Publication No. 01-127-164

THE SUBSTRATE SUITABILITY OF PHOSPHOGYPSUM COMPOSITES FOR MARINE HABITAT ENHANCEMENT

Prepared by
Louisiana State University

under a grant sponsored by

FIPR
Florida Institute of
Phosphate Research

January 1998

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FINAL REPORT

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in cooperation with Roger K. Seals
Principal Investigators

with

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Contract Manager: G. Michael Lloyd, Jr.
FIPR Project Number 95-01-127

January 1998

DISCLAIMER

PERSPECTIVE

In a world where recycle, reuse and conservation have become the norm it should not be surprising that there is interest in using phosphogypsum as a raw material for the production of oyster culch and other marine applications. With well over a billion tons on-ground inventory in the Gulf Coast states, low-cost phosphogypsum becomes a quite interesting potential raw material for construction applications when the finished product must compete with other low-cost materials.

The initial attempts to use a phosphogypsum cement mixture in the marine environment proved unsuccessful due to the poor physical stability of the culch and required the development of alternate formulations of phosphogypsum, cement, and fly ash mixtures. The new formulations proved satisfactory in the marine environment and were shown to support oyster growth. Due to the time required to develop the new formulations and to test the culch for physical stability, little or no efforts to determine the potential for toxic element accumulation in the food chain were possible.

At this point the question of toxic element accumulation in the food chain is largely academic when the economics for producing oyster culch using phosphogypsum are considered. The production cost for the phosphogypsum culch is higher than the cost of presently used materials and to date the phosphogypsum culch has not been shown to provide any advantages that could offset the higher costs. Until it can be shown that there is an economic incentive to continue this work, it would seem prudent to curtail activities in this area.

ABSTRACT

LSU researchers are studying the application of stabilized phosphogypsum (PG) blocks as artificial reefs and oyster substrate. The first study was focused on the mechanisms of preventing dissolution of PG and the mechanical properties of the stabilized PG blocks. It was found that 70%:30% PG:cement test blocks survived for more than one years while the 85%:15% PG:cement test blocks dissolved within two months of placement in the seawater. Optic imagery and microprobe analysis showed that a calcite ($CaCO_3$) layer formed on 70% PG/30% cement blocks that did not exhibit softening when submersed in saltwater. This $CaCO_3$ coating may act as a physical barrier to seawater intrusion, preventing block degradation. Ettringite formation was identified as the main reason for dissolution in 85% PG/15% cement blocks.

The mechanical properties studies were initiated to investigate the surface hardness and strength of PG block composites $\leq$ 15% and PG briquettes $\leq$ 3% that were subjected to various curing and seawater submergence times. Surface hardness results for both the blocks and briquettes indicated a significant decrease ($p>0.0001$) after the 30 day submergence period followed by little to no change between the 30 and 60 day submergence periods. Strength results were more variable between the blocks and briquettes. The interactions between composition and treatment were more apparent for the blocks. Surface hardness and compressive strength were not good indicators of the integrity of composite PG in marine applications.

The second study was focus on reducing the binding agent content and cost of the stabilized PG blocks. Lime and fly ash were added as other binding agents to reduce the cement content. It was found that the same total amount of lime and cement contents in cement/lime PG composites that endured 12 weeks of field submergence were identified to leach the least calcium in the laboratory. A gradual reduction in block size despite biological growth was observed in the field test, suggesting the addition of lime is not fully adequate. The incorporation of fly ash as an ingredient seems to be a good alternative, as demonstrated in additional studies where combinations of PG (55-62%), cement (3-10%), and fly ash (35-42%) showed little signs of deterioration after two years of seawater field submergence. The PG (62%), cement (3%), fly ash (35%) blocks are currently the lowest cost. Calcium leaching evaluated in the laboratory through dynamic leach test provides a good indication of how composites will perform in the field.

The economic analysis of the PG, cement, fly ash blocks indicates that the cost of such a briquette, based on a 4,500,000 ton per year facility, would be approximately the same cost as limestone (@ $13.00/ton). Limestone and shell are available for similar purposes on the open market. Although there is some question about the density of the resulting phosphogypsum product, it does appear to be competitive with the only other material available on the market in the gulf region. It is possible that with further engineering work the cost of producing the phosphogypsum briquettes may be reduced to some amount less than that of commercially available limestone.

ACKNOWLEDGMENTS

The research team would like to thank several persons and institutions involved in this phase of the project, LSU's Department of Geology for allowing the use of their valuable optic imagery equipment, the Louisiana Sea Grant College Program's Oyster Facility at Grand Isle and Dr. John Supan for assisting in the oyster settlement study, and openly accommodating the research team in the use of their facility for field submergence studies, IMC-Agrico Co. for providing the phosphogypsum, River Cement Co., Natchez Terminal, who donated the Type II Portland cement, Dravo Lime Co. for the lime, and Bayou Ash Inc. for the fly ash. Ms. Christine Kaiser who assisted in all water quality analysis. Dr. Rod Millward, Mr. Donald Anderson, Mr. T. Shane Sandefer, Ms. Sarah Jones, Ms. Autumn Hawke, Mr. Cedric Brown, Ms. Kara Zardiackas, and other students who assisted in fabricating the blocks, deploying them in the field, and assisting in data collection. Foremost, our sincere appreciation to the Florida Institute of Phosphate Research for its financial support and assistance in this phosphogypsum project.

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EXECUTIVE SUMMARY

In 1992, the Louisiana State University Department of Civil and Environmental Engineering, Coastal Fisheries Institute, and Department of Biological Sciences entered into an interdisciplinary program to evaluate the feasibility of using cement stabilized phosphogypsum as a source of marine substrate for oyster culch, artificial reefs, and stabilization of coastal erosion. These three research organizations brought together a team to evaluate the biological safety of stabilized phosphogypsum, engineering criteria important in designing an economically and biologically viable composite, and to determine the economic feasibility of the final product. The intent was to assist the Florida Institute of Phosphate Research and fertilizer industry in determining whether the industry by-product, phosphogypsum, was viable as an alternate source of marine substrate in lieu of its land-based disposal. Based on work conducted at LSU during 1990-93, the Florida Institute of Phosphate Research supported an effort to investigate engineering and biological integrity, and economics of cement stabilized phosphogypsum blocks.

The report is divided into three sections and begins with a study to investigate the stability and biological integrity of Type II Portland cement stabilized phosphogypsum. It was found that blocks constructed with cement levels less than 30% were unstable and rapidly dissolved in the marine environment largely due to ettringite formation. It was also found that oysters would use the material as site for settlement suggesting that it is a biologically acceptable source of substrate.

Due to the dissolution problem, the second study of this research was conducted to address the issue of PG block dissolution and to develop low-cost PG composites that maintain long-term structural integrity or durability under saltwater conditions while at the same time demonstrate suitability and provide no adverse impact to the aquatic environment. Specifically, the study objectives were to: (1) evaluate larval oyster setting on cement consolidated PG and river silt, (2) determine the mechanisms affecting the integrity of PG composites in saltwater conditions, (3) to determine the mechanic properties (stability, hardness, and compressive strength) of selected PG composites submerged in saltwater under laboratory and field conditions, and (4) to reduce the binding agent content and cost of the stabilized PG blocks while maintaining the structural integrity of the PG composites.

From results of the oyster set study, it is impossible to determine whether oyster failed to set on the PG briquettes or if the set was initially successful and the oyster were later sloughed during dissolution. The time series data show that if set did occur, they were quickly dislodged during the course of dissolution. Previous research has shown conclusively that oysters will set and grow robustly on cement consolidated PG. The lack of set oysters on PG briquettes in this study, therefore, is probably not due to any adverse effects strictly attributable to the constituent PG but from the material lost from dissolving PG briquettes.

Optic imagery and microprobe analysis showed that a distinct layer identified as calcite ($CaCO_3$) formed on 70% PG/30% cement blocks that did not exhibit softening when submersed in saltwater. This layer protected the block from seawater erosion and dissolution. Results and observations suggest that the coating must have formed in an environment of high pH>11 on the composite surface, and is mainly the byproduct of seawater and PG block reaction, not from the PG block content. On the other hand, ettringite formation was identified as the main reason for dissolution in 85% PG/15% cement blocks. Without the protection of a $CaCO_3$ coating, the permeability of the PG blocks is higher, which permits water to enter the PG composites and dissolve phosphogypsum crystals on the surface and in the pores. Ruptures develop as ettringite is formed, which further enhances the formation of ettringite. This cycle will continue until the PG blocks are fully eroded.

Surface hardness and strength was determined for four PG:cement block composites (5% cement, 10% cement, 15% cement and 5% cement/10%sand) and five PG:cement briquettes (0% cement/dihydrate PG, 1% cement/dihydrate PG, 3% cement/dihydrate PG, 0% cement/anhydrite PG and 3% cement/anhydrite PG) subjected to various air-curing and seawater submergence times. The PG blocks (193 cm^3) were used as surrogates for artificial reefs, while the briquettes (5 cm^3) were used as surrogates for oyster culch. The surface hardness results for both the blocks and briquettes indicated a significant decrease ($p>0.0001$) after the 30-day submergence period followed by little to no change between the 30- and 60-day submergence periods. The strength results were more variable between the blocks and briquettes. The strength of the briquettes actually increased for the 30- and 60-day submergence periods in comparison to the initial measurements. The interactions between composition and treatment were more apparent for the blocks. There was no correlation between the stability of PG blocks in saltwater and surface hardness or compressive strength. These physical characteristics are not good indicators of the integrity of composite PG in marine applications. The comparison between the calcium dynamic leaching test and field seawater submergence observations showed that calcium-leaching rate was a good indication of how composites will perform in the field.

Based on the above studies, other binding agents (lime and fly ash) were added to the PG/cement blocks to reduce the cement contents and the cost of the PG blocks. Fly ash is a solid waste from coal of oil combustion in electric power plants with the volume being much higher at coal-fired plants. Fly ash is a mixture of metallic oxides, silicates, and other inorganic particulate matter, which is produced during the burning of coal. When lime was added, it was found that the same total amount of lime and cement contents in cement/lime PG composites that endured 12 weeks of field submergence were identified to leach the least calcium in the laboratory. A gradual reduction in block size despite biological growth was observed in the field test, suggesting the addition of lime is not fully adequate. However, lime apparently helped as evidenced by the better performance of composites with similar cement but higher lime content. The incorporation of fly ash as an ingredient seems to be a good alternative as demonstrated in additional studies where combinations of PG (55-62%), cement (3-10%), and fly ash (35-42%) showed little signs of deterioration after two years of seawater field submergence. The PG (62%), cement (3%), fly ash (35%) blocks are currently the lowest cost. And there is a room for further reducing the binding agent contents and the cost of the PG blocks.

The third and final section of this report consists of an economic evaluation of the fly ash/cement/phosphogypsum composite, which was determined to be most feasible according to the engineering studies. This economic analysis indicates that the cost of such a briquette, based on a 4,500,000 ton per year facility, would be approximately the same cost as limestone (@ $13.00/ton). Limestone (and shell) is available for similar purposes on the open market. Although there is some question about the density of the resulting phosphogypsum product, it does appear to be competitive with the only other material available on the market in the gulf region. This cost analysis was based on a Crescent Technology report document looking at the feasibility of setting up a similar facility stationed at the Uncle Sam Plant on the Mississippi River near Baton Rouge, Louisiana.

It is possible that with further engineering work the cost of producing the phosphogypsum briquettes may be reduced to some amount less than that of commercially available limestone. Further investigation may indicate that the phosphogypsum briquettes are more desirable for marine colonization than other products commercially available. The feasibility of using phosphogypsum in the marine environment for oyster culch, artificial reefs, or other marine stabilization applications does appear to be economically, technically, and biologically feasible, however, further investigations will have to verify, through EPA protocol, whether this material would be allowed to be used in these applications.

PART ONE

THE SUBSTRATE SUITABILITY OF PHOSPHOGYPSUM COMPOSITES FOR MARINE HABITAT ENHANCEMENT

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INTRODUCTION

Phosphogypsum (PG) is a solid by-product from the production of phosphoric acid from phosphate rock. For each ton of phosphoric acid produced, 4.5-5.5 tons of PG is produced (FIPR 1980). Through the wet process, some impurities naturally present in the phosphate rock become concentrated in the phosphogypsum. One such impurity is radium 226 (Roessler et. al. 1979), the parent of radon 222. Thus, phosphogypsum is classified as a “Technologically Enhanced Natural Radioactive Material” (TENR), with other impurities including trace levels of heavy metals in an acidic medium (Taha and Seals 1991). The presence of these contaminants may pose a potential hazard to human health and the environment. The main disposal method is on-site stockpiling, which creates long-term management problems (May and Sweeney 1984; Berate 1990). Concerns over airborne emissions particularly of radon gas, groundwater leaching of trace metals, coupled with increasing land costs for stockpiles have promoted research on alternative beneficial uses of this solid waste that will result in applications considered protective of public health.

The long term goal of the phosphogypsum research at LSU is to provide an economical alternative use for PG that will be safe or safer from a public health point of view than the present stockpiling disposal methods stipulated by the Environmental Protection Agency (EPA). The researchers believe that utilization of phosphogypsum for aquatic applications provides the best means for minimizing public exposure because the airborne vector is significantly diminished if not eliminated. Many species of marine vertebrates and invertebrates are dependent on hard substrate for colonization, growth, and feeding. A pilot demonstration study conducted at Louisiana State University showed that PG/cement test blocks placed in the Gulf of Mexico supported a diverse population of surface-attached and burrowing organisms (Wilson 1996). Further research supported by the Louisiana Education Quality Support Fund (LEQSF) demonstrated the durability of PG composite blocks under uncontrolled environmental conditions and has indicated no significant impact on the surrounding microcosm (Malone et al. 1996). PG has good potential in the construction of artificial reefs, shoreline stabilization structures, and oyster settlement substrate.

In general, PG blocks with 30% cement content were stable but were shown to be not economical, while blocks with low cement content tend to soften and fall apart. This research was therefore conducted to address the dissolution issue and to develop low-cost PG composites that maintain long-term structural integrity or durability under saltwater conditions while at the same time demonstrate suitability and provide no adverse impact to the aquatic environment. The specific objectives of the study were: (1) to evaluate larval oyster setting on cement consolidated PG and river silt, (2) to determine the mechanisms affecting the integrity of PG composites in saltwater conditions, (3) to determine an optimum composition of ingredients that prevents dissolution of PG composites, and (4) to determine the stability, hardness, and compressive strength of selected PG composites submerged in saltwater under laboratory and field conditions.

METHODOLOGY

COMPOSITE PG BLOCKS AND BRIQUETTES FABRICATION

Raw Materials

Raw phosphogypsum (PG) was obtained from IMC-Agrico Co., Uncle Sam, Louisiana. Initially, the moist PG was spread out in a thin layer and air dried with fans. Then, the PG was oven-dried at 45-50oC for 6-12 hours, depending on moisture content. The oven temperature was checked twice a day and adjustments made if necessary. The dried phosphogypsum was crushed and passed through a 1.46-mm sieve. The fine phosphogypsum powder was mixed with dry, fresh Type II Portland cement and admixtures (lime and fly ash) at specified percentages (based on dry solids weight), depending on the treatment. Type II Portland cement used was from River Cement Co., St. Louis, Missouri; lime from Dravo Lime Co., Baton Rouge, Louisiana, and fly ash from Bayou Ash Inc., Erwinville, Louisiana.

Blocks Fabrication

To prepare the composites, the dry mixture of PG, cement, and/or other admixtures was thoroughly mixed, tap water added, and the mixture homogenized. During the earlier phases of the study, PG composite blocks were fabricated at 85% PG, 15% cement, and 15% moisture. Earlier research results indicated that 15% cement would be adequate to maintain the structural integrity of cement stabilized PG blocks (Fan 1997). Control blocks were fabricated at 83% sand, 17% cement and 8% moisture. The differences in cement and moisture content reflect the differing properties of the sand and the phosphogypsum. This study was conducted to examine the effect of fabrication pressure and compaction on block strength and hardness. Two molds of different length were used to fabricate the blocks. For mold #1, 360 grams of the PG/cement mixture were weighed and poured into a 5.08 cm diameter by 17.78 cm long steel mold, and compacted into a 9.53 cm long cylinder. The target dry density was 1.60-1.65 g/cm3. For the control blocks, 416 grams of the sand/cement mixture were added to the mold to obtain a target dry density of 2.0 g/cm3. The compacting load to achieve the desired dry density was approximately 3,640-4,545 kg (8,000-10,000 lbs), equivalent to 18-22 Mpa (2,546-3,183 psi). For mold #2, 390 grams of the PG/cement were poured into the mold and compressed into 5.08-cm diameter by 10.16-cm long cylinders. The target dry density was 1.60-1.65 g/cm3. For the control blocks, 446 grams were added to the mold to obtain a dry density of 2.0 g/cm3. The compacting load was also 3,640-4,545 kg.

In later studies, a standard procedure was followed in the fabrication of PG composites with cement and/or other admixtures. The blocks served as test specimens for investigating the use of PG for artificial reefs and oyster culch. About 96 grams of the resulting mixture were poured into a 3.81-cm diameter by 11.43-cm long steel mold, and compacted to a 3.81-cm long cylinder. The theoretical, target dry density was 1.9 g/cm^3. The compaction load to achieve the desired dry density was approximately 11,360 kg (25,000 lbs). This allowed the manufacture of the PG composites at a pressure of 98 MPa (14,150 psi), the actual attained pressure for full compaction of the PG, cement, and lime mixes. No notable compaction was achieved at any higher compaction pressures. The blocks were fabricated using a Soil Test Compression Testing Machine following the static compaction procedure (BS 1924). The molded blocks were withdrawn from the mold and allowed to air cure for one to two hours. The blocks were then placed in double-layered plastic bags, sealed, and cured at ambient temperature and 100% humidity for 28 days or longer prior to any testing.

Briquettes Fabrication

Briquettes of cement-consolidated PG and river silt (RS), and washed, aged clam (*Rangia cuneata*) shells, served as test culch materials for investigating the feasibility of using PG composites as oyster substrate. RS was chosen as a control because its size distribution was similar to PG. About 30% of PG particles were retained on a 210 µm sieve compared to 33% for RS. K.R. Komerack Briquetting and Research, Inc., Anniston, Alabama fabricated the briquettes. The PG briquettes were fabricated using 5% cement, 95% PG, and 4.2% moisture, while the RS briquettes contained 5% cement, 95% RS, and 6% moisture. The PG briquettes had a wet weight of 12.06 g, a volume of 5.64 cm^3, and a bulk density of 2.14 g/cm^3. The RS briquettes weighed 11.94 g, had a volume of 5.28 cm^3, and a bulk density of 2.26 g/cm^3. The briquettes were allowed to cure for 3 weeks prior to any testing.

OYSTER SETTLEMENT AND GROWOUT STUDY

The PG briquettes, RS briquettes, and clamshells served as experimental, control and normal culch materials, respectively. To isolate possible PG effects on oyster set, two separate setting systems were used. Each system consisted of a sump, a pump, seawater distribution pipes, a tank for immersion of three trays of PG or RS briquettes, and two trays of clamshell; two liters of the appropriate culch material were added to each setting tray. All three culch materials were soaked in filtered, ambient seawater (FAS at 25°C, 25 ppt) for 48 hours prior to addition of the larvae to allow biofilm accumulation.

Ten million pediveliger larvae of American oyster (*Crassostrea virginica* [Gmelin]) were reared and stored following standard methods (Breese and Malouf 1975, Dupuy et al. 1977, Supan 1991) at the Louisiana Sea Grant Program's Grand Isle Oyster Culture Facility. The larvae were equally distributed in 15 L of FAS; 1 L (approximately 0.666 x 10^6 larvae) of this mixture was evenly distributed atop each of the ten trays of submerged culch materials. Larval setting occurred in static seawater for 48 hours prior to commencement of 48 hours of downweller flow through the setting trays.

Nourishment for the oyster larvae was provided by the addition of algae (*Chaetoceros muelleri* clone CHAET 10) to each setting system; 100 g of reconstituted algal paste were used initially and 200 g after setting. The paste was weighed, washed with FAS through 75- and 40-micron screens to a volume of 15 L, then added in 7.5 L aliquots to the sump of each setting system. Natural food was also made available during two 48-hr seawater changes to both systems.

After 48 hours of downweller flow, the contents of each setting tray were emptied into individual upweller silos. All ten silos received equal flow (18.9 Lpm) of FAS. The silos were emptied and all culch materials rinsed clean with ambient seawater over a 400-micron screen every 48-72 hours as needed to remove accumulated silt. The culch and attached spat (young, metamorphosed oysters) were maintained in the upweller system until 30 October 1996. The silos were then emptied, the culch cleaned with freshwater, air-dried, and collected for subsequent analyses.

