.

We later tested newer foamed formulations of PC/silica, PC/BFS and PC for both rate of freshwater microalgae attachment and rate of gross photosynthesis as measured by O_2 production. Due to winter weather, these tests took place in an aquarium using lake water changed 3 times per week. Water from University Lake in Baton Rouge was again used. A bank of three 18" fluorescent lights simulated sunlight, and an aquarium pump was used to simulate the lake circulation. The recipes of the materials used (samples 63, 77, 83) are given in Appendix C. Results of this test (mg organic matter/cm^2 external surface area/day) are given in Table 5 below.

TABLE 5 - Organic Matter Attachment and Rate of Photosynthesis - Foamed Cement Samples

[1]SAMPLE	Attached Organic Matter mg/cm^2/day	Gross Productivity mg O_2/L/h
Blank (water only)	---	1.7
63A (PC/silica)	0.69	
63A	0.98	3.5
63B	0.58	
63B	0.78	4.5
77A (PC/BFS)	0.74	
77B	0.18	
77B	8.1	1.2
77E	5.3	
77E	8.5	0.77
83A (PC/silica)	0.13	
83B (PC/silica)	0.18	
83C	0.19	
83D	3.7	

[1] 63 has a w/c=0.55, 77 and 83 have a w/c=0.45; 83 is for 1 h mold time (vs. normal 2.5 h)
A=air set; B=CO_2 set, feed pressure ~900psi.
C=feed pressure 1500psi CO_2; D=feed pressure 2000 psi CO_2; E=feed pressure 2500 psi CO_2

Sample 63 is a foamed PC/silica with a recipe similar to the non-foamed sample 22 used in previous tests. It is clear that carbonation of this PC/silica did not improve its rate of microalgae attachment. Recipe 83 is almost the same as 22 and 63 except for a w/c (water/cement ratio) = 0.45; the mold time could be reduced to 1 h at the higher pressures, although the carbonate contents were unchanged. Even higher pressures showed few differences. However, there was evidently a dramatic effect on surface pH as the samples molded at the highest pressure showed a significantly higher rate of microalgae attachment.

We had determined that a 50% PC/50% BFS mixture (recipe 77) will harden in 1 h with an alkaline/surfactant activating solution of 0.55N NaOH, and is extensively carbonated to core pH~7. The carbonated samples here, with one exception, gave high rates of organic matter attachment. In fact, the rates for 77E and 83D were far higher than for previous tests done under actual sunlight.

Due to the small weights involved in this test, the accuracy is no greater than ±20%. This number was established through attachment tests on six blank cement samples representing different materials (PC, BFS, etc.).

These freshwater samples were also used to measure rates of CO_2 fixation by the “light and dark bottle” test (Appendix B). This is a well-established method for measuring CO_2 utilization in primary production by algae cells. Mann (1982), Livingston (1979), and Millero and Sohn (1992) discuss various aspects and methods of the light and dark bottle approach to measuring primary productivity using either the uptake of 14-C labeled carbon dioxide, unlabeled carbon dioxide, or release of oxygen (a product of photosynthesis). Where oxygen is being measured, for example, the increase in oxygen in the light bottles represents net photosynthesis and gross productivity is determined from the difference in the oxygen in the light and dark bottles where oxygen loss in the dark bottles is due to respirations. With this technique, transparent bottles (where photosynthesis and mineralization can occur simultaneously) and dark bottles (where only mineralization or organic matter decomposition will occur) are suspended in the photic zone of a water column for relatively short intervals. Where the objective is to compare data collected in different regions, or for the purposes of comparing different treatment effects under lab conditions, this approach typically works well. The gross productivity in terms of mg O_2/L/h, as given in Table 5 above, is directly proportional to the amount of CO_2 fixation.