The numbers of set oysters on 50 pieces of culch from each setting tray were enumerated under 7× magnification. Included in the counts were all larvae that set and failed to metamorphose and those that set, metamorphosed, and began somatic growth. All surfaces of the PG and RS briquettes were examined for set oysters. However, because the larvae had lost their ability to swim during normal growth prior to setting and settling, we suspected that differential setting might have occurred in the concave surfaces of the clamshell. Thus set oysters were counted only on the convex surfaces. To investigate the possible effects of the presence of the PG and RS briquettes on the setting of oysters on the associated clamshell, the clamshell replicates from the two setting systems were considered separate treatments. Mean numbers of set oysters from the four treatments (PG briquettes, RS briquettes, PG clamshell, and RS clamshell) were compared through analysis of variance and t-test procedures. Significance level for all comparative analyses was 0.05.

OPTIC MICROSCOPE IMAGERY

Optic microscope imagery (Goldstein et al. 1992) were conducted on 70/30 and 85/15 (% PG/% cement) blocks that had been previously submerged under natural saltwater conditions to help identify the physical and chemical processes responsible for surface softening. From a previous study, the 70/30 blocks were submerged for one year in experimental ponds at Grand Terre, LA, while the 85/15 blocks were submerged at Grand Isle, LA for one to two months. Scanning electron microscopy (SEM), polarized light microscopy (PLM), and microprobe analysis were used to examine, identify, and characterize the compounds present in the blocks. These procedures were conducted using equipment in LSU's Department of Geology. The SEM allowed the research team to identify distinct zones within the blocks and determine the physical and chemical stability. PLM allowed the research team to clearly determine the formation of a carbonate layer at the composite blocks' surface and at what point this layer formed. Microprobe measurements allowed a quantitative analysis of the surface layer's composition. It may be possible to form this coating during the fabrication process in order to minimize the dissolution process from occurring once the composites are placed in seawater.

A total of 3 samples each of 70/30 blocks and 85/15 blocks were analyzed. Two thin sections were prepared for each sample for optic imagery analysis. A precise and time consuming process, sample preparation required 8-10 man-hours to accomplish per specimen. Each preparation required cutting a 1-2 cm^3 section, coating and impregnating with epoxy, and drying for 24 hours. The epoxy-impregnated section is then ground and lapped until smooth and even. One side of the smoothened section is then set on a glass slide with epoxy and allowed to cure for 36 hours. The sample is then re-sectioned and carefully ground to about 100 microns. With increasingly finer grit glass plates, the section is reduced first to 40 microns, then 30 microns. The 30-micron specimen is then polished to an even sheen with 6-micron then 1-micron diamond paste, and with 0.3-micron then finally 0.05-micron aluminum oxide.

SELECTION OF COMPOSITE PG BLOCKS

There are many factors that affect the integrity, strength, and surface hardness of PG composites, including cement type and content, admixture type and content, moisture content, dry density, fabrication pressure, and curing and leaching times. Based on initial results of the optic image analyses, the researchers hypothesized that using PG-cement-lime-fly ash composites and fabrication of blocks at higher compaction pressures have the greatest potential to address the dissolution issue at little cost. In the design of experiments with mixture ingredients, the percentages of the ingredients must sum to 100%. The levels of one ingredient are not independent of the others, and the proportions of the ingredients in the mixtures can significantly affect the mechanical and chemical properties of the end mixture, on which statistical analyses of results are based. Previous studies indicated cement to be the cost-limiting factor, with 15% cement as about the economic maximum. Thus, an optimum ingredient composition with minimal cement and maximal PG was targeted. The search required the application of pseudocomponents with augmented simplex centroid statistical design (Hinkelmann et al. 1994 and Kuehl 1994). Essentially, the design determines mixture combinations for testing that are equidistant from each other, thus providing a good representation of all possible combinations.

Table 1. Composition of PG Blocks That Were Fabricated and Tested to Determine a Suitable Composition for Saltwater Stability.

No.	% PG	% Cement	% Lime
1	83	4	13
2	83	9	8
3	83	14	3
4	84.6	5.7	9.7
5	84.6	10.7	4.7
6	86.4	7.3	6.3
7	88	4	8
8	88	9	3
9	89.6	5.7	4.7
10	93	4	3
11	87	0	13
12	90	0	10
13	93	0	7
14	70	30	0
15	85	15	0

Thirteen composite treatments were identified and fabricated for laboratory and field testing, with PG concentrations ranging from 83-93%, cement from 0-14%, and lime from 3-13% (Table 1). Additionally, 85/15 and 70/30 blocks were fabricated. At least 20 blocks each of the identified PG composites were fabricated for laboratory and field testing purposes, which allowed all tests and measurements to be conducted in replicates of 2-5, with additional samples as needed.

SUBMERGENCE AND LEACHING TESTS

Laboratory Tests

Dynamic Leaching Test (DLT). Dynamic leaching tests were conducted on the 13 PG-cement-lime composites and the 85/15 and 70/30 blocks to evaluate the effects of lime on block integrity and calcium leaching. DLT (Environment Canada and Alberta Environmental Center 1986) is a modified version of the ANS-16.1 leach test (American Nuclear Society 1986) that is applied to low-level radioactive and hazardous wastes. The submergence medium was 18 ppt, artificial seawater (Instant Ocean™) to represent seawater conditions, at a saltwater volume/surface area (V/S) ratio of 8:1, (i.e., 547 mL of medium per 3.81-cm diameter x 3.81-cm long blocks). The samples were not aerated. Measurements/analysis of the saltwater media's pH, alkalinity, and calcium were conducted according to Standard Methods (APHA 1995). These measurements were conducted according to the DLT's standard medium renewal frequency of 2, 7, 24, 48, 72, 96, 120, 192, 264, 336, 504, and 672 hours. The replicated dynamic leaching tests were conducted at room temperature (23^{o}C), each using a randomly selected block of the composites tested.

Flow-Through Test. Another laboratory submergence test on the 13 PG-cement-lime composites was done in flow-through containers with 2 artificial saltwater (20 ppt) exchanges per day for 22 days to minimize leachate accumulation effects and approximate field submergence with little disturbance and no biological effects. This study was conducted to determine the impact on surface hardness and unconfined compressive strength. This laboratory submergence test was also performed at a saltwater volume/surface area (V/S) ratio of 8:1. Five blocks of each composition were randomly selected, tested, and evaluated for surface hardness and unconfined compressive strength.

Field Submergence

Field tests were conducted to evaluate how the natural marine environment affects the PG composites. At least four samples each of the composite PG blocks were randomly selected, randomly positioned (two per frame) and securely suspended with tie wrap and fish lines in two bread crate-PVC pipe frames (Figure 1), and fully submersed by the docks in the Louisiana Sea Grant Program's Grand Isle Oyster Culture Facility. The changes in length and diameter of blocks and their conditions were monitored at 3, 6, 9, and 12 weeks of submergence.

CHARACTERIZATION OF PG COMPOSITES

Surface hardness and unconfined compressive strength (or crushing strength for briquettes) were selected as important parameters to characterize the structural integrity of PG composites. It is presumed that certain strength and hardness levels may be established that are required for the PG composites to withstand destruction in marine environment. The strength and surface hardness of the samples were determined after curing (before the submergence tests), and after each of the submergence tests to determine the extent the composites are affected.

Surface Hardness

A cone penetrometer (Model No. WF21510, Humboldt Mfg., Inc.) was used to measure the penetration depth of the blocks and briquettes following the British Standard

Methods of Testing Soils for Engineering Purposes (BS1377:1975). The inverse of the penetration depth was used as a measure of the surface hardness of the composites. The hardness at six equidistant points along the length of each block (3 blocks per composition) was measured, while the surface hardness of the briquettes was measured at six random points.

Figure 1. A Bread Crate-PVC Pipe Frame Used in the Field Submergence Tests. The Blocks Were Suspended Using Tie Strap and 100-lb Test Lines.

Unconfined Compressive Strength and Crushing Strength

The unconfined compressive strength of the composite PG blocks (3 blocks per composition) was determined using the Matta universal testing machine in LSU's Department of Civil and Environmental Engineering following the Test for Cylindrical Cement Specimens (ASTM D1633-84). The machine automatically records the axial load and computes for the required pressure at the point of block failure.

The maximum amount of compressive force the briquettes could withstand before crushing was measured using a Soil Test Compression Testing Machine equipped with a proving ring (Material Test System 810).

RESULTS AND DISCUSSION

SURFACE HARDNESS AND STRENGTH OF PG COMPOSITES

The results of the earlier unconfined compressive strength and surface hardness tests on the PG blocks with 15% cement and control sand/cement blocks fabricated at 18-22 Mpa (2,546-3,183 psi) compaction pressure are summarized in Table 2. Mold #1 developed a slight bulge from the continual pressure put on it from the compaction machine resulting in slightly less uniform blocks.

Table 2. Unconfined Compressive Strength and Surface Hardness of PG Blocks Fabricated with Different Molds at a Compaction Pressure of 18-22 MPa. (Mean ± S.D.)

Composite	Wet Weight (g)	Volume* (cm^3)	Dry Density (g/cm^3)	Unconfined Compressive Strength (MPa)	Surface Hardness (mm^{-1})
PG/Cement (mold #1, n=10)	360 ± 8.04	198 ± 3.47	1.58 ± 0.01	7.89 ± 0.82	11.79 ± 1.45
PG/Cement (mold #2, n=10)	390 ± 3.76	206 ± 0.00	1.65 ± 0.01	8.82 ± 1.05	15.19 ± 1.75
Sand/Cement (mold #1, n=11)	416 ± 6.42	196 ± 2.81	1.97 ± 0.01	7.00 ± 0.98	11.90 ± 0.84
Sand/Cement (mold #2, n=10)	449 ± 3.62	205 ± 1.02	2.02 ± 0.01	12.91 ± 1.00	15.92 ± 0.78

* The blocks had a diameter of 5.08 cm. Mold #1 blocks were 9.53 cm while Mold #2 blocks were 10.16 cm long.

The results indicate that both unconfined compressive strength and surface hardness increased with the mold #2, indicating that the bulge may have had an effect on the compaction of the blocks. The PG blocks attained strength and hardness comparable to the sand/cement blocks. However, placement of the PG blocks in open saltwater conditions resulted in dissolution problems.

Table 3 summarizes the crushing strength and surface hardness of the PG and RS test briquettes. The briquettes also exhibited softening when submersed in saltwater.

However, when the surface layer was scraped off and the briquettes were dried and re-tested, the surface hardness and crushing strengths were as high or higher than the initial values. This observation led the researchers to believe that the briquettes may hold up as oyster culch material.

Table 3. Crushing Strength and Surface Hardness of Test Briquettes. (Mean ± S.D.)

Briquette	Crushing Strength (kN)	Surface Hardness (mm^{-1})
PG w/ 5% cement, dry (n=5)	0.805 ± 0.109	39.2 ± 11.34
PG w/ 5% cement, submerged/wet (n=5)	0.657 ± 0.143	13.4 ± 3.91
PG w/ 5% cement, submerged/dry (n=5)	1.051 ± 0.498	35.6 ± 4.34
River silt w/ 5% cement, dry (n=5)	0.474 ± 0.054	25.6 ± 2.51

The results suggested, however, that surface hardness and compressive or crushing strength are not sufficient indicators of durability in marine environment. Thus, the researchers undertook more fundamental studies to identify the factors affecting degradation of the PG blocks and determine a stable composite. Based on initial results of the optic image analyses, the researchers hypothesized that using PG, cement, and lime and fabrication of blocks at higher compaction pressures have the greatest potential to address the dissolution issue at little cost. Stronger and harder PG composites with cement and lime, which were fabricated at a higher compaction pressure of 98 Mpa (14,150 psi), were observed as shown in Table 4, although as before, strength and hardness did not indicate saltwater durability as will be discussed later.

Table 4. Surface Hardness and Unconfined Compressive Strength of PG Composites with Cement and Lime after Curing. The Blocks Were 3.81-cm Diameter x 3.81-cm Long, with a Dry Density of 1.9 g/cm^3. (Mean ± S.D.)

Composition, %			Surface Hardness (mm^{-1})	Unconfined Compressive Strength (MPa)*
PG	Cement	Lime		
70	30	0	111.11 ± 42.78	26.76 ± 6.60
85	15	0	61.85 ± 25.44	29.63 ± 3.85
84.6	10.7	4.7	99.07 ± 41.80	29.10 ± 1.50
84.6	5.7	9.7	79.07 ± 48.77	19.84 ± 1.06
88	4	8	77.78 ± 37.92	15.35 ± 1.35
88	9	3	72.59 ± 27.50	23.21 ± 11.02
89.6	5.7	4.7	70.00 ± 39.92	17.40 ± 1.53
83	4	13	68.89 ± 26.27	21.98 ± 0.66
86.4	7.3	6.3	67.96 ± 24.07	24.17 ± 0.98
87	0	13	67.59 ± 54.69	10.23 ± 1.82
90	0	10	65.74 ± 24.57	8.91 ± 1.08
83	9	8	64.82 ± 24.18	23.31 ± 1.34
93	0	7	58.15 ± 38.86	9.56 ± 0.20
83	14	3	54.63 ± 13.77	28.50 ± 4.41
93	4	3	48.33 ± 16.62	12.99 ± 0.98

* 0.006894 MPa = 1 psi

SETTLEMENT AND GROWOUT OF OYSTERS

Table 5 shows the results of the oyster setting experiment. Analysis of variance indicates a statistically significant difference ($P > 0.0001$) among the four treatments. A t-test of similarity of means defines three groupings as indicated above. Although variability was high within the last three treatments indicated in the table, the clamshell that was paired with the RS briquettes clearly experienced the highest success of oyster set. The RS briquettes and the clamshell paired with the PG briquettes exhibited similar sets but significantly less than the RS briquette-clamshell pair. None of the 150 PG briquettes evidenced any set oysters.

Table 5. Results of the Oyster Setting Experiment.

Treatment	n	Mean No. Set Oysters	t-test Grouping*
PG briquettes	150	0.00	a
PG clamshell	100	6.16	b
RS briquettes	150	8.43	b
RS clamshell	100	13.05	c

Notes: n = number of culch pieces examined; 50 pieces per replicate.
[*] Means with the same letter are not significantly different at % = 0.05.

Larval oysters will preferentially set on and attach to hard substrate materials that are high in calcium. As calcium sulfate is a major constituent of phosphogypsum (PG), we hypothesized that PG in cement consolidated form would be a reasonable substitute for the natural shell traditionally used. The total lack of set oysters on the PG briquettes is probably not due to any adverse effects strictly attributable to the constituent PG. The experiment was of necessity performed at the very end of the spawning season among natural populations of American oyster in Louisiana. Thus, there was some concern that the quality and vigor of the oyster larvae used may not have been optimal. Seasonal water temperatures at the lower extreme for growth may also have depressed setting rates of the larval oysters used. Physical or chemical inadequacies in the fabrication of the briquettes seemed to be the main problem, however. Even after as little as two days of immersion in FAS, the surfaces of the PG briquettes were becoming soft and showed signs of loss of material. A time series of 15 PG briquettes each harvested at days 4, 7, 11, and 15 of the experiment also held no set oysters and showed increasing loss of volume and mass. When the experiment was terminated on day 21, each of the PG briquettes had lost about 50% of both mass and volume due to dissolution. The absence of set oysters on the PG briquettes is thus attributed to the surface dissolution of the 95/5 PG/cement complex used in the formulation of the briquettes. From the data presented herein it is impossible to determine whether we had a failed oyster set on the PG briquettes or if the set was initially successful and the oyster were later sloughed during dissolution. The time series data show that if set did occur, they were quickly dislodged during the course of dissolution. Although our previous research has shown conclusively that oysters will set and grow robustly on cement consolidated PG, the oyster set on the clamshell paired with PG briquettes was significantly less than that on the clamshell paired with RS briquettes, which may indicate that the material lost from the PG briquettes had a deleterious effect on the oyster set.

INTEGRITY OF PHOSPHOGYPSUM COMPOSITES: OPTIC MICROSCOPE IMAGERY RESULTS

Observations of dissolution in PG blocks and briquettes with 15% cement or less prompted the research team to evaluate the physical and chemical mechanisms that may help identify an economic ingredient combination to build oyster substrate and artificial reef. The surface of the blocks is the first line of defense against seawater. With a high quality impermeable surface layer, the chemical effects of seawater can be limited. If the block becomes permeable, there is a wide opportunity for several harmful reactions, particularly PG dissolution. PG is easily soluble in seawater (Taha et al. 1991) and if the binding agent is not sufficient enough, the PG will dissolve.

From optic microscope images, PG blocks subjected to seawater leaching can be divided into three zones: Zone A--the surface zone contacting seawater or interface (Figures 2-6); Zone B--the transition zone (Figures 7 and 8), and Zone C--the PG block body (Figures 9 and 10). For blocks stabilized with 15% Portland cement, Zones A and B were each approximately 5 mm thick. For blocks stabilized with 30% cement, Zone A was about 2 mm thick, whereas Zone B was about 3 mm.

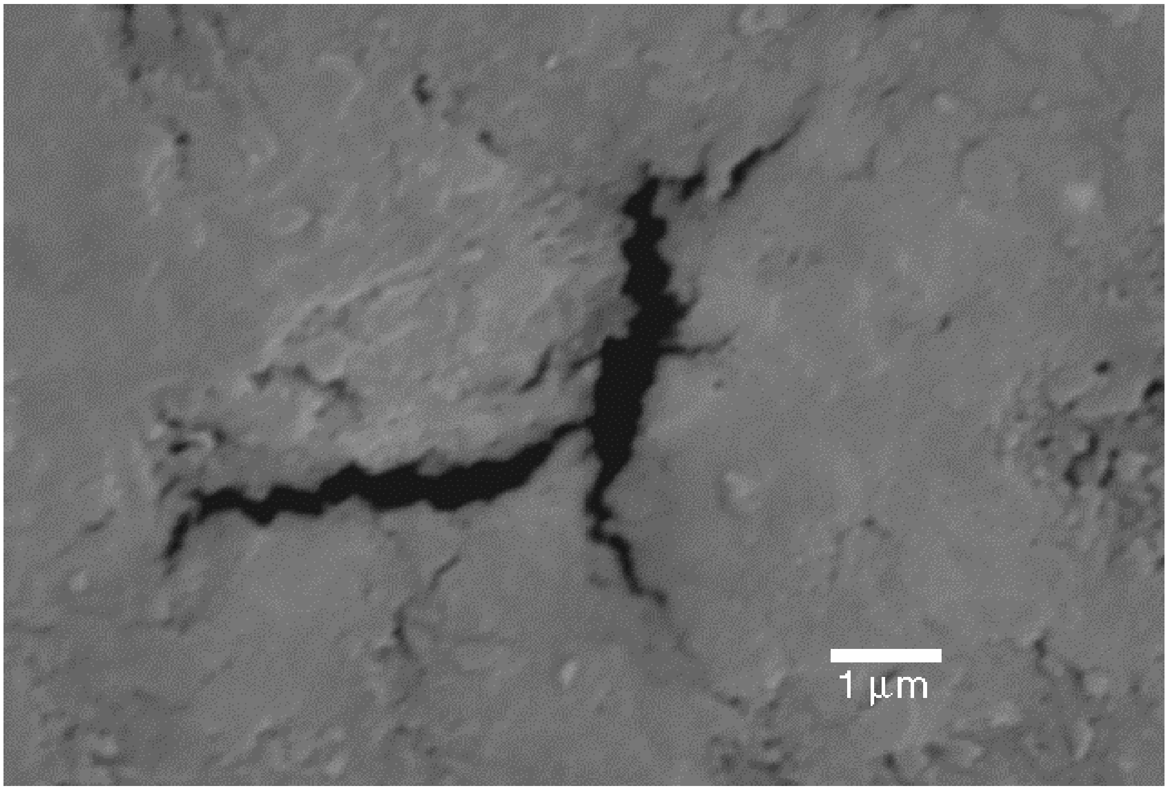

Figure 2. High Magnification SEM Image of Zone A of the 70% PG/30% Cement Block Showing <1-Micron Rupture.

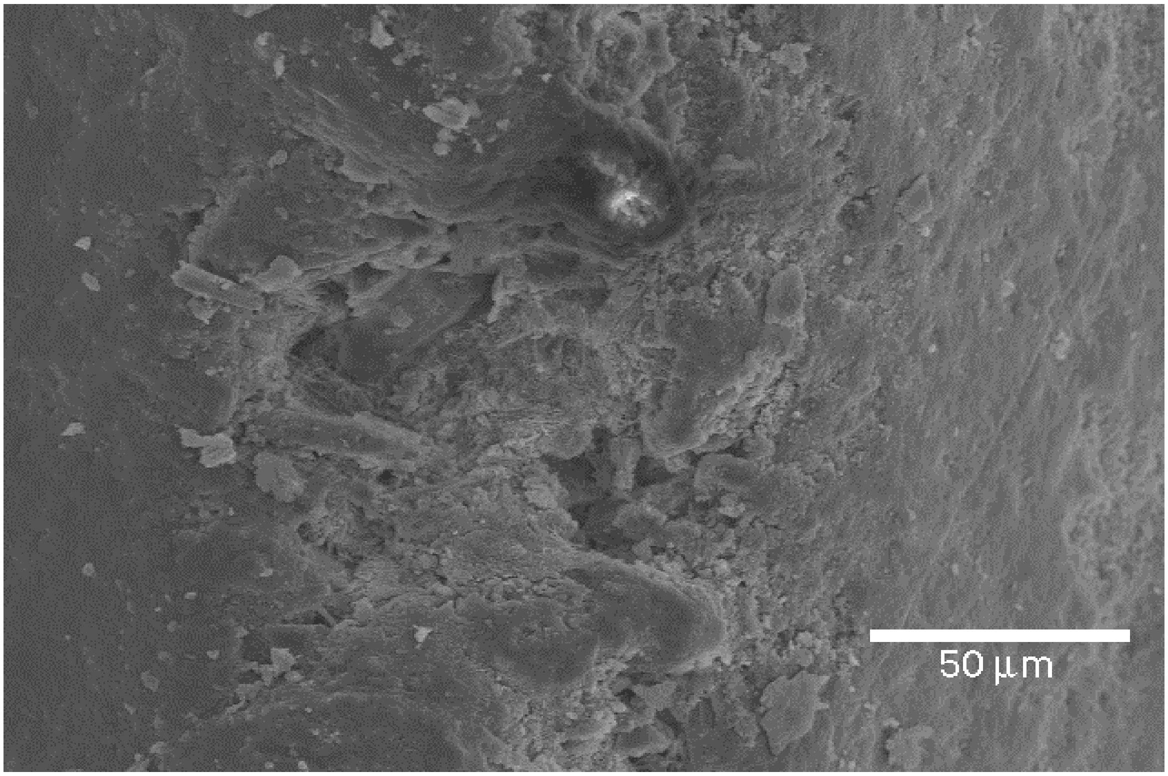

Figure 3. Ettringite Crystals (Slightly Left of Center) in Zone A of the 70% PG/30% Cement Block. On the Right is the Block Exterior.

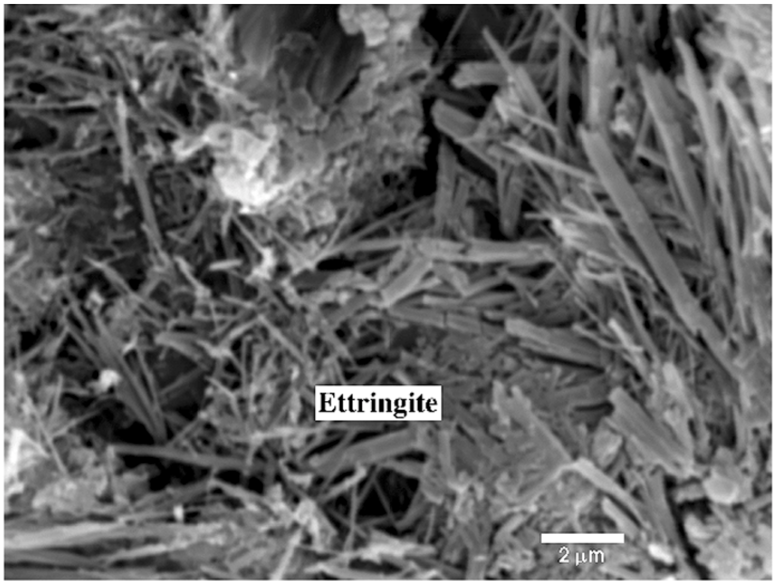

Figure 4. Higher Magnification of the Ettringite Crystals in Zone A of the 70% PG/30% Cement Block in Figure 3.

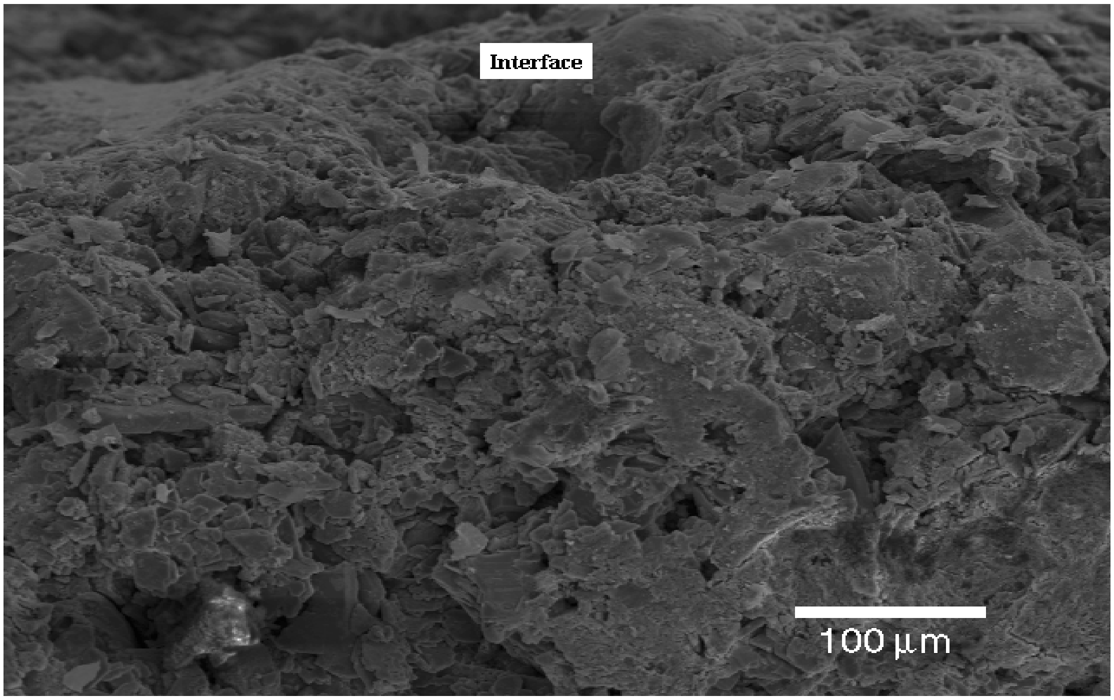

Figure 5. Zone A of the 85% PG/15% Cement Block. On Top is the Block Exterior.

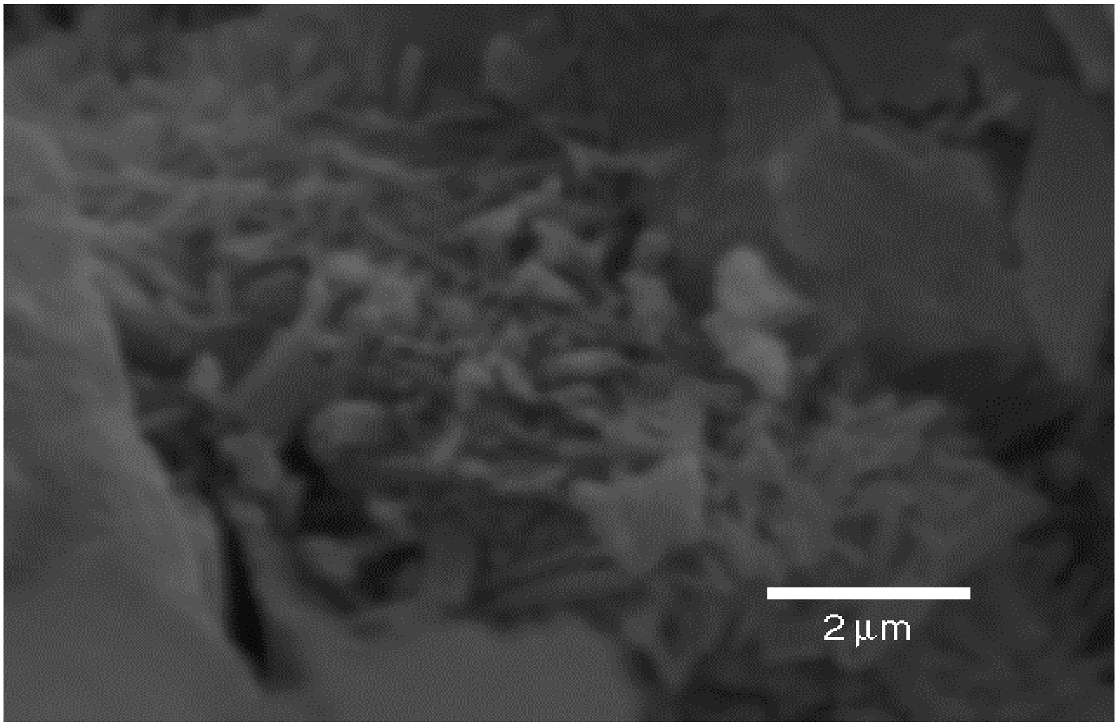

Figure 6. Ettringite Crystals in Zone A of the 85% PG/15% Cement Block.

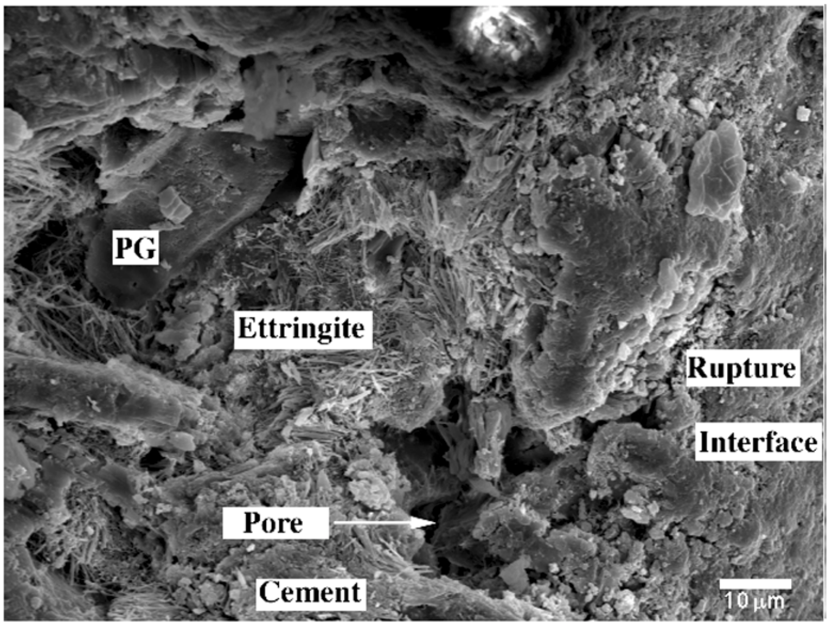

Figure 7. Zone B of the 70% PG/30% Cement Block. To the Right is Zone A.

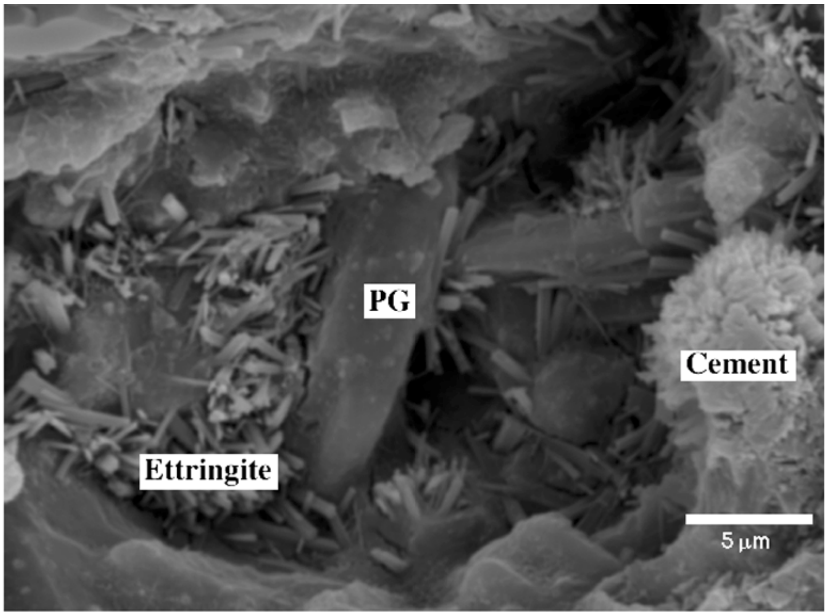

Figure 8. Ettringite Crystals throughout Zone B of the 85% PG/15% Cement Block.

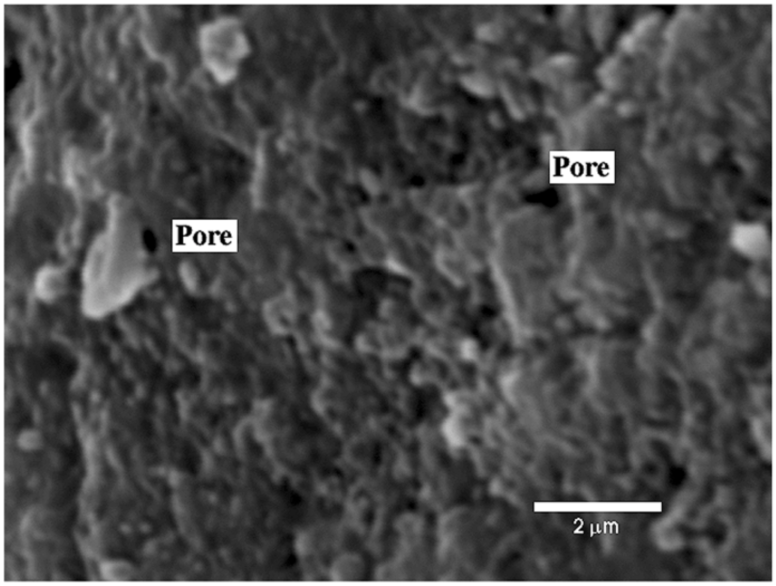

Figure 9. Zone C of the 70% PG/30% Cement Block. Hardly Any Pores Can Be Seen.

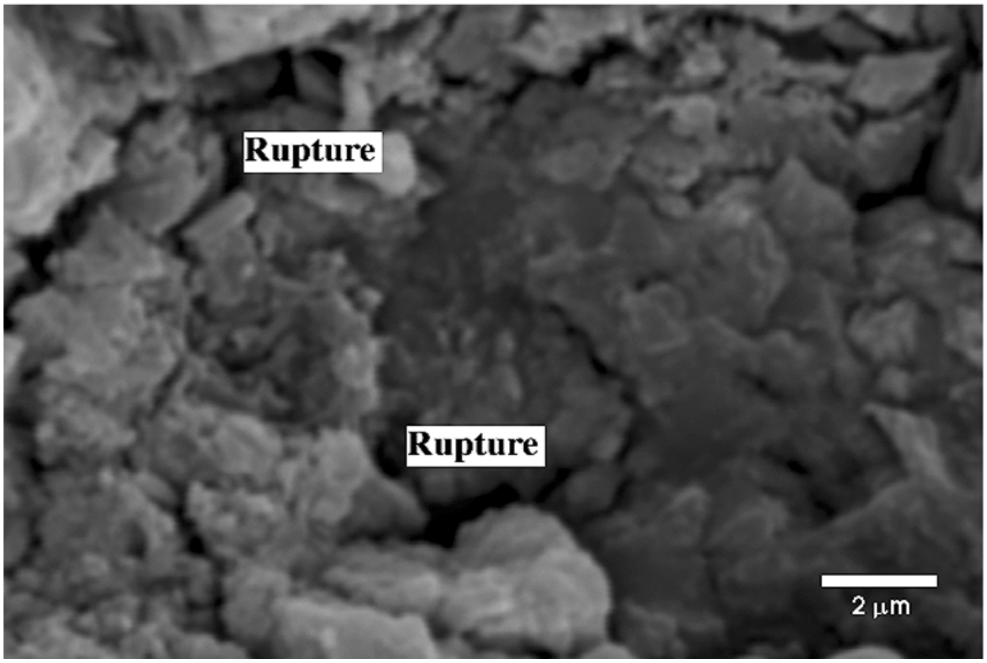

Figure 10. Zone C of the 85% PG/15% Cement Block. Pores and Ruptures Are Highly Visible.

The 30% cement PG blocks generally performed satisfactorily and did not exhibit significant surface softening. PLM observations and SEM images showed that a distinct layer identified as calcite ($CaCO_3$) formed on these blocks (Figure 11). This layer protected the block from seawater erosion and dissolution. Figure 11 was taken under crossed nicols from a polarized light microscope with a magnification rate of 100×. This image clearly showed the formation of a crystalline layer on the surface of the composite.

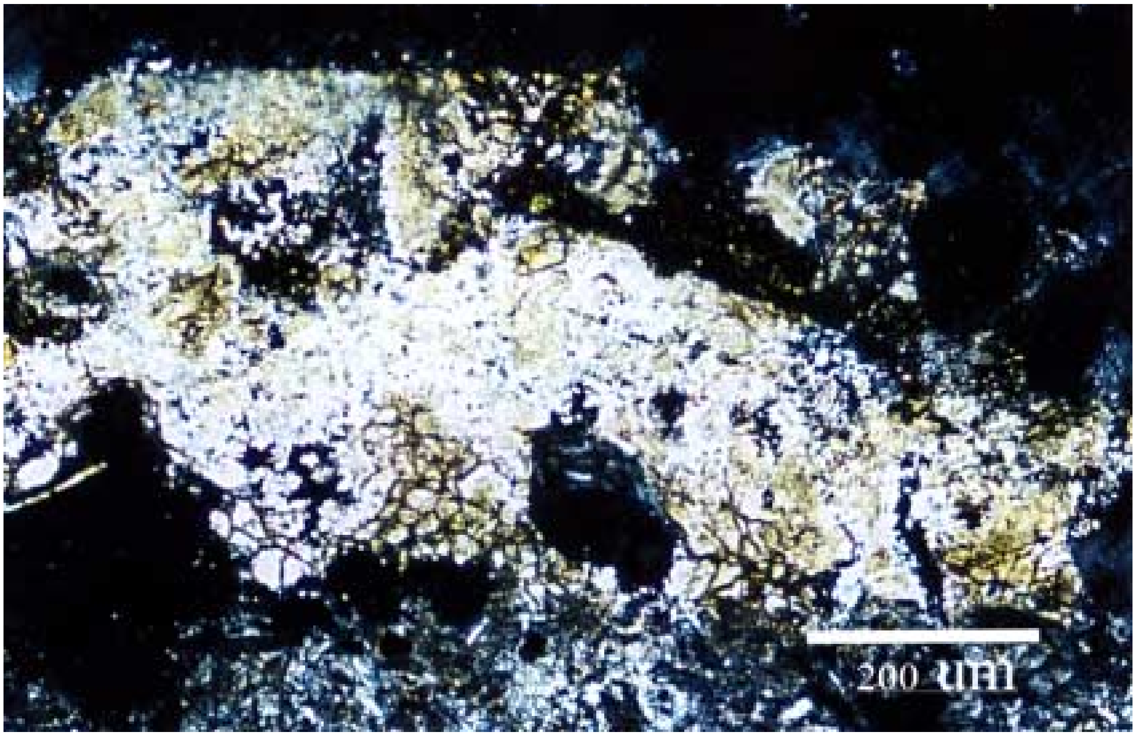

Figure 11. The PLM Cross Nicols Image of 70% PG/30% Cement Block Showing the Calcite Layer.

When an accessory plate (gypsum plate) was inserted, the high-order white interference color remained on the coating layer (Figure 12). When viewing this thin-section at a magnification rate of 600×, the flash relief phenomenon was observed. The high order white interference and flash relief phenomenon indicate that the coating layer is composed mainly of carbonates.