The initial photosynthesis tests (results, Table 5) were unsuccesssful. We could not understand why the gross productivities for the PC/silica samples were so high when their rates of algae attachment were not correspondingly high. Conversely, we did not know why the gross productivities of the PC/BFS were relatively low when their rates of attachment were high. Sediment attachment cannot explain these results, because the aquarium water was drawn from the lake and so had little sediment. The initial O_2 concentrations in the PC/silicas and the blank were well below the equilibrium value of 8.1 mg/L at 25EC (Drever, 1985), and this may have caused a problem with the test for these samples. For example, there may have been adsorption of O_2 by PC/silicas with subsequent gradual release of O_2 to the solution. Or possibly the operation of the dissolved O_2 probe was more disturbed by the presence of PC/silica than by the other samples. This would not explain the problem with the blank, however. In any case, the values obtained for the PC/silicas and the blank were abnormally high when compared to the solubility of O_2, suggesting the gross productivity results were unreliable at least for these samples. Later freshwater tests using this method gave far more credible results, however (see below).

The final freshwater attachment tests in month 10 were also conducted using fresh water from University Lake in Baton Rouge, changed 3 times per week. They were conducted outside the lab in sunlight because the weather had warmed to the point where outdoors algae growth was measurable. Unfortunately, some unusually cool weather for Baton Rouge intervened for almost a week, and the growth rates did not approach the levels found in the previous month's (indoors, artificial sunlight) work, which had been as high as 8 mg/cm^2/day. This does not invalidate the relative comparisons given below in Table 6, however, as all samples in this batch experienced exactly the same conditions.

TABLE 6 - Organic Matter Attachment and Rate of Photosynthesis - Foamed Cement Samples

	Attached Organic Matter mg/cm^2/day	Gross Productivity mg O_2/L/h
Blank (water only)	---	1.2
63A (PC/silica)	0.12	
63B	0.39	
63B	0.45	1.4
83C (PC/silica)	1.6	1.3
72A (PC/FAC)	0.01	
72B	0	
73A (FAC)	0	
73B	0	
75A (PC/BFS)	0	
75B	0	
77C (PC/BFS)	0.19	

63 has a w/c=0.55, 64 etc. have a w/c=0.45
A=air set; B=CO_2 set, feed pressure ~900psi.
C=feed pressure 1500psi CO_2; D=feed pressure 2000 psi CO_2; E=feed pressure 2500 psi CO_2

In contrast to some previous attachment tests, it was clear in these results that carbonation of the PC/silica (63) did improve its rate of microalgae attachment. Recipe 83 is almost the same as 22 and 63 except for a w/c (water/cement ratio) = 0.45; the mold time could be reduced to 1 h at the higher pressures, although the carbonate contents were unchanged. However, there was evidently a dramatic effect on surface pH as the samples molded at the higher pressure again showed a significantly higher rate of microalgae attachment. This is in complete agreement with the freshwater results from the previous month and suggests that an excellent surface for algae attachment is PC/silica molded at low water/cement ratio.

While 77C (50% PC/50% BFS) performed satisfactorily here (in agreement with previous work), sample 75 performed poorly. This was expected from its low carbonate content (Table 1). All of the fly ash-containing samples also performed poorly. Therefore FAC would not be suitable for freshwater algae attachment. This is in contrast with the successful results for FAC in saltwater (months 3-4).

These freshwater samples were also used to measure rates of CO_2 fixation by the "light and dark bottle" test (Appendix B). The gross productivity in terms of mg O_2/L/h, as given in Table 6 above, is directly proportional to the amount of CO_2 removed. These tests were conducted over a 4 h period using water from University lake sufficient to fill a 250 mL bottle containing (except for the blank) the 25 g cement disk sample.

Although our previous experience (month 9) with this test was spotty, the results in the table above do not suffer from obvious anomalies. In particular, the gross rates of photosynthesis for the samples which attached algae successfully exceeded that of the blank. This improvement could be the result of more careful calibration of the dissolved O_2 meter, or of better standardization of test procedures. Future tests will prove if we have solved the problems associated with this test, as appears to be the case.

The initial O_2 concentrations in the PC/silicas and the blank were only about 25-30% of the equilibrium value of 8.1 mg/L at 25EC (Drever, 1985), which shows that the lake has been relatively stagnant. The stagnancy at this time of year may have contributed to the relatively low rates of algae growth in this test when compared to last month's tests, which were performed in the lab under artificial sunlight and with water circulation.

Task 4.

Based on results from tasks (2)-(3), we developed a preliminary technical and economic assessment of the novel technology for enhanced CO_2 fixation.