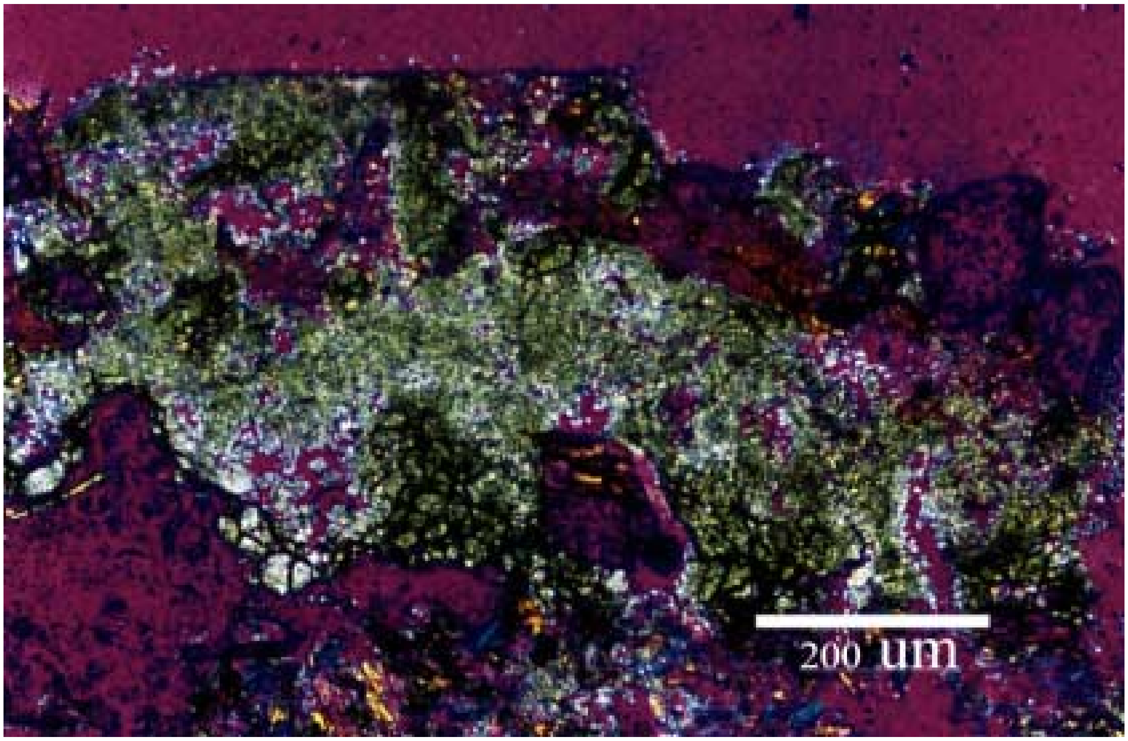

Figure 12. **The PLM Cross Nicols Image of the Same 70% PG/30% Cement Block in Figure 11 but with an Accessory Plate Inserted. The High-Order White Interference Color Remained, Suggesting that the Layer was Mainly Carbonates.**

The elemental content images (100×) of S and Ca for the 70/30 composites are presented in Figure 13.

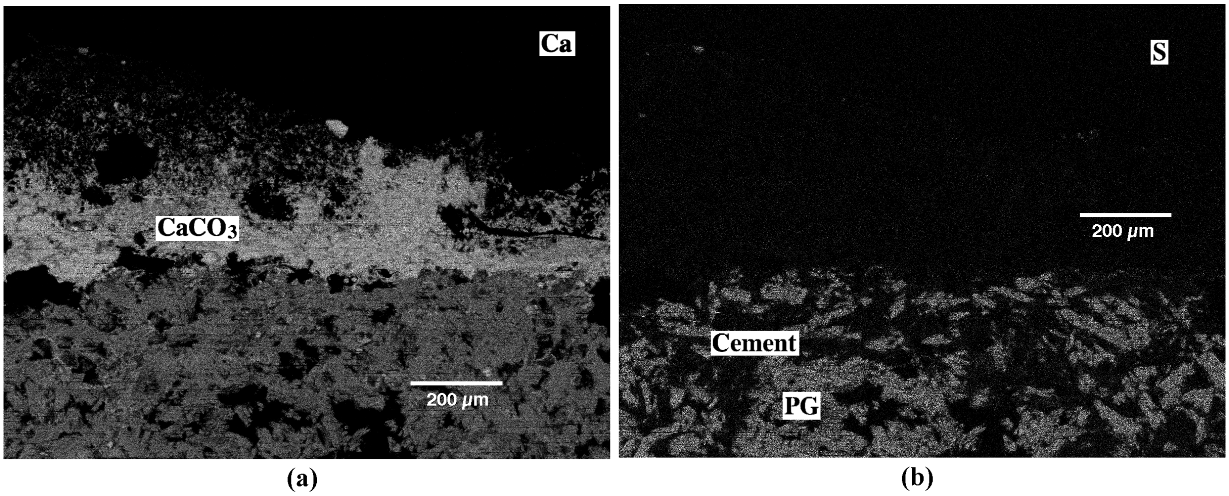

Figure 13. **The PLM Cross Nicols Image of 70% PG/30% Cement Block Showing the (a) Calcite Layer and (b) the Absence of Sulfur in the Calcite Layer.**

The Ca content image shows that the coating on the PG block surface contains a higher content of Ca than observed in the PG block body. Additionally, the Ca content in the coating is uniform, indicating that the coating is a mineral not a mixture. The S content image shows that the coating does not contain sulfur, and the sulfur content in the composite body is not uniform. The non-uniform distribution of S implies that the composite body is a mixture of minerals with high S content and low S content, which coincides with the materials making up the block. The cement does not contain significant S, while PG ($CaSO_4 \cdot 2H_2O$) does. The back-scattered electron image (1500×) of the coating is presented in Figure 14.

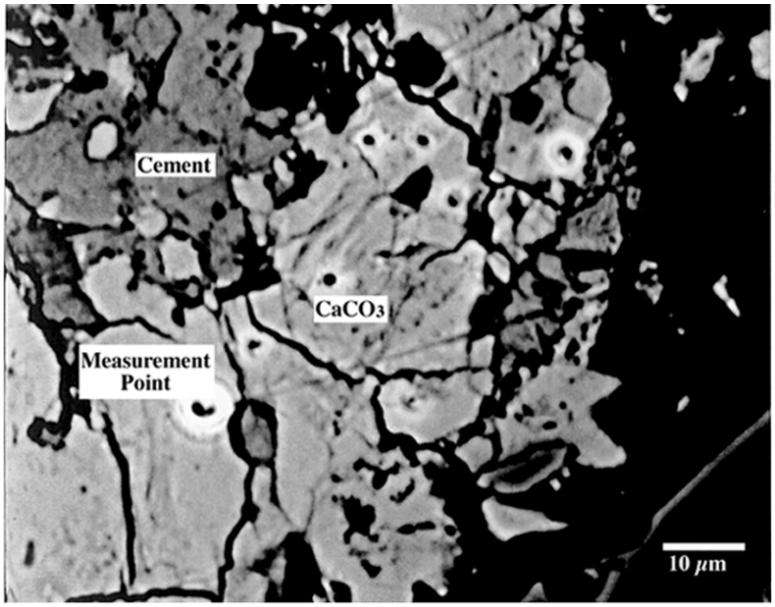

Figure 14. The Back-Scattered Electron Image (1500×) of the Carbonate Coating Showing Seven Measurement Points with their Circular White Rings that Were Formed by Electron Beams during Microprobe Quantitative Analysis.

It shows seven measurement points with their circular white rings that were formed by electron beams during microprobe quantitative analysis, whose results are presented in Table 6. The coating must be $CaCO_3$ with a 0.5% weight of $MgCO_3$. Since the coating sample was very small, the crystal forms of the $CaCO_3$ could not be identified exactly; i.e. calcite or its allomorph aragonite cannot be distinguished. However, the observed CaO content of 53.3% is close to the 55.3% CaO content of USNM No. 136321 calcite ($CaCO_3$) mineral provided by the Smithsonian Institution, Washington, DC.

Table 6. Quantitative Microprobe Analysis of the Surface Calcite Layer in PG/Cement Blocks.

Measurement	% CaO	% MgO
1	52.74	0.2844
2	53.39	0.1836
3	54.58	0.4504
4	53.46	0.3639
5	53.76	0.2596
6	52.00	0.2915
7	52.59	0.2704
Mean ± S.D.	53.22 ± 0.32	0.30 ± 0.03

Carbonates found in marine environments consist of $CaCO_3$ and about 5% $MgCO_3$ by weight (Andersen and Malahoff 1977; Drever 1977). The semi-quantitative analysis shows that there exists a Mg content gradient from the surface to the inner zones. The PG composite surface has high content of Mg while the PG composite center has lower Mg content. In an estuary bottom-water environment, $CaCO_3$ (calcite) is supersaturated at the saturation index of 590% (Guo et al. 1989). The pH value on the PG block surface is above 11 based on our measurements. The higher pH and supersaturated condition with respect to calcite would result in the precipitation of $CaCO_3$. The above results and observations suggest that the coating must have formed in an environment of high pH>11 on the composite surface. Therefore, the reactants Ca^{2+}, Mg^{2+}, and CO_3^{2-} are mainly from seawater not from the PG/cement composite.

In contrast, no evidence of calcite formation was found in 15% cement PG blocks. Or even if a calcium carbonate coating was formed as observed in laboratory tests, this coating most probably was not strong enough to resist water current and fell apart. Without the protection of a $CaCO_3$ coating, the permeability of the PG blocks is higher, which permits water to enter the PG composites and dissolve phosphogypsum crystals on the surface and in the pores. Well-developed ettringite was observed in the larger pores and ruptures (100-micron diameter pores and 50-micron wide ruptures in Zone A in the 15% blocks compared to <1 micron in the 30%; Figures 2-6), which explains why there was dissolution. Cracks extended to Zones B and C in 15% cement blocks (Figure 8 and 10). According to the double-layer theory, the solution on the PG block wall will reach saturation state. The high concentration of sulfate ions in PG can react with C_3A (tricalcium aluminate; $3CaO{\cdot}Al_2O_3$) to form ettringite crystals. This reaction is:

$$C_3A + 2CS'H_2 + 26H \longrightarrow C_3A{\cdot}3CS'H_{32}$$

When this reaction is completed the volume increases by 227% (Neville 1995). When the volume increase exceeds the tolerance-expanding limit of the hardened hydrated cement paste, ruptures develop. The ruptures increase the dissolution of the phosphogypsum that in turn will further enhance the formation of ettringite. This cycle will continue until the

PG blocks are fully eroded. Although ettringite formation was the main reason for dissolution, magnesium salts can also react with Portland cement paste in seawater resulting in the formation of brucite (magnesium hydroxide) and soluble products like calcium chloride and calcium sulfate. In old concrete, a magnesium silicate ($4MgO \cdot SiO_2 \cdot 8H_2O$) has been identified resulting from ion exchanges between seawater and calcium silicate hydrates present in hydrated Portland cement (Mehta 1991). This substitution makes concrete weak and brittle.

The above results indicated the need to minimize ettringite formation and enhance calcite formation to maintain the integrity of the PG blocks. Among possible solutions identified were:

a) Using low C_3A content cement (e.g., Type V or pozzolan blended cement);
b) Incorporating mineral admixtures to enhance the formation of stable hydration products (e.g., mixing lime, coal, fly ash, waste quarry fines/silt);
c) Increasing fabrication pressure to reduce pore spaces and rupture size,
d) Use of a polymer binding agent,
e) Surface coating of PG blocks, and
f) Some combination of the above.

Enhancing the formation of calcite using admixtures and fabrication at higher pressures were decided to have the greatest potential to address the dissolution issue at low cost. Hence, composites of PG with cement, lime, and/or fly ash were tested, and the blocks were fabricated at a compaction pressure of 98 MPa compared to 22 MPa at the most in previous research. As mentioned earlier, no notable compaction was achieved at any higher compaction pressures.

SUBMERGENCE AND LEACHING TESTS RESULTS

Table 7 shows the diameter of the blocks as measured after 3, 6, and 9 weeks of field submergence at Grand Isle, Louisiana. The 3-week results were encouraging, with three PG/cement/lime composites (% Cement/% Lime of 4.0/13.0, 5.7/9.7, and 9.0/8.0) showing the least erosion and actually supporting biological growth, primarily marine algae, oysters, and barnacles.

Table 7. Diameters of Phosphogypsum-Cement-Lime Blocks after 3, 6, and 9 Weeks of Seawater Submergence. The Original Diameter of All Blocks Was 38.1 mm. A Larger Diameter Means that the Block Supported Biological Growth.

Composition			Mean Diameter ± SD (mm) after a Submergence Period of:			
% Cement	% Lime	% PG	3-weeks	6-weeks	9-weeks	12-weeks
4.0	13.0	83.0	38.68 ± 0.49	38.84 ± 0.87	34.99 ± 3.78	33.70 ± 0.38
5.7	9.7	84.6	38.60 ± 0.05	36.28 ± 0.82	35.01 ± 2.48	33.40 ± 0.63
9.0	8.0	83.0	38.56 ± 0.15	38.24 ± 0.92	34.98 ± 2.80	33.04 ± 1.53
14.0	3.0	83.0	38.11 ± 0.34	34.67 ± 0.45	29.66 ± 2.73	25.11 ±4.28[*]
10.7	4.7	84.6	37.31 ± 0.8	35.06 ± 0.35	31.71 ± 0.65	29.84 ±2.55
7.3	6.3	86.4	37.64 ± 0.41	33.98 ± 0.33	28.90 ± 2.27	30.16 ±5.03[*]
9.0	3.0	88.0	36.20 ± 0.86	30.99 ± 0.43	25.57 ± 2.28	29.40 ±1.58[*]
4.0	8.0	88.0	35.96 ± 0.76	30.49 ± 0.55	27.13 ± 1.15	Fell apart
0.0	13.0	87.0	37.42 ± 1.23	33.78 ± 0.31	28.23 ± 0.73	29.76 ±.73[**]
5.7	4.7	89.6	33.89 ± 2.30	30.87 v 0.91	25.50 ± .19[**]	25.50 ±.61[*]
4.0	3.0	93.0	32.79 ± 3.02	30.83 ± 1.31	Fell apart	Fell apart
0.0	10.0	90.0	34.53 ± 2.60	29.72 ± 0.84	Fell apart	Fell apart
0.0	7.0	93.0	29.81 ± 1.46	Fell apart	Fell apart	Fell apart

* Only one sample left.

** Only two samples left.

This was reflected earlier as an increase in diameter after 3 weeks from the original 38.1-mm. Deterioration was apparent, however, after longer periods of submergence as can be seen in the changes in diameters in Table 7. An illustration of a deteriorating block is shown in Figure 15. Edges tend to erode first, gradually rounding the blocks until they eventually fall off or break apart. Only 3 composites had an average diameter of about 35-mm after 9 weeks (4.0/13.0, 5.7/9.7, and 9.0/8.0). The same composites had diameters of 33 mm or more after 12 weeks.

Figure 15. An Example of a Deteriorating PG/Cement/Lime Block Submersed at Grand Isle, LA. Edges Tend to Erode First, Rounding the Blocks.

It will be noted that the same composites leached less calcium in the dynamic leaching tests, results of which are shown in Figure 16. It can also be seen that the 10.7/4.7 composite performed well in the DLT. It did not do very well in the field test (in terms of size/erosion) but held up to the 12-week test. The 14.0/3.0 composite was good after 3 weeks but clearly deteriorated later. With concurring results, it becomes apparent that calcium leaching evaluated in the laboratory through dynamic leach test provides a good indication of how composites will perform in the field. During the DLT, calcite formation was observed to begin after about 7 hours in all composites. However, this was sustained only in blocks that maintained integrity (i.e., 4.0/13.0, 5.7/9.7, and 9.0/8.0 cement/lime, and the 70/30 PG/cement), where complete coatings were observed after about 2 days.

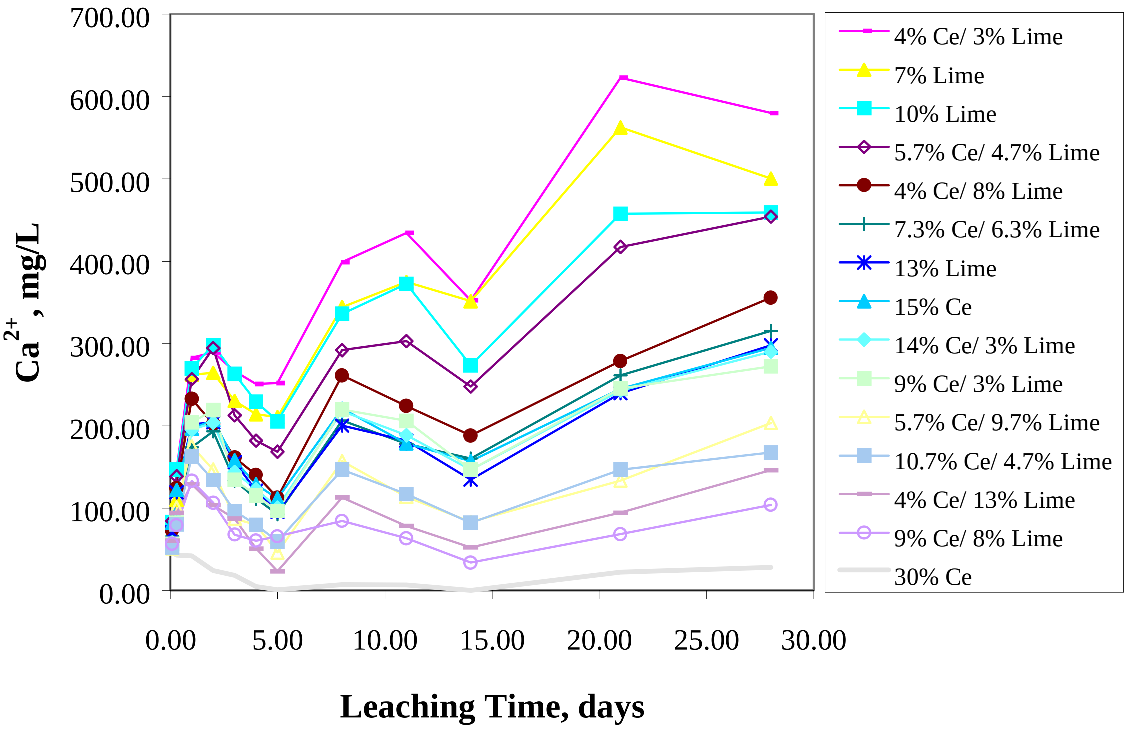

Figure 16. **Changes in Calcium Concentration with Time during the Dynamic Leaching Test. The Blocks that Leached Less Calcium Held Up Better in the Field Submergence Test.**

The surface hardness of the PG/cement/lime composites before and after the flow-through and dynamic leaching tests are shown in Table 8. Surface hardness of the 70/30 PG/cement blocks was not affected by submergence compared to the nearly 17-fold decline in that of the 85/15 blocks. There is no direct correlation between initial surface hardness values and block integrity of the PG/cement/lime composites. The hardest composite (10.7/4.7 cement/lime), pre-submergence, did not do very well in both field submergence and flow-through test. Likewise, the three composites (4.0/13.0, 5.7/9.7, and 9.0/8.0) that endured 12 weeks of field submergence have varying hardness before and after submergence, with the 83% PG, 4% cement, and 13% lime composite showing most promise.

Table 8. Surface Hardness of Phosphogypsum-Cement-Lime Blocks after a Standard 28-Day Curing Process, a 22-Day Flow-Through Test, and a Dynamic Leaching Test (DLT).

Composition			Mean Surface Hardness ± SD (mm^{-1})		
% Cement	% Lime	% PG	Cured	Flow-Through	DLT
10.7	4.7	84.6	99.07 ± 41.80	26.99 ± 20.71	18.47 ± 18.34
5.7	9.7	84.6	79.07 ± 48.77	22.18 ± 8.94	28.94 ± 21.03
4	8	88	77.78 ± 37.92	27.59 ± 9.84	12.43 ± 11.84
9	3	88	72.59 ± 27.50	26.58 ± 11.15	16.39 ± 16.71
5.7	4.7	89.6	70.00 ± 39.92	13.99 ± 6.18	4.44 ± 5.13
4	13	83	68.89 ± 26.27	30.71 ± 27.32	36.11 ± 24.57
7.3	6.3	86.4	67.96 ± 24.07	29.05 ± 10.25	21.66 ± 18.19
0	13	87	67.59 ± 54.69	17.06 ± 11.31	20.22 ± 28.85
0	10	90	65.74 ± 24.57	15.95 ± 8.97	6.53 ± 13.76
9	8	83	64.82 ± 24.18	28.27 ± 11.94	29.05 ± 22.45
0	7	93	58.15 ± 38.86	13.34 ± 7.09	2.31 ± 1.96
14	3	83	54.63 ± 13.77	29.09 ± 12.99	17.09 ± 16.74
4	3	93	48.33 ± 16.62	11.84 ± 23.24	4.79 ± 4.73
15	0	85	61.85 ± 25.44	Not tested	3.73 ± 2.85
30	0	70	111.11 ± 42.78	Not tested	109.72 ± 45.20

Hardness of submersed PG/cement/lime blocks were generally 2-5 times less than initial values, but had very poor correlation with initial hardness (Figure 17). It will be noted that the PG/cement/lime composite with most cement (14/3) did not perform any better than those with less cement. However, lime apparently helped as evidenced by the better performance of composites with similar cement but higher lime content.

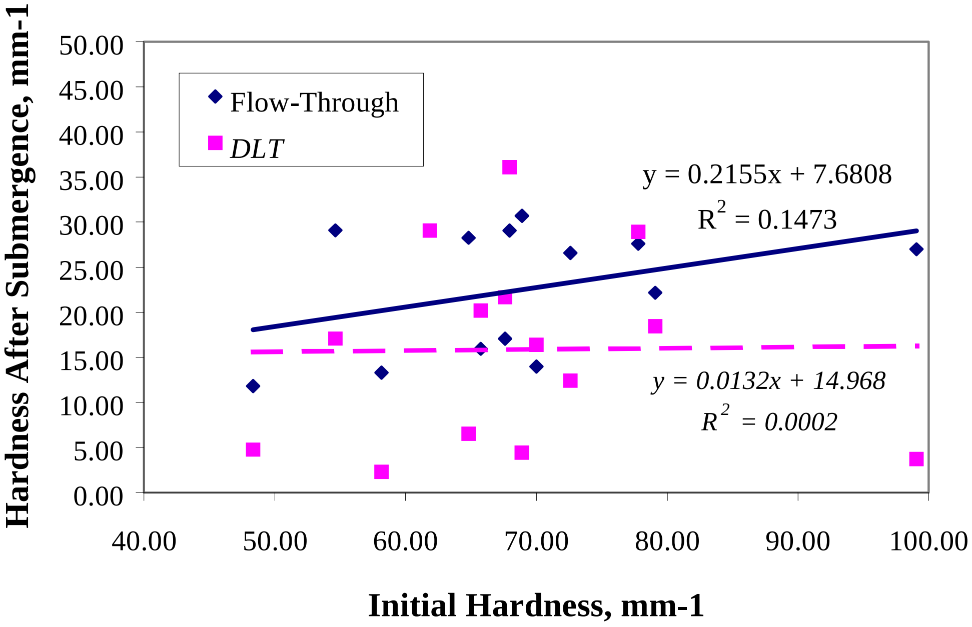

Figure 17. Poor Correlation between Block Hardness Before and After Submergence Tests.

Similarly, the stability of blocks is difficult to predict using unconfined compressive strength (UCS). Table 9 presents the PG/cement/lime composites in order of decreasing UCS. The hardest composite, 10.7/4.7 cement/lime, had highest UCS, but was not stable in saltwater. The stable composites (4.0/13.0, 5.7/9.7, and 9.0/8.0) had varying degrees of UCS, which also illustrates the limitation of this physical characteristic as an indicator of block stability.

Table 9. Unconfined Compressive Strength (UCS) of Phosphogypsum-Cement-Lime Blocks after a Standard 28-Day Curing Process, a 22-Day Flow-Through Test, and a Dynamic Leaching Test (DLT).

Composition			UCS ± SD (MPa)		
% Cement	% Lime	% PG	Cured	Flow-Through	DLT
10.7	4.7	84.6	29.10 ± 1.50	14.92 ± 2.63	11.48 ± 1.21
14	3	83	28.50 ± 4.41	14.21 ± 0.86	14.78 ± 1.74
7.3	6.3	86.4	24.17 ± 0.98	10.90 ± 0.79	9.23 ± 1.06
9	8	83	23.31 ± 1.34	15.32 ± 0.82	16.08 ± 1.39
9	3	88	23.21 ± 11.02	7.97 ± 0.91	10.57 ± 0.68
4	13	83	21.98 ± 0.66	10.21 ± 1.36	11.12 ± 1.36
5.7	9.7	84.6	19.84 ± 1.06	10.50 ± 1.27	7.71 ± 1.11
5.7	4.7	89.6	17.40 ± 1.53	6.54 ± 1.24	5.87 ± 0.85
4	8	88	15.35 ± 1.35	7.98 ± 2.16	6.71 ± 0.20
4	3	93	12.99 ± 0.98	3.82 ± 0.50	6.32 ± 1.24
0	13	87	10.23 ± 1.82	3.75 ± 0.07	4.73 ± 0.76
0	7	93	9.56 ± 0.20	2.96 ± 0.23	3.92 ± 1.24
0	10	90	8.91 ± 1.08	3.67 ± 0.80	5.16 ± 1.67
15	0	85	29.63 ± 3.85	Not tested	12.64 ± 1.09
30	0	70	26.76 ± 6.60	Not tested	26.09 ± 4.48

However, there was a strong correlation between initial UCS and UCS after submergence as shown in Figure 18, with consistent trends in both the flow-through and dynamic leaching test.

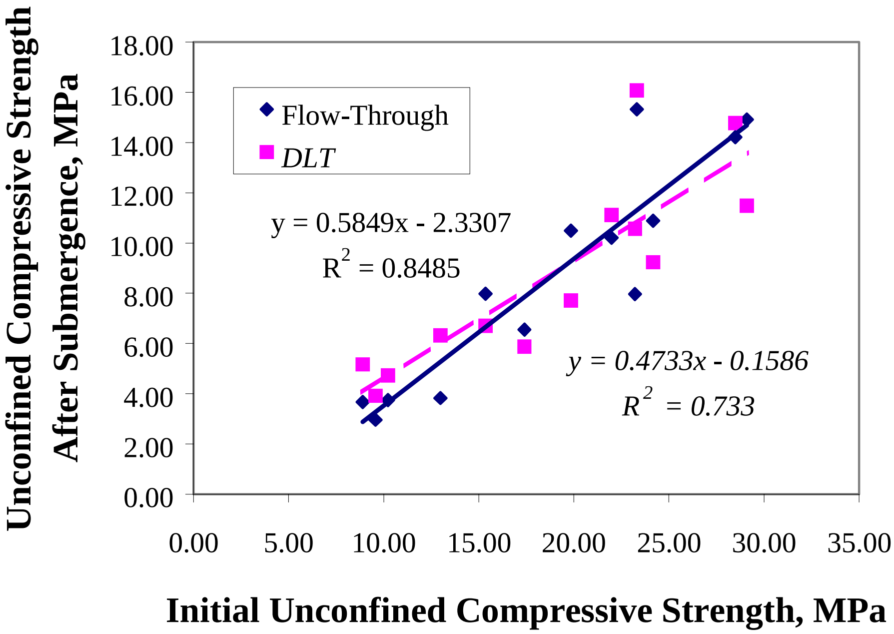

Figure 18. Good Correlation between the Unconfined Compressive Strength of Blocks before and after Submergence.

CONCLUSIONS AND RECOMMENDATIONS

The importance of preventing dissolution of phosphogypsum to make it an effective material for artificial reefs, shoreline stabilization structures, and oyster settlement substrate has been demonstrated. From results of the oyster set study, it is impossible to determine whether we had a failed oyster set on the PG briquettes or if the set was initially successful and the oyster were later sloughed during dissolution. The time series data show that if set did occur, they were quickly dislodged during the course of dissolution. Our previous research has shown conclusively that oysters will set and grow robustly on cement consolidated PG. The lack of set oysters on PG briquettes in this study, therefore, is probably not due to any adverse effects strictly attributable to the constituent PG but from the material lost from dissolving PG briquettes.

Optic imagery analysis showed that a distinct layer identified as calcite ($CaCO_3$) formed on 70% PG/30% cement blocks that did not exhibit softening when submersed in saltwater. This layer protected the block from seawater erosion and dissolution. Results and observations suggest that the coating must have formed in an environment of high pH>11 on the composite surface, and is mainly the byproduct of seawater and PG block reaction, not from the PG block content. On the other hand, ettringite formation was identified as the main reason for dissolution in 85% PG/15% cement blocks. Without the protection of a $CaCO_3$ coating, the permeability of the PG blocks is higher, which permits water to enter the PG composites and dissolve phosphogypsum crystals on the surface and in the pores. Ruptures develop as ettringite is formed, which further enhances the formation of ettringite. This cycle will continue until the PG blocks are fully eroded.

There was no correlation between the stability of PG blocks in saltwater and surface hardness, as well as compressive strength. These physical characteristics are not good indicators of the integrity of composite PG in marine applications. Calcium leaching evaluated in the laboratory through dynamic leach test provides a good indication of how composites will perform in the field. The same cement/lime PG composites (4.0/13.0, 5.7/9.7, and 9.0/8.0) that endured 12 weeks of field submergence were identified to leach the least calcium in the laboratory. A gradual reduction in block size despite biological growth was observed in the field test, suggesting the addition of lime is not fully adequate. However, lime apparently helped as evidenced by the better performance of composites with similar cement but higher lime content.

The incorporation of fly ash as an ingredient seems to be a good alternative as demonstrated in additional studies where combinations of PG (55-62%), cement (3-10%), and fly ash (35-42%) showed little signs of deterioration after field submergence. Further intensive tests with fly ash and other admixtures to identify an optimum ingredient combination is recommended, including an economic analysis to identify the most favorable combination that can be manufactured at least-cost.

PART II. COMPOSITE STABILITY

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June 1998

INTRODUCTION

Phosphogypsum (PG), a solid by-product of wet process phosphoric acid manufacturing, has been classified as a "Technologically Enhanced Natural Radioactive Material" (TENR) because it contains radionuclides and some trace metals in concentrations that may pose a potential hazard to human health and the environment. The main disposal method, on-site stockpiling, has resulted in some problems. Environmental concerns associated with PG disposal, coupled with increasing land costs for stockpiles, have promoted research on alternative beneficial uses of this solid waste that will result in applications considered protective of public health. Two such applications are artificial reefs and oyster substrate.

The researchers feel that utilization of phosphogypsum for underwater applications provides the best means for minimizing public exposure because the airborne vector of transmission of radon gas is eliminated or, at least, significantly diminished. An initial, informal pilot demonstration study conducted at Louisiana State University showed that PG/cement test blocks placed in the Gulf of Mexico supported a diverse population of surface attached and burrowing organisms, indicating the potential of using PG for offshore artificial reefs. Further research supported by the Louisiana Education Quality Support Fund (LEQSF) demonstrated the durability of PG composite blocks under uncontrolled environmental conditions and has indicated no significant impact on the surrounding microcosm (Malone et al. 1996). However, these blocks were fabricated using a high Portland cement content and would not be economically feasible.

The long-term goal of phosphogypsum research at LSU is to provide an alternative use for PG that will be safe or safer, from a public health point of view, than the present stockpiling disposal methods stipulated by the Environmental Protection Agency (EPA). One area that requires considerable research is the development of composite blocks/briquettes that maintain their structural integrity (durability) over the long term under seawater conditions. There are many factors that affect the durability, including cement type and content, admixture type and content, moisture content, dry density, fabrication technique, and curing and leaching times. This study was conducted to determine the effect of submergence time on the strength and surface hardness of different PG-sand-cement composite blocks and briquettes. PG blocks (5.08 cm diameter x 9.53 cm cylinders, 193 cm^3) were used as surrogates for artificial reefs, while briquettes (5 cm^3) were investigated for use as oyster substrate.

METHODOLOGY

COMPOSITE PG BLOCK AND BRIQUETTE FABRICATION

Raw Materials

Raw phosphogypsum (PG) was obtained from the IMC-Agrico Co. phosphogypsum stack in Uncle Sam, Louisiana. Initially the wet PG was air-dried to remove most free water, then it was oven-dried at 45-50°C for 6-12 hours. The oven temperature was checked twice daily and adjustments made if necessary. The dried phosphogypsum was crushed and passed through a 1.46-mm sieve. The cement was a Type II Portland cement provided by the River Cement facility in Natchez, Mississippi.

Block Fabrication

To prepare the composites, the dry mixture of PG, Portland cement, and sand were thoroughly blended at the specified percentages based on dry solids weight, depending on the treatment (Table 10). Tap water was added at 15% of the total dry solids weight, and the mixture homogenized. Next, 376 grams of the resulting mixture were poured into a 5.08 cm diameter by 17.78 cm long tapered, steel mold, and compacted to a 9.53 cm long cylinder. The target dry density was set at 1.65-1.70 g/cm^3. The compaction load to achieve the desired dry density was approximately 3,182-3,636 kg (7,000-8,000 lbs), equivalent to 15-18 Mpa (2,228-2,546 psi). The blocks were fabricated using a Soil Test Compression Testing Machine following the static compaction procedure (BS 1924). The molded blocks were withdrawn from the mold and allowed to air cure for one to two hours. The blocks were then placed in double-layered plastic bags, sealed and cured at ambient temperature and 100% humidity for 28 days.

Table 10. Composition of Cement-Stabilized PG Test Blocks.

ID	Cement (%)	Sand (%)	PG (%)	Moisture (%)	Diameter (cm)	Height (cm)	Weight (wet, g)	Cement (g)	PG (g)	Sand (g)	Water (g)
1	5	0	95	15	5.08	9.53	376	16.4	311	0	49
2	10	0	90	15	5.08	9.53	376	32.8	294	0	49
3	15	0	85	15	5.08	9.53	376	49.2	278	0	49
4	5	10	85	15	5.08	9.53	376	16.4	278	32.8	49

Briquette Fabrication

Five briquette treatments were chosen to investigate the effects of percent cement and phosphogypsum form [dihydrate ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$)] on the structural integrity of the briquettes (Table 11). The briquettes were fabricated by K.R. Komerak Briquetting and Research, Inc., Anniston, Alabama. The briquettes were allowed to cure under sealed, ambient laboratory conditions for 14 days. The rough briquette edges were trimmed prior to any testing in order to better assess the structural integrity and chemical stability of the briquettes.

Table 11. Composition of Phosphogypsum Test Briquettes.

ID	Cement (%)	PG (%)	Moisture (%)	Surface Area (cm^2)	Volume (cm^3)	Drying Temperature (^oC)	PG Form
1	0	100	0	23.03	6.00	50	Dihydrate
2	1	99	3.5	16.75	4.35	50	Dihydrate
3	3	97	3.5	16.75	3.88	50	Dihydrate
4	0	100	0	23.03	6.48	80	Anhydrite
5	3	97	5.5	16.75	3.94	80	Anhydrite

SUBMERGENCE AND LEACHING TESTS

Phosphogypsum Blocks

The PG blocks were subjected to one of five treatments following the 28-day high humidity curing process. Three treatments were air curing for one, two, or five days, and two treatments were seawater submergence for 30 or 60 days. All treatments were run in triplicate. For each treatment, six PG blocks were placed in 60 cm (length) by 40 cm (width) by 20 cm (depth) covered, aerated, plastic containers. To represent field conditions, 40 liters of 35 parts per thousand (ppt) artificial seawater (Instant Ocean) were used as the submergence medium in each container. Three of the six blocks were removed after 30 days submergence and the other three after 60 days. The blocks were air-dried for a period of two days and tested for unconfined compressive strength and surface hardness.

Total dissolved solids in the submergence medium were measured to investigate possible dissolution of the PG composites with time. During the 30- and 60-day seawater submergence tests, 500 mL water samples were analyzed for total dissolved solids according to Standard Methods (APHA 1995).

Briquettes

The briquettes were subjected to a 30- and 60-day submergence test, which was similar to the blocks. Six briquettes were placed in two-liter bottles with a V/S (extraction fluid volume/briquette surface area) ratio of 8:1. The samples were not aerated. The submergence medium was 20 ppt, artificial seawater (Instant Ocean) to represent conditions observed in oyster planting areas. Three briquettes from each run were removed from the bottles after 30 and 60 days, air dried for 24 hours, and tested for crushing strength. One-half of the extraction fluid was removed following 30 days to maintain an 8:1 V/S ratio. A control containing 20 ppt artificial seawater only was also run to correct for evaporation. In addition, briquettes were placed in two-liter bottles containing 20 ppt artificial seawater at a V/S ratio of 8:1 and placed on a shaker table for 14 days. Briquettes from this study were removed from solution and tested wet.

CHARACTERIZATION OF PG COMPOSITES

Surface hardness, unconfined compressive strength for the blocks and crushing strength for briquettes were selected as important parameters to characterize the structural integrity of PG composites. It is presumed that optimum strength and hardness levels may be established that are required for the PG composites to withstand degradation in the marine environment. The strength and surface hardness of the samples were determined after curing (before the submergence tests), and after each of the submergence tests to determine the extent the composites are affected.

Surface Hardness

A cone penetrometer (Model No. WF21510, Humboldt Mfg., Inc.) was used to measure the penetration depth of the blocks and briquettes following the British Standard Methods of Testing Soils for Engineering Purposes (BS1377:1975). The inverse of the penetration depth was used as a measure of the surface hardness of the composites. The surface hardness of each block was measured at six equidistant points along the length and three blocks per composition were measured, while the surface hardness of the briquettes was measured at six random points.

Unconfined Compressive Strength and Crushing Strength

The unconfined compressive strength of the composite PG blocks was determined in triplicate using the INSTRON 8500 ServoHydraulic Machine in LSU's Department of Mechanical Engineering following the Test for Cylindrical Cement Specimens (ASTM D1633-84).

The maximum amount of compressive force the briquettes could withstand before crushing was measured using a Soil Test Compression Testing Machine equipped with a proving ring (Material Test System 810).

STATISTICAL ANALYSIS

Two-factor (composition and submergence/curing treatments) replicated analyses were conducted to compare the surface hardness and unconfined compressive strength of the PG-cement-sand blocks (or crushing strength for briquettes), using the General Linear Models procedure (GLM, assuming a 5 percent level of significance; SAS Institute, Inc., 1990). All statistical analyses were done using the SAS System for Windows Release 6.12, SAS Institute Inc., Cary, North Carolina (SAS Institute, Inc. 1990).

RESULTS AND DISCUSSION

SURFACE HARDNESS

Phosphogypsum Blocks

Table 12 shows the surface hardness of the PG blocks for different cure times in air following the 28 day standard curing process and different submergence times in 35 ppt artificial seawater. Surface hardness improved with air curing, with 2-days air curing generally sufficient to attain maximum hardness. Surface hardness decreased significantly after 30-days of seawater submergence, with the surface hardness of PG blocks with 5% cement, 10% cement, and 5% cement with 10% sand reduced by about 10 times, and that of 15% cement by about 6 times. There was no significant difference between surface hardness at 30-days and 60-days submergence for each block composite. Since the submergence water was not replaced, it was not clear if further softening or complete dissolution would occur at longer submergence periods. It was strongly suspected that chemical equilibria between the blocks and the seawater prevented further dissolution after 30 days. However, the results suggest that softening will be apparent within 30 days.

Table 12. The Surface Hardness ± SD (mm^{-1}) of Composite PG Blocks for Different Cure Times in Air and Different Submergence Times in 35 ppt Seawater (C = Cement, S = Sand).

ID	Compo-sition	1 Day Cure (n=2)	2 Day Cure (n=2)	5 Day Cure (n=2)	30 day Submergence (n=9)	60 day Submergence (n=4 to 6)
1	5% C	5.54 ± 0.60	7.86 ± 2.40	7.71 ± 0.85	0.78 ± 0.04	0.79 ± 0.07
2	10% C	5.62 ± 0.54	14.2 ± 3.82	12.9 ± .49	1.37 ± 0.33	1.48 ± 0.32
3	15% C	9.77 ± 0.12	17.4 ± 6.58	18.5 ± .00	3.27 ± 1.18	3.21 ± 0.03
4	5%C /10%S	3.75 ± 0.34	5.94 ± 0.53	6.44 ± .62	0.75 ± 0.05	0.77 ± 0.05

Since highly significant differences ($p>0.0001$) were obtained between composition and treatment, which also had highly significant interactions, the results need to be discussed on a case by case basis. Figure 19 illustrates the treatment versus the mean surface hardness for the four compositions. It is apparent that the interactions between composition and treatment were greater for the 15% cement and 5% cement 10% sand compositions than for the other two composites.