The high-pressure CO_2 "one step" molding technology can be conveniently adapted to the production of artificial reefs. As noted above we anticipate the eventual manufacture of hollow reef balls™ (trademark of Reef Ball Development Group, Ltd.), of roughly hemispherical shape, - 1 m diameter x 3 cm thick, with a weight of -450 kg, and an active surface area for bacteria and microalgae growth of -10^4 m^2. The thickness of - 3 cm is thick enough to ensure needed strength, but thin enough to ensure sunlight penetration into the pores in all “blue water” applications. The molded spheres will contain several large openings, approximately 7-12 inches in diameter, to allow for enhanced fish growth.

The technical assessment was discussed in the Results of Tasks 1 and 2. The economic assessment is discussed below. Once the reef balls are placed in the ocean or intercostal waterways they will continue CO_2 removal indefinitely without additional maintenance costs.

In the following calculations we assume each reef ball contains 1000 pounds of concrete. No time value of money ($i = 0$) will be used. Basis - one reef ball.

Manufacture of Cement

According to Simatupang and Habighorst (1993) the manufacture of 1000 pounds of cement will result in 136 pounds of carbon dioxide being released to the environment.

Production of Reef Ball

1. Cost of Cement

$$\frac{\$\ 0.05}{1\text{ lb cement}} \quad * \ 1000\text{ lbs cement} \quad = \quad \$\ 50.00\text{ (cost of cement)}$$

2. Cost of carbon dioxide.

In the proposed process, CO_2 at 900 psi will be compressed to a higher pressure and contacted with the cement. The key here is the reaction of CO_2 with the cement will produce $Ca(CO_3)$ and other carbonates. Our Phase I experiments showed that CO_2 capture during the high pressure neutralization process will be about 10% of the cement weight using optimal materials. To treat and neutralize a 1000 lb reef ball, about 100 lbs of CO_2 will be needed, costing $5.

3. Molding system.

As part of Phase II we will determine the best way to manufacture reef balls of carbonated cements. Two methods are currently under evaluation. In the first process the reef ball mold would be filled with cement at low pressure and then the mold would be treated with high pressure CO_2. The second process consists of reactive extrusion, with high pressure mixing and reaction of the cement and CO_2 in the barrel of the extruder. The pressure would be reduced to near atmospheric and the reef ball mold would be filled. The key to the second process is controlling the amount of setting in the extruder.

For either system, high pressure molding or reactive extrusion, we estimate the capital costs at $10,000. For the high pressure molding system this includes the cost of a compressor ($6,000) to generate high-pressure CO_2 and the high pressure containment system ($4,000) to hold the reef ball during the molding/treatment process. For the reactive extrusion process the primary cost will be a high-throughput vented extruder ($9,500) and a low-pressure mold ($500).

This capital cost can be amortized over the expected 5-year life of the equipment. We assume 250 day operation per year and a conservative estimate of 12 reef balls produced per day.

Capital cost = $10,000/5 years * 1-year/250 days * 1-day/12 reef-balls = $0.7/ reef ball

Including instrumentation, maintenance, and utilities at 20% of the capital cost, an estimate of ~$1/ reef ball is obtained. We estimate labor costs at $40/reef ball produced.

Installation of the Reef Ball

We estimate that one boat and diver can install 12 reef balls per day. The cost for a boat and diver is $2000/day.

Installation cost = $2000 boat and diver/12 reef balls = $167/reef ball (installation)

Total Cost of Material and Installation per Reef Ball

$50 (cement) + $5 (CO2) + $ 1 (equipment) + $40 (labor) + $167 (installation) =

$263 Total Cost/Reef Ball

In this analysis it is assumed the manufacture of the reef balls results in no net CO_2 release to the atmosphere. The CO_2 emitted during the manufacture of the reef balls, including cement manufacture, is nearly equal to the amount of CO_2 bound in the cement (as carbonates) during the neutralization process. It is also important to realize this $263/reef ball can be substantially reduced by certain manufacturing technologies. For example, if we can use reactive extrusion technology, it may be possible to manufacture the reef balls nearer to destination, which could lower the installation and labor costs per reef ball.

CO_2 Sequestered

According to Carter (1988) coral reefs result in 1,700 - 2,500 g of fixed carbon/m^2-year. This m^2 is gross or external coral surface area, not accounting for the surface area created by the microporous structure of the coral. Reef balls are ~4 ft wide, 3 ft high. The external surface area of a hemisphere with these dimensions would be ~70 ft^2. Because reef balls are microtextured the true surface area is much higher but as noted above only the external surface area should be considered. The availability of the base of the reef ball to grow microalage increases the estimate of the available external surface area in the reef ball to about 100 ft^2 or 10 m^2 .

2000 g of fixed carbon/m^2 - year * 10 m^2 = 20,000 g fixed carbon / year - reef ball

20,000 g fixed carbon * 3.66 g CO_2 fixed / g fixed carbon =

73 kg captured CO_2/ reef ball-year = 0.073 tonne CO_2 avoided / reef ball-year

The single-year cost is therefore,

$263/0.073 tonne of CO_2 = $3603/tonne of CO_2 avoided

If we take a reasonable lifetime of 100 years for the reef ball, this cost becomes:

$3603/tonne of CO_2 avoided * 1/100 year reef ball life = <u>$36.03/tonne of CO_2 avoided</u>

One way to put this number in perspective is to consider that one proposed carbon tax is $50/tonne of CO_2 produced. If we use the Reef Ball Development Group estimate of a 500 year lifetime this number is reduced to <u>$7.21/tonne of CO2 avoided</u>.

<u>Task 5.</u> Preparation of a report summarizing results of the assessment, and the preparation of a work plan with costs and schedule to further develop the concept in Phase 2.

The Work Plan with costs and schedules was included in the Phase II proposal (Vol II), which was submitted to DOE-FETC on January 14, 1999. Vol. III of this proposal consisted of the Cost Plan. The preliminary Final Report on this project was also submitted on January 14, 1999.

iii. CONCLUSIONS

(1) In terms of short curing times, high extents of carbonation, low CO_2 feed pressures, and low surface pH, PC and fly ash are the best materials in non-foamed applications. Portland Cement (PC)/silica will require longer cure times (>2 h) or higher pressures.

(2) Foamed samples (vs. non-foamed) show increases in extent of carbonation; $Ca(CO_3)$ wt% can increase by a factor of 4. Going to higher CO_2 feed pressures also increases extent of carbonation and decreases cure times for silica- and blast furnace slag (BFS)-PC mixtures to ~ 1 h or less.

(3) In terms of short curing times (~1 h), high extents of carbonation (>20wt% in some cases), and low surface pH (~7), PC/silica, PC/BFS and fly ash all behave excellently in foamed molding applications.

(4) Carbonated, non-foamed samples have low porosity and low internal surface area, and are optimal for low leaching rates. Carbonated, foamed samples have high porosity and surface area (10 m^2/g common) and should be better for algae attachment.

(5) All classes of samples showed increases (in some cases >100%) in the 7-day unconfined compressive strength upon carbonation. In artificial reef applications, this could prove important in withstanding wave and tidal action.

(6) In saltwater organic matter attachment tests, non-carbonated cement samples attach some algae, but far less than carbonated samples. Conservatively, ~50% of their attached organic matter is from barnacles.

(7) Carbonated PC/silicas, fly ash, and some BFS all show high algae attachment rates in initial colonization in saltwater (~0.009 mg/cm^2Cday).

(8) Carbonated PC/silicas and PC/BFS show high initial algae attachment rates in initial colonization in fresh water.

(9) Economic analysis shows that if we take a reasonable lifetime of 100 years for a reef ball (an engineered reef structure), the cost in \$/tonne of CO_2 avoided becomes: \$36.03/tonne of CO_2 avoided. If we use the Reef Ball Development Group estimate of a 500 year lifetime this number is reduced to \$7.21/tonne of CO2 avoided.

PATENT DECLARATION

We have not patented or filed any disclosures of invention on any of the technology developed under this Phase of the project.

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H. LIST OF ACRONYMS AND ABBREVIATIONS

BFS	Blast furnace slag
BTB	Bromothymol blue
FAC	Fly ash cement
LSU	Louisiana State University
PC	Portland cement
SCF	Supercritical fluid
TGA	Thermogravimetric analysis
w/c	water/cement weight ratio
XRD	X-ray diffraction

APPENDIX A - ORIGINAL STATEMENT OF WORK

A. OBJECTIVES

PHASE 1-

(1) Test pH-neutral cements of different types (portland cements, fly ash, blast furnace slags) for microalgae attachment. Determine which compositions lead to enhanced algal densities.