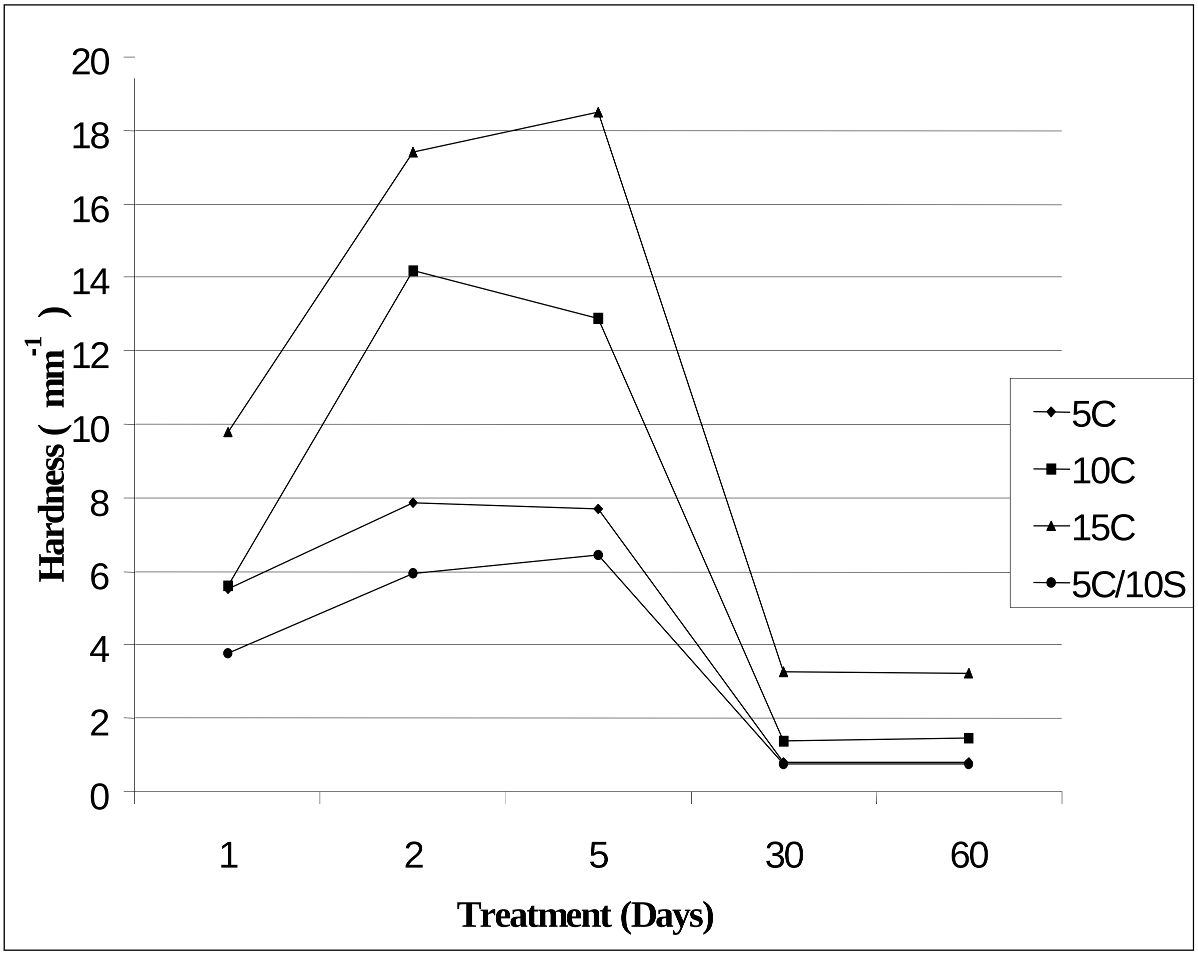

Figure 19. Surface Hardness versus Treatment for the Four Block Compositions.

Briquettes

Surface hardness of the briquettes was measured after a two-week curing time, 30- and 60-day submergence, and 14-day submerged shaking tests. The results are summarized in Table 13. For this test, the briquettes, initially and after submergence, proved to be harder than the PG-cement blocks, presumably due to the differences in fabrication technique. Like the blocks, the briquettes experienced a significant ($p>0.0001$) reduction in hardness when exposed to the artificial seawater, and this effect was most noticeable in the 14-day submergence with shaking test.

Table 13. Summarized Results of the Surface Hardness for Five Briquette Compositions Subjected to Various Tests (mm^{-1}) ± SD.

Composition	Initial (n=5)	14-day Submergence with shaking (n=3)	30-day Submergence (n=3)	60-day Submergence (n=3)
1 (0 cement; dihydrate)	55.2 ± 6.64	11.7 ± 2.96	14.3 ± 1.45	14.7 ± 0.33
2 (1% cement; dihydrate)	46.4 ± 2.91	9.0 ±2.52	15.7 ± 1.33	16.0 ± 1.53
3 (3% cement; dihydrate)	42.4 ± 1.12	12.7 ± 0.33	28.3 ± 3.53	19.3 ± 2.40
4 (0 cement; anhydrite)	42.8 ± 1.96	14.0 ± 0.00	16.7 ± 1.86	22.3 ± 0.88
5 (3% cement; anhydrite)	48.0 ± 2.07	2.0 ± 0.00	12.0 ± 0.58	10.7 ± 0.88

The circulation and water movement caused by the shaking activity most likely increased the diffusion process. The briquettes that were fabricated using dihydrate PG yielded harder briquettes than those made with anhydrite PG. However, the results suggest that 3% cement is insufficient to maintain briquette hardness high enough to offset degradation process, including erosion and burrowing organisms. The interactions between composition and treatment were highly significant (p>0.0001) and even more pronounced than for the blocks (Figure 20).

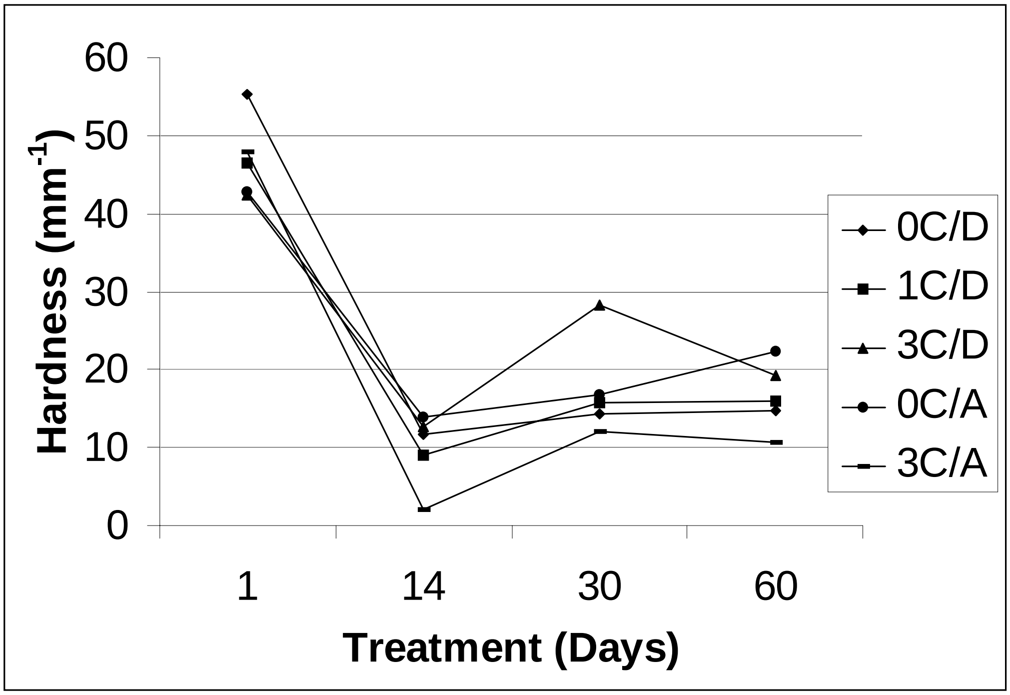

Figure 20. Surface Hardness versus Treatment for the Five Briquette Compositions.

UNCONFINED COMPRESSIVE STRENGTH OF BLOCKS

Table 14 shows the strength of PG blocks for a 65 day air curing period after the 30 day curing process in plastic bags and after different submergence times in 35 ppt artificial seawater. It can be seen that 30 days submergence in 35 ppt seawater greatly reduced the strength of PG blocks in the 5% cement, 10% cement, and 5% cement/10% sand. After 60 days submergence the strength of the 5% and 10% cement PG blocks increased to about the strength of 65 day cure in air. For 5% cement/10% sand PG blocks, the strength of 60 day submergence was about the same as that of 30 day. The 30-day and 60-day submergence in 35 ppt seawater did not change the strength of PG block with 15% cement. All strengths of the tested PG blocks meet the minimum desired strength of 500 psi for use as artificial reefs (Chen et al. 1995). However, 10% to 15 % cement appears more appropriate to ensure long term integrity, and because the seawater was not replaced during the entire submergence tests, the effect of chemical reactions and equilibrium on the blocks cannot be discounted. Interactions between composition and treatment were more apparent for the 30- and 60-day submergence tests than for the initial and 65-day air curing treatments (Figure 21). Highly significant differences ($p > 0.0001$) were obtained between compositions and treatments, which also had highly significant interactions. Again, however, since the medium was not replaced, the extent of the interactions is hard to determine.

Table 14. The Strength ±SD (psi) of Composite PG Blocks for 65 Day Cure in the Air, After 30 Day Cure in Plastic Bags and After Different Submergence Times in 35 ppt Seawater (C = Cement, S = Sand).

Composition	Presubmergence (n=3)	65-Day Cure in Air (n=5)	30-Day Submergence (n=9)	60-Day Submergence (n=5)
5% C	691 ± 123	1210 ± 167	703 ± 156	1135 ± 159
10% C	1603 ± 146	1911 ± 415	1522 ± 188	1951 ± 223
15% C	1344 ± 164	2218 ± 292	2285 ± 250	2141 ± 126
5%C/10%S	567 ± 80	983 ± 223	744 ± 137	774 ± 72

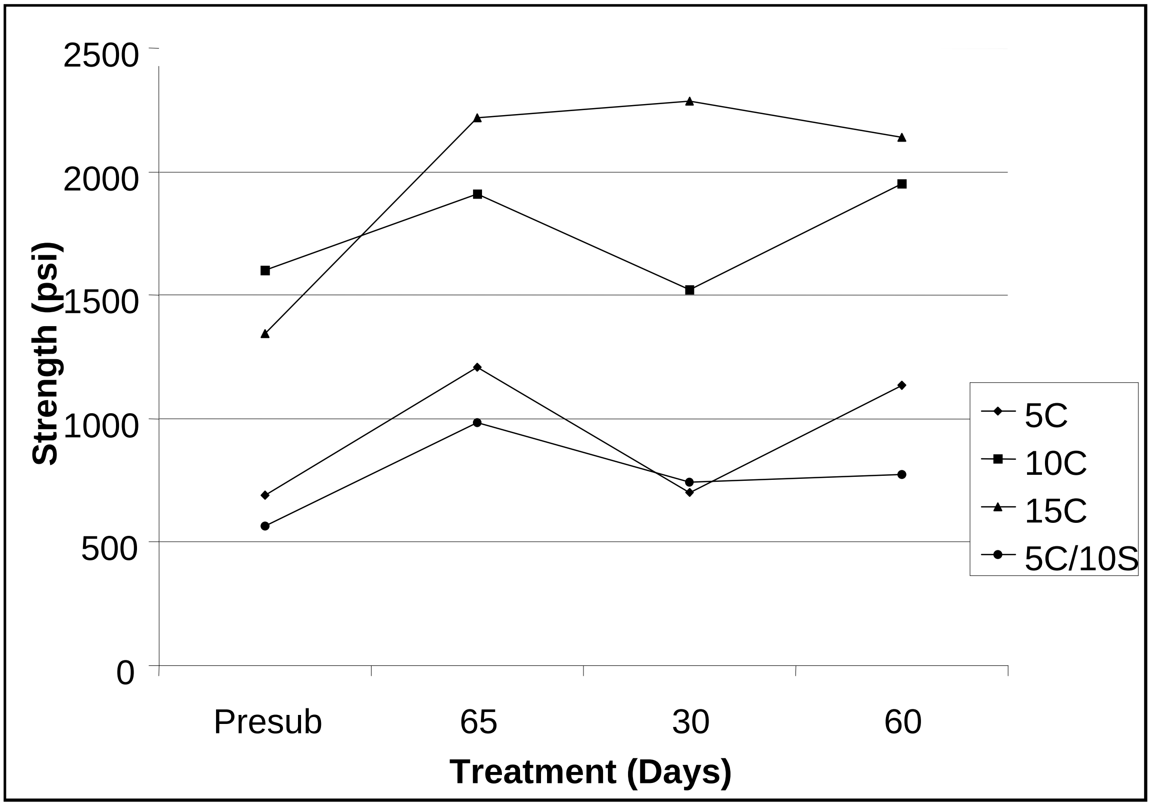

Figure 21. Strength (psi) Versus Treatment for the Four Block Compositions.

CRUSHING STRENGTH OF BRIQUETTES

While the briquettes were harder, their crushing strength was much lower than the unconfined compressive strength of the cement-PG blocks (Table 15). The decline in crushing strength of the PG-cement briquettes very much followed the trend observed with the briquettes' hardness. Softening and dissolution was apparent in the 14-day submergence with shaking test, which among the tests conducted best simulated field submergence. Similar to the blocks, the interactions (Figure 22) between composition and the 30- and 60-day submergence treatments were highly significant ($p>0.0001$).

Table 15. The Crushing Strength ± SD (psi) of PG Briquettes Subjected to Submergence Tests.

Composition	Initial (n=5)	14-day Submergence with Shaking (n=3)	30 - Day Submergence (n=3)	60 - Day Submergence (n=3)
1 (0 cement; dihydrate)	246.65 ± 31.18	72 ± 36.77	249.5 ± 14.85	317.7 ± 24.83
2 (1% cement; dihydrate)	134.88 ± 16.54	63.7 ± 21.03	221.7 ± 25.7	230.33 ± 8.08
3 (3% cement; dihydrate)	138.74 ± 16.71	74 ± 25.51	218.67 ± 42.85	267.33 ± 10.07
4 (0 cement; anhydrite)	198.69 ± 19.69	48.3 ± 11.68	374.5 ± 382.54	561.7 ± 17.90
5 (3% cement; anhydrite)	163.11 ± 23.34	16.5 ± 2.12	52.3 ± 30.62	88 ± 4.00

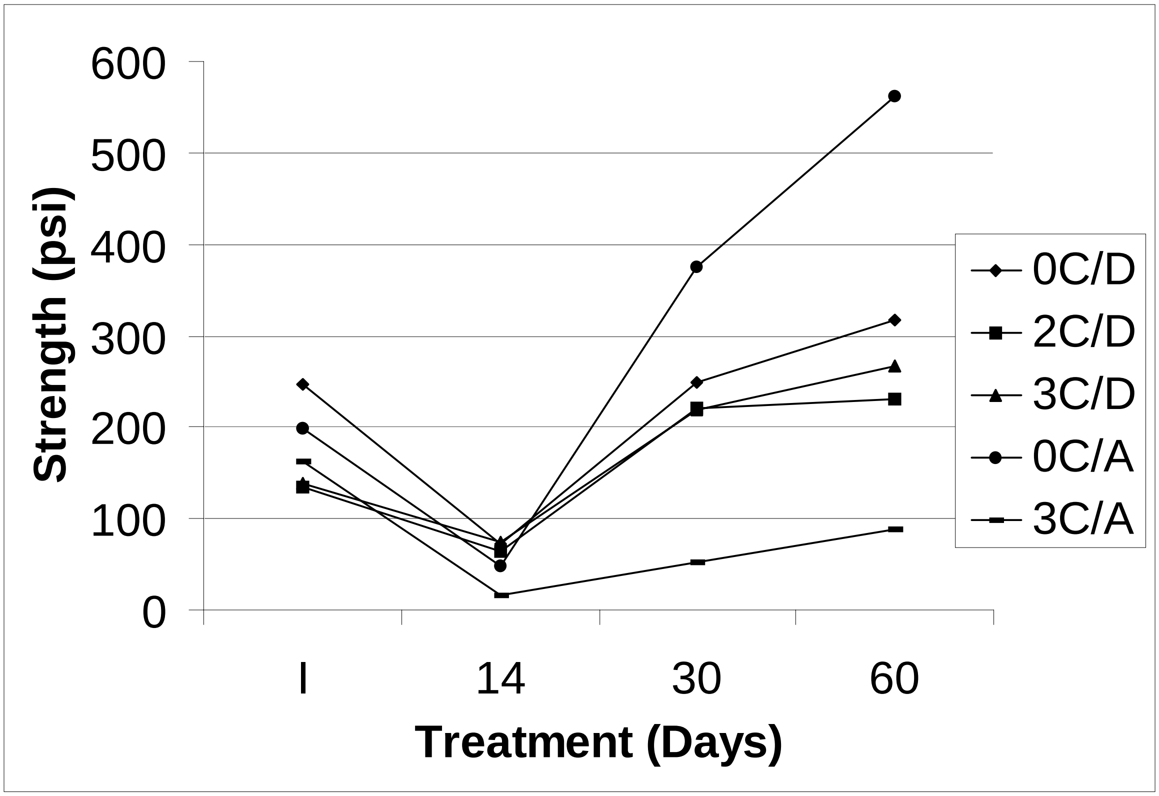

Figure 22. Strength (psi) Versus Treatment for the Five Briquette Compositions.

TOTAL DISSOLVED SOLIDS

Tables 16 and 17 show the results of the total dissolved solid (TDS) measurements of the artificial seawater solution in which the blocks and briquettes were submerged. The data show a large variation in results due in part to the lack of sensitivity of the test at the high level of TDS present in the seawater samples. However, the 30-day submergence results indicate a high solubility of the 5% and 10% cement blocks and the increase in concentration of TDS approaches the expected solubility of gypsum in seawater which is reported to be in the range of 5000 mg/l (James 1992). TDS increase is lower for 30-day submergence seawater that contained the 15% cement-PG blocks and 5%cement/10% sand. Between the 30-day and 60-day submergence, there was a reduction in TDS for the solution containing the 5% and 10% cement-PG blocks, while there was an increase in TDS for the solution containing the 5% cement/10% sand-PG blocks.

Table 16. The Net Change of Total Dissolved Solids ± SD (mg/L; n=3) in Artificial Submergence Seawater, (C = Cement, S = Sand).

Composition	30-Day Submergence	60-Day Submergence
5%C	4260 ± 3110	3690 ± 1540
10%C	4110 ± 1410	3310 ± 856
15%C	2820 ± 3450	2980 ± 1060
5%C and 10%S	2340 ± 1560	3730 ± 609

Similar increases in TDS were observed in all the briquettes submergence water. Increase in TDS may be attributed to the continuing dissolution of the 5% cement/10% sand-PG blocks and all the briquettes beyond 30 days. PG is easily soluble in seawater (Taha and Seals 1991), and if there is not enough cement, the PG will dissolve.

Table 17. Total Dissolved Solids ± SD (mg/L; n=3) for the Briquette Submergence Tests.

ID	30-Day Submergence	60-Day Submergence
1 (0 cement; dihydrate)	19,700 ± 213	20,600 ± 234
2 (1% cement; dihydrate)	18,800 ± 326	19,800 ± 202
3 (3% cement; dihydrate)	18,400 ± 146	19,900 ± 775
4 (0 cement; anhydrite)	17,900 ± 1690	20,800 ± 356
5 (3% cement; anhydrite)	17,600 ± 273	20,200 ± 287

On the other hand, reduction in TDS in the cement-PG blocks submergence seawater suggest the possibility of chemical reactions that impact the integrity of composite PG blocks, for instance, the formation of a thin coat layer that was observed on some of the blocks.

It is likely that a chemical equilibrium was attained in the 15% cement-PG block medium that can explain why there was hardly any change in TDS from 30 to 60 days submergence. What is not clear, however, is the inconsistent observations on the changes in TDS and the changes in hardness and compressive strength.

CONCLUSIONS AND RECOMMENDATIONS

This research has indicated that composition is critical to the maintenance of block/briquette integrity when used for underwater applications. The data indicates that dissolution and diffusion processes are taking place at the block/water interface. The extent and rate of these processes could not be estimated from the experiments conducted. Based on the results obtained under this funding, the following recommendations are being made for future research in this area:

1. Investigate the mechanisms leading to block degradation. Status: This work was undertaken under FIPR funding to LSU (contract #95-01-127). The results indicated the presence of a $CaCO_3$ coating on the blocks that exhibited no degradation when placed in a saltwater regime. Further studies are needed to pinpoint the exact mechanisms of the reactions taking place.

2. Investigate other materials such as lime and fly ash as potential additives. Status: Again, this work was initiated under FIPR contract #95-01-127. This work has continued beyond the ending date of that grant. Results indicate that PG/cement/fly ash composites (cement as low as 4%) have showed little or no degradation after placement under natural seawater conditions for 11 months. This work is continuing.

3. Investigate the diffusion rate of calcium from the composites as a mechanism to determine potential block degradation.

4. Following determine of optimum ingredients to maintain composite integrity, re-evaluate the economic feasibility of fabricating composites known to withstand degradation over a period of one year.

5. Re-initiate bioaccumulation studies using optimal ingredient composites.

6. Develop risk assessment model to determine long-term effects of radium-226 and radon gas release from the composites.

PART III. ECONOMIC ANALYSIS OF THE USE OF PHOSPHOGYPSUM/FLY ASH BRIQUETTES FOR ENHANCEMENT OF FISHERIES HABITAT

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July 1999

INTRODUCTION

The northern Gulf of Mexico, as well as other U.S. coastal regions, is faced with a number of fishery habitat issues that are being, and will continue to be, resolved through habitat enhancement. The oyster industries of many coastal states, for example, compensate for insufficient natural reef with manmade substrate to support oyster growth. As a second example, artificial reef programs are increasingly turning to manmade substrates to support and create artificial reefs. As a final example, while the natural ecosystem may work best to prevent coastal erosion, anthropogenic-induced degradation (as well as natural processes) of many of the states coastal ecosystems has resulted in the use of alternative hard substrates as a means of reducing, or reversing, the effects of coastal erosion. A common thread amongst all of these activities is that they call for the use of shell-like material to achieve the desired goal and, in the process, create fish habitats.

While the demand for suitable substrate material is likely to advance in relation to increases in the types of activities outlined above, the supply of traditional hard substrate materials, and in particular *Rangia* shell, is more uncertain due, at least in part, to institutional constraints. In 1989, for example, a prohibition on the dredging of *Rangia* shell in Lake Pontchartrain was initiated. The impact of this prohibition was to increase the price of the product, which made it economically unattractive for use in some activities, given the relative availability of other, less costly, substrate materials.   More recently, a prohibition on shell dredging in the Atchafalaya has further curtailed the available supply of *Rangia* shell. The purpose of this report is to explore the economic feasibility of stabilized phosphogypsum as a hard substrate for use in the marine environment. Primary emphasis of this economic exploration was the role that stabilized phosphogypsum might play in meeting hard substrate demands by the Gulf of Mexico oyster industry. Demand for hard substrate in coastal activities (e.g., artificial reefs, coastal restoration projects, etc.), however, may make demand by the oyster industry insignificant should the phosphogypsum composite material prove to be biologically and economically feasible.

USES FOR SUBSTRATE MATERIALS

Substrate Material to Enhance The Gulf Of Mexico Oyster Reefs

In general, oyster reef substrate material is used by state agencies for the purpose of enhancing public reefs and by individual fishermen to enhance private reefs that are leased from the state. Current use of substrate materials by these two groups is briefly examined below.

State Agencies. As noted by Leard et al. (in press), the effort to replace and increase the amount of hard-bottom substrate has become one of the most important functions of state oyster management programs throughout the Gulf of Mexico. Initial efforts focused on the use of processed oyster shells, which were stockpiled during the winter months and scattered over the reefs in the summer months. As alternative demands for the processed oyster shell expanded, primarily for the use in roadbeds, the oyster industry increasingly turned to other substrate enhancing materials. Most prominent materials included dredged oyster shell, dredged *rangia* shell and, more recently, limestone.

States in the Gulf of Mexico Region are responsible for maintenance of fishery habitats with emphasis on oyster habitat. Several states require oyster shell that results from shucking operations be returned to areas leased to private lease holders to continue to cycle of oyster spat settlement growth and harvest. Louisiana has no such requirement. Most of the states which have such laws only have need for sponsored shell planting in the event of natural and anthropogenic disasters that lead to loss of shell substrate. In states without the re-stocking laws, the state and private leaseholders periodically pay to have culch (a hard material upon which oyster larvae set and grow) placed in specific areas to improve conditions for oyster grow out. In Louisiana, for example, the state is responsible for maintaining state seed grounds. In essence, this is an oyster culch one-way process where the substrate is placed on the oyster seed grounds, harvested by the commercial oystermen, and transported to private lease grounds for oyster spat grow out. The material is then harvested with the oysters. These same state agencies also sponsor culch plantings in response to natural disasters such as hurricanes and floods.

Historical usage of processed oyster shell, dredged oyster shell, and *Rangia* clam by respective Gulf of Mexico states in planting activities (through 1994) is presented in Tables 18 through 20.

Table 18. Processed Oyster Shell Planting Activities by State, 1986-1994 (Cubic Yards).

	Florida	Alabama	Mississippi	Louisiana	Texas
1986	26,801	-----	-----	-----	-----
1987	14,901	-----	-----	-----	-----
1988	9,104	-----	3,076	-----	-----
1989	10,013	3,399	3,514	-----	-----
1990	7,297	16,589	2,345	-----	-----
1991	-----	-----	137	-----	-----
1992	2,100	-----	-----	-----	-----
1993	6,250	5,961	2,000	-----	-----
1994	2,363	6,954	2,000	1,784	-----

Table 19. Dredged Oyster Shell Planting Activities by State, 1986-94 (Cubic Yards).

	Florida	Alabama	Mississippi	Louisiana	Texas
1986	-----	-----	-----	-----	NA
1987	-----	-----	-----	-----	NA
1988	-----	-----	-----	-----	NA
1989	-----	-----	-----	-----	NA
1990	4,300	-----	-----	-----	NA
1991	3,650	-----	-----	-----	NA
1992	3,950	-----	-----	-----	NA
1993	6,222	-----	-----	-----	NA
1994	4,380	------	-----	100,420	NA

Source: Leard et al. (in press). NA = information not available.

Table 20. *Rangia* Clam Planting Activities by State, 1986-94 (Cubic Yards).

	Florida	Alabama	Mississippi	Louisiana	Texas
1986	4,785	84,402	-----	-----	-----
1987	48,780	22,588	20,876	-----	-----
1988	5,631	-----	10,424	-----	-----
1989	6,900	-----	3,616	59,652	-----
1990	-----	-----	3,146	-----	-----
1991	-----	-----	-----	-----	-----
1992	-----	-----	-----	-----	-----
1993	-----	-----	-----	-----	-----
1994	-----	-----	-----	1,785	-----

Total shell planting activities are presented in Table 21. As indicated, total shell planting activities, when expressed on a cubic yard basis, are highly variable when examined on a year-to-year basis. In general, publicly financed shell planting activities increase in relation to natural disasters. Florida, for example, intensified shell-planting activities in 1986 and 1987 to refurbish oyster-producing grounds impaired by Hurricane Elena in 1985. Likewise, Louisiana initiated significant shell planting activities in 1994; financed primarily with Federal disaster money associated with Hurricane Andrew.

Table 21. Total Shell Planting Activities[a] by State, 1986-94 (Cubic Yards).

	Florida	Alabama	Mississippi	Louisiana	Texas	Total
1986	31,586	84,402	-----	-----	NA	115,988
1987	63,681	22,588	20,876	-----	NA	107,145
1988	14,735	-----	13,500	-----	NA	28,235
1989	16,993	3,399	7,130	59,652	NA	87,174
1990	11,597	16,589	5,491	-----	NA	33,677
1991	3,650	-----	137	-----	NA	3,787
1992	6,050	-----	-----	-----	NA	6,050
1993	12,472	5,961	2,000	-----	NA	20,433
1994	6,743	6,954	2,000	103,989	NA	119,686

[a] Excludes some calico scallop plantings in Florida.

In total, state shell planting activities in the Gulf of Mexico averaged approximately 60 thousand cubic yards annually during 1986-94. This translates into a historic usage of approximately 80 thousand tons of shell plants annually, based on a conversion factor of 1.4 tons of shell per cubic yard.[1]

In addition to shell plants, more recently limestone aggregate has been used in planting activities in the Gulf Region. Its use has been limited due to the fact that its costs have not been competitive with available oyster and clamshell. Its use, however, has increased, as the supply of shell becomes more restrictive. The cost of # 67 limestone aggregate in 1996 was $13.50 per ton of shell material. For transportation and unloading in the New Orleans to Houma area by Pontchartrain Materials Corporation cost was increased by approximately $13.75 per ton for total cost of $27.25 per ton. Our primary interest is in the figure for the material which $13.50 per ton because transportation and unloading costs would be approximately the same for phosphogypsum pellets. The primary method of deployment of shell or limestone in these applications is by high-pressured water jets from a barge. Typically the barge is brought on the site with a tugboat and high-pressure water jets are used to blow the shell off of the barge onto the designated bottom.

Private Leaseholders. With the exception of Louisiana, leasing of water bottoms for oyster production is relatively insignificant in the Gulf of Mexico Region. Combined leasing activities in Florida and Mississippi, for example, equal only slightly more than one thousand acres. About 2,300 acres are currently leased in Texas. By comparison, more than 360 thousand acres are currently under lease in Louisiana.

While statistics regarding shell-planting activities by private leaseholders are unavailable, such activities are known to take place. According to Mr. Ron Dugas of the Louisiana Department of Wildlife and Fisheries (personal telephone communication), private shell planting activities utilizing purchased shell are less than 10 thousand cubic (14 thousand long) yards per year in Louisiana and tend to be directly associated with the dockside oyster price. By and large, most culch material utilized by private leaseholders in Louisiana is derived from the public seed grounds. The dockside price of Gulf of Mexico produced oysters when adjusted for inflation has been relatively low since 1991 suggesting that current demand for substrate material by lease holders is also relatively low under prevailing conditions.

Substrate Material for the Establishment of Artificial Reefs

The demand for fishing opportunities in coastal states throughout the United States and in several countries throughout the world has led to the development of a number of artificial reef programs. In fact, most coastal state agencies house artificial

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[1] The effect of a prohibition on the dredging of *Rangia* shell in Lake Pontchartrain on the use of that substrate material by the Gulf of Mexico oyster industry can be seen with the aid of the information in Tables 18 through 21. After the ban in 1989, specifically, the use of *Rangia* shell was significantly reduced (Table 20) with a substitution toward processed oyster shell.

reef programs. This demand for fishing opportunities was “loud” enough to culminate in an National Artificial Reef Plan (1986) created under the National Fishing Enhancement Act (1984). The primary purpose of the Act was to promote the development of artificial reefs along most of the coastal U.S. states.

Concomitant with the desire for creating fishing opportunities and associated artificial reefs has been in demand for material. States have relied on materials of opportunity such as vessels, cars, railroad boxcars, bridge rip-rap, army tanks, and even oil-and-gas platforms. One constraint regarding the use of these materials is that their size and stability restrict their use to specific areas. State agencies are now turning to other materials that are dependable, available, predictable in their size and construction, and are biologically safe, particularly in the shallow marine environment accessible to the majority of marine recreational anglers. An example of such an effort is the artificial reef sites created by the Louisiana Artificial Reef Program where dredged *Rangia* shell was used to create three one-acre shell pads to serve as shallow water fishing habitat.

Given the number of states that have artificial reef programs on the Atlantic and Gulf coasts and the apparent desire of these programs to create artificial reefs, the demand for this type of material is likely to be significant.   However, quantity demanded is inversely related to price suggesting that as price increases, the quantity demanded for materials will decline, *ceteris paribus*. As noted, use of materials for artificial reefs to date have largely been “opportunistic” in nature with state agencies bearing little costs for the material other than, possibly, those costs related to placement of the material in the appropriate marine setting. One would expect that use of these materials for artificial reefs would have been substantially less had the state agencies been required to pay the prevailing market price (even if the price is for scrap material) for materials used.

Substrate Material for Coastal Erosion Projects

A third area of opportunity for hard substrate concerns the worldwide problems of coastal erosion. Due to demand for coastal property, there has been a focus in recent years on land loss along coastal boundaries. A number of different techniques have been proposed to stabilize this land loss including jetties, break waters, and rock lining of waterways. Indeed, one can travel to almost any coastal state and find areas where shell, small rock, gravel, and large rock is used to halt or stem the erosion that occurs due to anthropogenic and natural wave force, particularly along waterways.

Substrate Material for Oil and Gas Activities

A less significant use for stabilized phosphogypsum is in the oil and gas industry. For over forty years the oil and gas industry has been operating in the Louisiana coastal zone. Associated drilling operations require the support of hard substrate in this very soft bottom environment. This hard substrate was created with shell in the form of large pads or mounds up to 10 feet thick. George Douglass of Ponchartrain Materials Corp. reported that demand for shell in this application ranged from 30,000 cu yds per month during the peak of industry operations to its current level of about 3, 000 cu yds per month.

POTENTIAL DEMAND FOR SUBSTRATE MATERIALS

As noted, state shell planting activities have historically averaged approximately 80 thousand tons annually in recent years with private plantings adding somewhat less to the total. While private leaseholders have historically planted only moderate amounts of (purchased) shell, the potential for significant increases is apparent. As noted by Leard et al. (in press), when culch is deposited on existing reefs it is done so at a density of from 100 to 150 cubic yards per acre. If ten percent of the leased (private) acreage in Louisiana were to be "seeded" annually with suitable culch material, approximately 4.5 million cubic yards (6 million tons) of the material would be required each year. A price for a product more in line with costs associated with the transport of shells from the public seed grounds would be a strong incentive for leaseholders to use an alternative culch material. If suitable culch is available at no cost, the Louisiana Department of Wildlife and Fisheries could use up to 500,000 cubic yards (700,000 tons) per year on state seed grounds (Ron Dugas, personal communication).

A second potential use for increased culch/substrate material reflects desires by the Louisiana Department of Natural Resources to relocate oyster lessees who will be displaced by proposed coastal restoration projects. This currently represents about seven thousand acres. Leard et al. suggests the use of at least 250 cubic yards per acre in the development of new reefs or replenishment of severely depleted reefs. This suggests the need for approximately 2 million cubic yards of material with the potential need for significantly more as compensation for lost leases increase as a result of coastal restoration projects in the state of Louisiana.

As discussed above, other potential uses of phosphogypsum composites is for the construction of artificial reefs, stemming coastal erosion, and oil and gas activities. For the purpose of illustrating potential use of alternative substrate material, we offer the following discussion with respect to the construction of artificial reefs and coastal erosion projects. Although this is speculative, it does point out that there is a demand for significant amounts of such material should the cost be within the means of the organizations proposing to build the artificial reef sites or the state/federal agencies in need of coastal erosion preventing substrate.

By example, we can illustrate the volume of material required for a shallow water artificial reef by using a reef creation project in Louisiana. In 1991, the Louisiana Artificial Reef Program created three one-acre shallow water artificial reef sites using shell. These test sites were designed to evaluate shell plants as fish habitat. The reefs covered a one-acre area and were two feet thick. They consisted of thirty-five hundred cubic yards of shell (5,000 tons). Given the soft substrate characteristics of Alabama, Mississippi, Louisiana, and part of Texas, one could envision the demand for fifty to one hundred such shell plants per year along the Gulf Coast. Since the reefs would be placed in shallow water soft sediments, they would likely require re-nourishment every three to five years. Regardless of the specific numbers, the significant amount of recreational fishing suggests that there would likely be a strong demand for substrate-enhancing materials if price (cost) of the material is acceptable. Having said this, however, the paucity of current artificial reef building activities using existing substrate materials (shell and limestone) suggests that prevailing prices of these products are above those that would encourage the creation of artificial reefs using materials of this nature. Instead, the bulk of materials currently being used in artificial reef development are procured by the organizations at little or no cost to the organization. Therefore, the delivered price of stabilized phosphogypsum to these organizations would likely have to be significantly below the prevailing price of shells or limestone to encourage its use. At no cost to the organization (agencies), we anticipate that the demand for a stabilized phosphogypsum material would be significant and on the order of 250 thousand to 500 thousand tons per year.

A similar case could be made for demand of materials for reducing coastal erosion. Such figures, like the above scenario, would be speculation at best, but could be on the same order of magnitude. A major distinction, however, should be made. Specifically, state/federal agencies pay the prevailing market price for many of the materials used in restoration projects. Hence, stabilized phosphogypsum that is competitive with shell or limestone in price, *ceteris paribus*, may be considered a viable substitute for which demand exists at a price in line with the costs of production.

In summary in consideration of all the above numbers, immediate demand for shell material is roughly 80,000 tons of oyster culch per year in the Gulf Region. This estimate is based on historic usage. If the material were available at no-cost, based on Ron Dugas' comments (Louisiana Department of Wildlife and Fisheries), an additional seven hundred thousand tons per year could be used on the state seed grounds and up to six million tons on private leases (10% of the leased area in Louisiana alone). In the more near term 2 million tons of material could be used in the Davis Pond Diversion alone to restore reef material being impacted by this diversion project. Artificial reef construction scenario explained above could use up to 500 thousand tons of shell material annually. So all combined, one could envision a total demand of one time at 10 million tons of shell material could be used in the Gulf Region and an annual level of 1-2 million tons, mostly in Louisiana. Since the density of phosphogypsum composites is approximately twice that of *Rangia* shell, therefore these figures should be doubled to illustrate potential demand.

COST ESTIMATE OF GYPSUM PELLET PRODUCTION AND COMPARISON

The primary objective of research at Louisiana State University over the past four or five years was to examine both the biological and physical stability of phosphogypsum blocks/pellets. Our research led us to the most recent report by Guo and colleagues (Guo et al. 1999) that illustrated that the combination of cement and phosphogypsum would only work if the cement levels approached thirty percent. Obviously this was cost prohibitive, so Dr. Rusch and her colleagues pursued the use of Type C fly ash which had significant cementing properties. Based on the most recent study, it found that a mixture of 35% fly ash, 3% cement, and 62% phosphogypsum produced an aggregate block that has persisted in the marine environment for over two years (Guo 1998). Although further work needs to be done to "fine tune" these numbers, this was the formula used in the following economic discussions. This new mixture introduces another cost element into the calculation, as there is a cost associated with purchasing and transporting fly ash to a phosphogypsum composite producing facility. For discussion purposes we continue the work initiated by Crescent Technologies (Appendix).

A study conducted by Crescent Technology Inc. (Appendix) can be used to assess the feasibility of using phosphogypsum as culch/substrate enhancing material. The 1996 updated analysis conducted by Crescent Technology was based on two primary factors: (1) the production facility was scaled to 4.5 million tons of output per year, and (2) cement used in the production of pellets equaled three percent of the total product weight.

For our analysis The Crescent Technology analysis was modified to include the additional costs incurred by adding Type C fly ash to the composite. The Type C fly ash is available locally and would be provided by Cajun Electric and Southwestern Electric Power Company. Both power companies are on the Mississippi River and within one-day barge travel to the Uncle Sam Plant. Current costs quoted by Cajun Electric are $18/ton delivered to Uncle Sam.

Manufacturing costs are comprised of capital and operating costs. Capital costs for 4.5 million annual tons of production, exclusive of finance charges, were estimated to equal $26.0 million in 1999 dollars. Financing capital costs at 8% per annum over a ten-year period yields total capital outlays equal to $35.0 million. Expressed on a per ton basis over the 10-year finance period, capital costs would equal $0.77 per ton (i.e., $35.0 million to produce 45 million tons)[2] without adjusting for inflation.

Total annual operating costs at 4.5 million tons of output were estimated to equal $50.0 million (Table 22), or $11.96 per ton of pellets produced. Cement costs represented approximately 25% of the total and fly ash 50% of the total.

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[2] It could be argued that a 10-year life expectancy period may be somewhat excessive in estimating annual capital costs associated with some fixed factors of production (e.g., trucks). More realistic estimates of life expectancy of different components comprising capital costs category would likely not significantly impact final per ton estimates.

Table 22. Cost of Producing Phosphogypsum/Fly Ash/Cement Pellets (64%/33%/3%) at Different Costs of Cement and Fly Ash*.

Cement per ton	Fly Ash per Ton						
	18.00	19.00	20.00	21.00	22.00	23.00	24.00
90.00	$ 11.72	$ 12.05	$ 12.38	$ 12.71	$ 13.04	$ 13.37	$ 13.70
100.00	$ 12.02	$ 12.35	$ 12.68	$ 13.01	$ 13.34	$ 13.67	$ 14.00
110.00	$ 12.33	$ 12.66	$ 12.99	$ 13.32	$ 13.65	$ 13.98	$ 14.31
120.00	$ 12.63	$ 12.96	$ 13.29	$ 13.62	$ 13.95	$ 14.28	$ 14.61
130.00	$ 12.93	$ 13.26	$ 13.59	$ 13.92	$ 14.25	$ 14.58	$ 14.91

* see Appendix 1, Table 18 for cost breakdown.