(2) Compare CO_2 fixation rates for unattached vs. attached algae populations. Determine which cement compositions lead to enhanced fixation rates.

B. SCOPE OF WORK

Preliminary experiments performed at LSU have shown that supercritical CO_2 can rapidly carbonate any cement-based product - portland cements, fly ash, or blast furnace slag. This technology will allow the development of hardened concrete structures of nearly neutral pH, which can be used as artificial reefs. It is known that attached (to coral reefs, e.g.) microalgae and algal beds are 20 times more efficient, on an areal basis, for the fixation of CO_2 when compared to the open ocean. The questions which must be answered by the proposed research are: (a) What density of microalgae can be attached to pH neutral cements?; (b) How can the surface compositions of the cements be altered to enhance attachment densities and rates of photosynthesis?; (c) What locations where temperature, light penetration, nutrient status, and perhaps other factors affect algae productivity will be most favorable for further enhancement of rates of photosynthesis associated with fixed algae?; (d) How can the surface areas of the cements be increased without sacrificing minimal required strength?

This project involves a team of researchers with backgrounds in cement technology, supercritical fluid technology, materials science, oceanography and wetland biogeochemistry. We will address each of these questions in Phases 1 and 2, and then proceed to demonstration technology using prototype artificial "reef hemispheres" in Phase 3.

APPENDIX B - EXPERIMENTAL AND TEST PROCEDURES

Molding Non-Foamed Samples:

The recipe was mixed and stirred in a beaker, then poured into the mold (cylindrical, piston-opererated, sealed on outer surface by silicone rubber O-rings). CO_2 gas (-900 psi) is introduced below the piston. The pressure above the piston is rapidly increased using water as the driver fluid (to -2000 psi) to initiate molding. As the piston moves rapidly toward the sample the pressure above the sample rose to equalize; simultaneously the CO_2 was reacting with the cement, tending to moderate the pressure rise. The samples, cylinders 39 mm diameter and 13 mm height, were typically molded for 2 h, although molding times were varied from 0.67-4 h. The amount of CO_2 added to the cement matrix was controlled by adjusting the initial height of the piston (using spacers) above the cement.

Molding Foamed Samples:

1. Put mold cell together.
2. Place dry cement powder into mold
3. Normal thickness of cement disk not foamed was approximately 13 mm. We wanted to increase the volume by ~50%, such that the thickness was ~19 mm. The dry powder was compressed to this thickness.
4. Take required amount of surfactant mixture and pour on top of cement. Let liquid disperse throughout cement. Depending on the surfactant mixture, hardening time varied.
5. After initial set to paste (from 1 min to ~ 1 h), connect to CO_2 for 2.5 h (if ~900 psi CO_2 used, shorter at higher CO_2 pressures).

Not compressing the dry powder down to a 50-70% volume increase will cause the cement to become flaky. Beyond 70% expansion the cement is brittle.

Cement Sample pH with Bromothymol Blue Indicator Solution

1. Dissolve 1 g Bromothymol Blue/99 g absolute ethanol.
2. Place ~30 mL solution in glass beaker. Place beaker on a white paper background.
3. Gently place sample in solution. Make observations immediately and every min for 10 min. Color changes that don't take place immediately represent core pH, since the solution penetrates the structure. If no color change after 10 min, pH neutral throughout.

No color change represents a pH of approximately 7. A color change to blue indicates a pH at or above 7.6.

TGA, XRD, Surface Area and Porosity (Void Volume) Tests

Surface areas were estimated using the one-point BET method at 30% relative saturation, using a Micromeritics 2700 Pulse Chemisorption apparatus. Water was first removed under vacuum at 1 torr for 24 h at 100EC, then under flowing N_2/He for at least 2 h. The surface areas of selected samples were checked by the full BET N_2 adsorption method using an Omnitherm (model Omnisorp 360) adsorption apparatus. The pore volume was determined in water by displacement (Archimedes' principle). All specimens used in density and porosity measurements were dried under vacuum at 1 torr at ambient temperature prior to measurement.

A Scintag PAD-V X-ray powder diffractometer (XRD) using Cu Ka radiation was used to identify crystalline phases in the specimens. Samples were step-scanned from 3-60E 2?, at 0.02E step size, 3 s/step. A Perkin Elmer thermogravimetric analyzer (TGA) operating at atmospheric pressure was used to quantify the weight losses due to water evolution (from hydrates), hydroxide (e.g., $Ca(OH)_2$) to oxide conversions, and carbonate (e.g., $CaCO_3$) to oxide conversions. The carrier gas was He, and the temperature program was 200-700EC, 5EC/min, then hold at 700EC. The peak for calcium carbonates appears at > 450EC.

The key result in XRD analysis is the ratio of the portlandite (crystalline $Ca(OH)_2$) to calcite (crystalline $Ca(CO_3)$) peak heights. The portlandite peak is at 18.1E 2? and the calcite peak at 29.5E. This ratio is not strictly quantitative, because detailed calibration of peak height vs. weight of a given phase was not performed, and also because careful microtome sectioning procedures were not used. But it is a useful qualitative measure of both carbonate formation and of the extent of cure.

Organic Matter Attachment Test

1. Place sample in a glass jar of at least 250 mL.
2. Place jar in oven at 75EC for 7 days (7 days determined during first run, samples weighed every day until constant weight). Make observations about sample (barnacle, sediment attachment).
3. Remove and weigh sample in clean work area. Dried algae sometimes falls off during handling and has to be re-added to scale.
4. After weighing, place sample back in jar. Add ~30 mL (enough to cover sample) aqueous H_2O_2, place in fume hood. Add H_2O_2 while sample is still hot from oven, so samples are weighed and treated individually.
5. After sample in jar stops foaming (usually 15-20 min), rinse and clean with DI water. Add H_2O_2 again and if there is visible algae still on the surface place in oven at 75EC for 20 min. If no visible algae on the surface add H_2O_2 for 10 min or until foaming stops but do not place in oven.
6. After second H_2O_2 treatment remove sample, rinse and clean with DI water. Soak in DI water 10 min.
7. Empty water and place back in oven for 7 days at 75EC.
8. Re-weigh; weight difference between step 3 and 8 is organic matter weight.
9. Measure surface area of sample in cm^2.
10. Determine amount collected in g/(cm^2-day). Number days = days samples exposed to algae in water.

CO_2 Fixation Measurements Using the “Light and Dark Bottle” Test

1. Algae is grown on sample.

2. Four bottles will be used, two clear and two covered with aluminum foil to inhibit sunlight.

3. Measure the O_2 concentration (the initial O_2 concentration of the water in the bottles) of the water in the aquarium with a dissolved oxygen meter. The meter must be of ±0.05 mg O_2/L precision.

4. Two samples of the same type will be placed in a clear bottle and a dark bottle, respectively. The bottles will be filled to the top with water. The other two bottles will be filled to the top also and all bottles covered with a lid.

5. Samples will be left alone for 4 h, then the O_2 concentration of each bottle will be measured.

6. From the initial value obtained previously and the O_2 content of the clear bottles, the amount of photosynthetically formed oxygen is obtained. New O_2 concentration minus initial O_2 concentration gives the amount of oxygen formed and thus the average amount of CO_2 removed. A comparison of bottles can be made to determine if the bottles with the extra algae on the cement actually remove more CO_2.

Appendix C - Detailed Cement Mix Recipes

Non-Foamed Sample Recipes

2B - FLY ASH	2A - FLY ASH
25g Class C Fly Ash	25g Class C Fly Ash
10.0g 5.0N NaOH	10.0g 5.0N NaOH
2 h CO_2 mold time	2 h air mold time

19B	19A
25g BFS	25g BFS
10.0 g 5N NaOH	10.0 g 5N NaOH
2 h CO_2 mold	2 h air mold time

22B	22A
22.4g Type I Portland Cement	22.4g Type I Portland Cement
6.2g Sodium Metasilicate ($Na_2SiO_3 \cdot 9H_2O$)	6.2g Sodium Metasilicate ($Na_2SiO_3 \cdot 9H_2O$)
9g DI H_2O	9g DI H_2O
CO_2 mold time varied	Air mold time varied

42B
0.67 h mold time, same recipe as 22B except 1500 psi CO_2 during mold.