Substantial cost savings could be realized if the pellets can be fabricated with less than three percent cement or less than 33 % fly ash (Table 23). Cost estimates at alternative prices for cement and fly ash are presented in Table 22. In general, the information in Table 22 suggests the cost is relatively insensitive to relatively large changes in the prices of the inputs used to produce the final product. Cost estimates are much more sensitive to formulation (Table 23). For example reducing the percentage of fly ash to 20% and increasing the amount of cement to 5% would yield a production cost of $10.50 per ton. The primary cost issue associated with the use of phosphogypsum as culch/substrate material is whether it is competitive with some of the more frequently used products including oyster shell and limestone.

Table 23. Cost of Production of Phosphogypsum/Fly Ash/Cement Pellets Using Different Percentages of Fly Ash and Cement Using 1999 Cost Figures*.

Percent Cement	Percent Fly Ash				
	0.35	0.3	0.25	0.20	0.15
0.02	$ 11.36	$ 10.46	$ 9.56	$ 8.66	$ 7.76
0.03	$ 12.36	$ 11.46	$ 10.56	$ 9.66	$ 8.76
0.04	$ 13.36	$ 12.46	$ 11.56	$ 10.66	$ 9.76
0.05	$ 14.36	$ 13.46	$ 12.56	$ 11.66	$ 10.76

*see Appendix 1, Table 1 for cost breakdown.

Raw material limestone cost is approximately $13.5 per ton (varying by type of limestone), suggesting that gypsum pellets can be produced for about the same cost of limestone. Transportation and unloading costs associated with phosphogypsum should be about the same as limestone.

While limestone has been found to be an excellent culch material, its use in the Gulf of Mexico Region has been limited primarily to an experimental basis due to its cost relative to dredged or processed oyster shells. The quoted price for dredged oyster shell is \$17.50 per cubic yard (\$12.50 per ton) or about \$1.00 less per ton than limestone. The estimated cost of phosphogypsum pellets (@\$12.00 per ton) is equivalent to that of dredged shell.

A significant variable in evaluating this cost analysis is the history of fly ash use. Over the past ten years Type C fly ash has gone from being a disposal problem to a product with some demand. If the price of fly ash continues to increase the feasibility of phosphogypsum composite production becomes less attractive to some extent (see Table 22) but likely still remains competitive with the limestone given the uncertainty of the estimates.

OTHER ISSUES FOR CONSIDERATION

Our analysis suggests that phosphogypsum pellets can be produced at a cost that is in the range of that required to secure oyster shell or limestone. This analysis did not directly address the issue of "sinkage" which is an important consideration in the natural marine environment. Specifically, the water bottoms off Louisiana in particular, but also other areas of the northern Gulf of Mexico, tend to be soft mud in nature and any solids placed on the bottoms tend to sink, with the overall level of sinkage depending upon the density and the surface area of the solid. Sinkage of alternative substrate materials in a Louisiana setting was examined by Soniat et al. (1991), the findings for which are presented in Table 24. As indicated, clamshell had both a relatively low density and a high surface area when compared to other substrate materials. The "sinkage coefficient" assigned to clamshell was set equal to (i.e., standardized) one.

Table 24. Physical Measurements of Culch Materials Used in Field and Laboratory Experiments.

	Clamshell	Limestone	Gravel	Concrete
Liquid volume of one dry liter of material (ml)	385.0	512.9	562.1	489.3
Weight of one dry liter of material (kg)	0.69	1.30	1.67	0.93
Surface area of one dry liter of material (cm^2)	2671	2036	2310	1434
Volume (yd^3) of culch required to cover an acre with 3 cm of material, adjusted for sinkage	174.8	375.7	453.4	535.2
Sinkage coefficient (standardized to clamshell)	1.0	2.5	3.0	3.2

Other substrate materials, because of higher densities and lower surface areas, had sinkage coefficients significantly in excess of one (i.e., the standard). The sinkage coefficient of limestone, equal to 2.5, suggesting that it would take 2.5 times more limestone (in volume) than clamshell to cover a given area. As indicated in the table, for example, about 175 cubic yards of shell would be required to cover an acre with three cm of material, after allowing for sinkage. By comparison, about 376 cubic yards of limestone would be required.

It is impossible to state the sinkage factor for the stabilized phosphogypsum in the absence of experimental data. However, some very "ballpark" estimates can be made based on preliminary briquetting work previously performed since preliminary studies investigated the practicality of briquetting as a method of forming PG composites. The initial work by Rusch et al. in Part II of this report focused on PG and cement. These briquettes weigh approximately 1.2-1.4 Kg per liter and have a corresponding surface area of 1,700 cm^2 per dry liter (K. Rusch, personal telephone communication). These figures suggest a weight similar to limestone with a surface area equal to approximately 85% of that of limestone. Hence, the sinkage coefficient for limestone should be a good first approximation for that of PG briquettes.[3] Further experimentation with briquettes could potentially optimize the surface area to weight ratio so that briquettes have a sinkage coefficient equal to or less than limestone.

Another consideration that should be examined in the use of stabilized phosphogypsum concerns the broad issue of "risk and uncertainty." While no quantitative discussion with respect to risk and uncertainty can be presented in our analysis due to lack of data, a qualitative discussion can be offered. Specifically, traditional substrate materials, such as shell and to a lesser extent limestone, have proven track records. With respect to use by the oyster industry, both substrate materials are known to be conducive for spat set (see Soniat et al. 1991) and have a long life in the marine environment. Preliminary studies indicate that oyster spat did not differentiate between PG briquettes and clam shells during the set though additional in-depth studies are needed to corroborate these initial findings. One must be cognizant of the fact, however, that industry and state/federal agencies know little about stabilized phosphogypsum. Hence, even if the product can perform the same functions as shell and/or limestone and is cost competitive, demand for the product, at least in the short run, will likely be limited unless it can be offered at a price below that of the more "traditional" substrate materials; particularly limestone given its wide availability at present. Unfortunately, no information can be offered as to what the discount would have to be for it to be considered an acceptable substitute.

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[3] One additional issue not considered is the rate of sinkage. Specifically, one would expect a more pyramid shaped object to sink at a faster rate than, say, a rectangular shaped object, all other factors being equal.

SUMMARY

Our preliminary analysis has shown that phosphogypsum pellets are competitive with commercially available culch materials in terms of cost of production. Based on historic use patterns, there is an potential market for 1-2 million tons of shell per year or 2-4 million tons of phosphogypsum pellets, though demand is likely to be much more limited if price is tied to the cost of production plus some additional margin for profit. Specifically, current use of substrate material appears to be relatively limited due to price. If price were to fall, use would likely increase. Since culch planting in Louisiana, in particular, is constrained by funding, much more culch could be used if acquisition costs drop. It is likely that other Gulf states are in the same position. Given that costs to produce stabilized phosphogypsum is roughly equivalent to that needed to secure limestone, there is no reason to expect that offering the stabilized phosphogypsum for sale at, say, the current cost of production will increase demand for substrate material by the oyster industry.

While there appears to be significant potential use for stabilized phosphogypsum in development of artificial reefs, price of the product, if tied to costs required to produce it, will effectively “choke out” all potential demand for the product. Specifically, much of the product currently being used in artificial reef development is secured by the appropriate organizations at little or no cost to these organizations. To be competitive, therefore, the stabilized phosphogypsum would have to be offered at a price well below estimated production costs. To the extent that the creation of inshore reefs using traditional substrate materials (e.g., shell and limestone) is extremely limited, furthermore, one would have to conclude that the costs of conducting such activities are excessive at the prevailing prices of the substrate materials. Hence, stabilized phosphogypsum, if sold for the same price as the more traditional substrate materials, will not result in any increased demand for substrate material for inshore reefs.

Finally, there may exist demand for stabilized phosphogypsum for coastal erosion projects. Again, however, current demand appears to be marginal, at best, given that the cost of producing the product provides no advantage to that of limestone and limestone is a more widely recognized product.

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APPENDIX

CRESCENT TECHNOLOGY, INC. REPORT

Crescent Technology, Inc. reported on cost estimates for a 4,500,000 tpy Gypsum Pellet Production Facility. A cover letter by Mr. Hugh Manson presents assumptions. Table A-1 is a summary of costs adjusted to include fly ash and inflation.

Table A-1. Update of Crescent Technology Inc Economic Analysis for Fabrication of Phosphogypsum Composites to Account for Fly Ash and Inflation. Cost Estimates Are in 1999 Dollars.

Capital costs from Crescent Technology Inc. report	$21,870,000.00
Modified materials blending facility to include fly ash	$ 2,340,000.00
Total capital costs	$24,210,000.00
Inflation to 1999 dollars	$26,001,540.00
Operating costs from Crescent Technology Inc. report	$21,870,000.00
Inflation to 1999 dollars	$23,488,380.00
Additional operating costs for fly ash	$26,730,000.00
Annual operating costs	$50,218,380.00
Annual interest and principle payment (10 yr payout)	$ 3,587,960.00
Total annual costs	$53,806,340.00
Cost of production per ton	$ 11.96

CRESCENT TECHNOLOGY INC.

International Environmental, Safety, Engineering, and Analytical Services

1615 Poydras Street
New Orleans, Louisiana 70112
Telephone: (504) 582-4305
Facsimile: (504) 582-1832

April 15, 1996

Mr. Russ Olivier
IMC-Agrico Company
Exit 7250, Hwy 44
Uncle Sam, LA 70792

cc (w/attachments): J. Jolly
Roger Seal
File 2700-3

Re: Phosphogypsum Studies - Estimates for a
4,500,000 tpy Gypsum Pellet Production Facility

Dear Russ:

Attached are order of magnitude capital and operating estimates for a 4,500,000 ton per year phosphogypsum pellet production facility at the Uncle Sam plant. The estimated capital cost is $21,870,000 and the estimated annual operating cost is $22,860,000 These estimates are based on the March 1986 estimates by Messrs. M. A. Steele and M. S. Salvatore. The costs have been modified to reflect the deletion of facilities to handle red mud (alumina tails), the escalation to 1996 dollars and the increase of the production capacity from 3,942,000 tons per year to 4,500,000 tons per year. I have also included the "Operating Manpower Estimate" and the "Criteria and Description" for the facilities.

The estimates are based on reclaiming gypsum from the existing stack. No comparison has been made to the cost of transporting the gypsum directly from the filters in the phos-acid plant. As per our discussion, this will be investigated in the course of the other estimates. You may also note that the annual operating cost increase was only 15 % over that of the 1986 estimate. This is due to the following:

- The percentage of cement used in the pellets was 3% in the 1996 estimate and 5% in the 1986 estimate, so despite an increase in capacity and a significant (+ 65%) increase in cement cost, the annual cost of cement actually dropped slightly.
- The unit cost of power did not increase over the 10 year period.

At this time I will focus on the costs to estimate the remaining six of the phosphogypsum facilities that we have discussed. I will split these out into two groups. The first will consist of those that are associated with the Louisiana coastline restoration. The second will consist of those dealing with other products from phosphogypsum (revetment, levee armoring poured in place, and plastic lumber).

Please contact me if you have any questions or would like to discuss the estimates submitted. I can be reached at (504)582-4464.

Sincerely,

Hugh Manson

Hugh Manson
Sr. Project Engineer

CRITERIA AND DESCRIPTION
FOR A 4,500,000 TONS PER YEAR
GYPSUM PELLET PRODUCTION FACILITY
AT THE IMC/AGRICO UNCLE SAM PLANT

1) Criteria.

- Pellet Capacity - 4,500,000 tpy nominal (4,536,000 tpy actual)
- Feed Stocks

  Phosphogypsum (20 % water) - 4,400,000 tpy dry

  Cement, Type II (dry) - 136,000 tpy (3% of the mix)
- Bulk densities

  Phosphogypsum - 75 pcf

  Cement, Type II - 85-94 pcf.
- Storage Capacities.

  Phosphogypsum feed bin - 250 ton

  Cement silos (2) - 300 tons total, 150 tons each (19 hours)

  Pelletizer feed bin - 1040 tons (2 hours)

  Pellet Stockpile - 62,000 tons (5 days).

2) Gypsum reclaim facilities - The estimate is based on four large wheel loaders (Cat. 988's, 10 ton capacity) feeding 7 - 25 ton haul trucks. The trucks dump into a hopper feeding the gypsum reclaim conveyor. Operation is 24 hours per day, 365 days per year. The equipment included has the capacity to move the quantities necessary, however, another arrangement may prove more practical. Optimization would be required for an AFE grade estimate.

3) Gypsum reclaim conveyor - The reclaim conveyor runs from the hopper discussed in 2 above to the phosphogypsum feed bin in the blending plant.

4) Blending plant - The blending plant contains two 400 tph pug mills that are fed by separate feed belts. These belts are fed from the phosphogypsum feed bin via two vibrating weigh feeders and from the cement silos via rotary valves. Cement will be furnished, shipped and unloaded by the cement supplier. Cement supply trucks will be unloaded pneumatically and the dust will be captured in baghouses and transferred to the pug mills. Both pug mills discharge onto a single belt conveyor to the pellet plant.

5) Pelletizing Plant - A single belt conveyor from the blending plant feeds a long pelletizer feed hopper via a belt tripper. The 15 pelletizers (42 tph capacity each) are then fed via 15 separate screw feeders. The pelletizers include product air coolers, and they discharge on a single belt conveyor to outside storage.

6) Pellet storage - Pellet storage is fed via a conveyor from the pelletizing plant. This conveyor discharges on a stacker conveyor that can either discharge the pellets on the 120 ft. x 1000 ft. x 30 ft. ht. outside storage pile, or transfer the material to a conveyor feeding the barge loading facility at the dock. The storage pile can hold approximately 62,000 tons of pellets, 5 days production. Truck loading from the pile is handled by 2-10 ton wheel loaders (Cat. 988's).

7) Dock loading facilities - The present barge mooring system would be relocated and expanded to handle the pellet system. With the proposed arrangement, four dolphins would serve for moving barges under a single stationary ship loader. One dolphin supports the loader. A 36" conveyor transports the pellets from the pellet storage area to the loader. The conveying and loading systems are sized for full production capacity.

8) General - All facilities are based on continuous operation. All facilities are outdoors except for a partially open building over the pelletizer plant, a small office and a switchgear building.

ORDER OF MAGNITUDE COST ESTIMATE
FOR A 4,500,000 TONS PER YEAR
GYPSUM PELLET PRODUCTION FACILITY
AT THE IMC/AGRICO UNCLE SAM PLANT

I.	GYPSUM RECLAIMING FACILITIES	1,940,000
	a. Site preparation	20,000
	b. Approach ramp from stack	15,000
	c. Hopper and grizzly feed to gypsum conv.	30,000
	d. Control feeder belt	15,000
	e. Four front end loaders, 10 tons each (Cat. 988's)	1,280,000
	f. Seven haul trucks, 25 tons each	430,000
	g. E & I	140,000
	h. Painting	10,000
II.	PHOSPHOGYPSUM RECLAIM CONVEYOR	850,000
	a. Site preparation	15,000
	b. Foundations	65,000
	c. Conveyor and structural support with walkway 36" x 780 L.F.	640,000
	d. E & I	80,000
	e. Painting	50,000
III.	MATERIALS BLENDING PLANT	1,170,000
	a. Site preparation/piling	75,000
	b. Concrete foundations	30,000
	c. Phosphogypsum feed bin (250 T)	95,000
	d. Phosphogypsum bin discharge feeders (2)	55,000
	e. Two conveyors to pug mills 175' x 24"	95,000
	f. Two pug mills - 400 tph capacity each	340,000
	g. Two cement storage silos - 150 ton capacity each	135,000
	h. Four baghouses	80,000
	i. Four screw conveyors	45,000
	j. Four rotary valves	20,000
	k. E & I	125,000
	l. Road construction	50,000
	m. Drainage	25,000
IV.	PELLETIZING PLANT	7,280,000
	a. Site preparation/piling	90,000
	b. Concrete	120,000
	c. Structural steel, walkways, etc.	300,000
	d. Building 50' x 150' x 45' eave openside	600,000
	e. 250 Foot supply conveyor 36"	185,000
	f. Traveling tripper	30,000
	g. 15 Pelletizers (42 tph each), with screw feeders and product coolers	4,920,000
	h. Pelletizer feed bin 25'w x 125'l x 12'd	275,000
	i. E & I/control center	650,000
	j. Painting	60,000
	k. Office	20,000
	l. Drainage	30,000

ORDER-OF-MAGNITUDE OPERATING COST ESTIMATE FOR A 4,500,000 TONS PER YEAR GYPSUM PELLET PRODUCTION FACILITY AT THE IMC/AGRICO UNCLE SAM PLANT

I.	MATERIAL COSTS		$12,380,000
	a.	Portland cement purchase and delivery 136,000 tpy @ $91.00/ton	12,380,000
II.	MANUFACTURING COSTS		9,860,000
	a.	Labor, Incl. OH, 85 persons @ (53,000 x 1.35)	6,080,000
	b.	Utilities, electric power	1,830,000
	c.	Utilities, other	150,000
	d.	Maintenance	1,800,000
III.	ADMINISTRATION & FINANCIAL COSTS		620,000
	a.	Salaries, 6 persons (405,000 x 1.35)	548,000
	b.	Insurance, fire and liability (.3% cap)	64,000
	c.	Taxes on Inventory	8,000
IV.	ANNUAL OPERATING COST		$22,860,000

NOTES:

1. Costs are quoted in 1996 dollars.
2. Not included are charges for depreciation and interest
3. Patent royalties and payments to third parties are not included
4. Plant capacity is based on the production rate of 15 pellet machines at an operating factor of .822.
   15 x 42 x 24 x 365 x 0.822 = 4,536,000 tpy
5. Cost for Type II cement is from Blue Circle Cement in New Orleans and is negotiable.
6. The operating manpower estimate is attached.
7. Electric power consumption is based on 80 % of the projected installed capacity of 8200 kw. The other utilities costs are for nominal amounts of natural gas and water.
8. The six administration personnel consist of: 1 manager, 1 general superintendent, 2 foremen, 1 clerk, and 1 secretary.

ORDER OF MAGNITUDE COST ESTIMATE
FOR A 4,500,000 TONS PER YEAR
GYPSUM PELLET PRODUCTION FACILITY
AT THE IMC/AGRICO UNCLE SAM PLANT

V.	PRODUCT STORAGE CONVEYOR & FACILITIES	2,210,000
	a. Piling	110,000
	b. Concrete	30,000
	c. Structural steel/conveyor 1,350 LF	890,000
	d. Traveling tripper double boom	110,000
	e. Two front end loaders, 10 ton each (Cat. 988's)	640,000
	f. Scale	80,000
	g. Levee around storage pile 2,300 LF	30,000
	h. Painting	80,000
	i. E & I	140,000
	j. Road construction	70,000
	k. Drainage	30,000
VI.	RIVER DOCK LOADING FACILITIES	3,870,000
	a. Dock (5 dolphins, walkway)	1,020,000
	b. 3,200 LF Conveyor 36"	2,180,000
	c. Loading tipple tower	140,000
	d. E & I	140,000
	e. Painting	220,000
	f. Weightometer	30,000
	g. Environmental	140,000
VII.	CONSTRUCTION EXPENSE	4,550,000
	a. Salaries (U.S. Personnel)	70,000
	b. Other	140,000
	c. Engineering design	2,000,000
	d. Engineering field	1,470,000
	e. Auto mileage	30,000
	f. Service Eng'r.	40,000
	g. R&D Testing & Permits	200,000
	h. Spare Parts	600,000
VIII	TOTAL CAPITAL COST	$21,870,000

NOTES:

1. Costs are in 1996 dollars.
2. No allowance for contingency is included.
3. All operations and storage are outdoors except for an open, or partially open-sided building over the pelletizing machine and a small office and switchgear building

HPM:04-15-96

OPERATING MANPOWER ESTIMATE
FOR A 4,500,000 TONS PER YEAR
GYPSUM PELLET PRODUCTION FACILITY
AT THE IMC/AGRICO UNCLE SAM PLANT

Item	Description (and men required per shift)	Total Men
I	Gypsum reclaim facility Loading -4 men Hauling - 7 men	51.7
II	Blending plant Operator - 1 man	4.7
III	Pelletizing plant Supervisor/operator - 1 man Operator - 1 man	9.4
IV	Storage facility and truck loading Operators - 2 men	9.4
V	River dock barge loading facility Supervisor/operator - 1 man Operator - 1 man	9.4
VI	Total men required - 18 men per shift	84.6

Notes:

1. Operating cost is based on 24 hours per day, 365 days per year operation. For each man required per shift, 4.7 men will be required on the payroll to maintain 3 shifts per day, seven days per week, 365 days per year. This includes 4.2 men to fill the position and .5 men to fill in for vacations, illness and holiday relief.

2. The maintenance facilities will require 12 men. Use of the Uncle Sam shop is assumed for required shop work.

HPM:4-15-96