24B	24A
24g Type I Portland Cement	24g Type I Portland Cement
12g DI H_2O	12g DI H_2O
3 h CO_2 mold time	3 h air mold time

3B	3A
25g Type I Portland Cement	25g Type I Portland Cement
8g H_2O	8g H_2O
3 h CO_2 mold time	3 h air mold time

Foamed Sample Recipes 63A, 73A, 75A, 77A, 83A, 87A, 88A same as "B" except no CO_2 used - set in air only.

<u>85C - PC, 0.5 h mold</u>
22.9g Type I Portland Cement
12.8g Silicate Surfactant D
w/c=0.45, CO_2 introduction prior to set. Sample not completely hardened at bottom (need >1 h).

<u>63B - PC/silica, 2.5 h CO_2 mold</u>
22.4g Type I Portland Cement
15.2g Silicate Surfactant D Solution, w/c = 0.55

74B - PC/silica, 1 h set in air, 2.5 h CO_2 mold

22.9g Type I Portland Cement
12.8g Silicate Surfactant D
w/c=0.45, immediate CO_2 introduction prior to set

83B - PC/silica, 1 h CO_2 mold (83C, feed P = 1500 psi; 83D, 2000 psi; 83E, 2500 psi)

22.9g Type I Portland Cement
12.8g Silicate Surfactant D
w/c=0.45, immediate CO_2 introduction prior to set

84C - PC/silica, 1 h set in air, 1 h CO_2 mold, feed P = 1500 psi (84D, feed P = 2000 psi)

22.9g Type I Portland Cement
12.8g Silicate Surfactant D
w/c=0.45, immediate CO_2 introduction prior to set

87B- PC/Silica - 1 h CO_2 mold (87D, feed P = 2000 psi)

22.9g Type I PC
12.8g Silicate Surfactant D
w/c=0.45, allowed to set to paste in air first

75B - PC/BFS, 1 h air set, 2.5 h CO_2 mold

12.5g Type I PC
12.5g BFS
10g 0.55N NaOH Surfactant D solution

77B - PC/BFS, 1 h CO_2 mold (77C, feed P = 1500 psi; 77D, 2000 psi; 77E, 2500 psi)

12.5g Type I Portland Cement
12.5g Slag
10g 0.55N NaOH Surfactant D solution
CO_2 introduced immediately (before set). Very hard after 1 h, but some cracking.

88B- PC/BFS - 1 h CO_2 mold

12.5g Type I PC
12.5g BFS
10g 0.55N NaOH Surfactant D solution
allowed to set to paste in air first

72B - PC/Fly Ash, 1 h air set, 2.5 h CO_2 mold

12.5g Type I PC
12.5g Fly Ash
10g 5N NaOH Surfactant D solution

78B - PC/Fly Ash, 1 h CO_2 mold

12.5g Type I Portland Cement

12.5g Fly Ash
10g 0.55N NaOH Surfactant D
CO_2 introduced immediately (before set). Not fully hardened, need ~2.5 h, or more concentrated activating solution (~1.0 N NaOH).

80B - PC/Fly Ash, 1 h air set, 1.5 h CO_2 mold
12.5g Type I PC
12.5g Fly Ash
10g 0.55N NaOH Surfactant D solution

64B - Fly Ash
25g Fly Ash
10g 5N NaOH Concentrated Surfactant D solution

73B - Fly Ash, 1 h air set, 2.5 h CO_2 mold
25g Fly Ash
10g 0.55N NaOH Surfactant D solution

Surfactant D (wt%)
2% Igepal CA-210 (polyethoxylated alcohol nonionic surfactant)
0.5% Polyoxyethylene-3, methyl ether
Balance 0.55N NaOH or whatever normality desired.

Silicate Surfactant D (wt%)
80.7% H_2O
16.8% Na_2SiO_3
0.5% Polyoxethylene-3, methyl ether
2% Igepal CA-210

Surfactant E (wt%)
15.2% Na_2SiO_3
1% Aliquat 336 (a cationic quaternary amine surfactant)
1% Igepal CA-210
1% sodium lauryl sulfate
balance water