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Biorock: Calcium Carbonate Deposition and Oyster Growth in the Fishers Island Sound

I. Rationale

The purpose of these experiments is to test the effect of DC voltage/current applied to a steel geodesic dome has on mineral deposition and oyster growth. This is done by constructing three steel geodesic domes and running low DC voltage/current through them using solar panels as a power source.

II. Problem Statements

- Experiment 1: Will DC voltage/current affect mineral accretion/deposition on a steel geodesic dome?
- Experiment 2: Will DC voltage/current affect oyster growth inside a steel geodesic dome?

III. Introduction

In 1976, the Biorock system was invented as a way of increasing sediment deposition in coral reefs through the science of electrolysis (Biorock Website). The Biorock acts as a large electrolytic cell. The outer frame acts as a cathode and reduces calcium carbonate and other ions out of solution, which then attach to the dome in a process called electrodeposition (Hilbertz). The first experiments in electrodeposition involved depositing calcium carbonate on galvanized mesh by attaching power to the mesh (cathode) and a lead anode that was also submerged (Hilbertz). Significant deposition was observed in these and other experiments (Hilbertz). This is applicable to the Biorock dome because the deposition will strengthen and "grow" the structure. About 1-2 cm of calcium carbonate can be grown per year, in any shape dictated by the metal structure (Goreau, 275). In addition, parts of the structure with less accumulation, for example a section where some calcium carbonate broke off, grow faster than the surrounding structure. This allows the Biorock structures to “self-heal” (Goreau, 278). Even more important to the long-term effectiveness of the growth is the fact that the accumulation of calcium carbonate does not slow down as sediment increases because the calcium carbonate is 20% porous so the electrolysis continues (Goreau, 279). This was found to be true with deposition as much as 30 cm thick (Goreau, 279).

The equations that cause this electrodeposition are given below.

At the anode (the positive end), water is broken down in this oxidation reaction (Goreau, 279):

$2H_2O = O_2 + 4H^+ + 4e^-$

At the cathode (negative) water is broken down in the following reduction reaction (Goreau, 279):

$4\ H_2O + 4e^- = 2H_2 + 4OH^-$

The two reactions, as one balanced equation, can be written as (Goreau, 279):

$6H_2O = 2H_2 + O_2 + 4H^+ + 4OH^-$

The hydrogen gas released at the cathode will bubble to the surface, and these visible bubbles are an indication that the electrolysis is working correctly and make the calcium carbonate porous enough that the reactions continue. The oxygen gas, produced at the anode, dissolves into the water when released. This increased oxygen content of water near the Biorock structure can help increase the productivity of the surrounding area by providing this essential substance to nearby organisms (Goreau, 279). The hydrogen synthesized at the anode is in the form of H^+ ions, which dissolve in water. When these ions encounter limestone in the surrounding environment, they react to form bicarbonate and calcium ions (Goreau, 279).

$H^+ + CaCO_3 = Ca^{2+} + HCO_3^-$

The dissolved calcium ions then react with bicarbonate and hydroxide at the cathode to reform calcium carbonate and water in this reaction (Goreau, 280):

$Ca^{2+} + HCO_3^- + OH^- = CaCO_3 + H_2O$

This series of reactions simply moves limestone ($CaCO_3$) from sediments near the anode to the cathode, where it accumulates again as a solid, and is driven by the electrolysis of water which forms the hydrogen and hydroxide ions necessary for the reactions.

There are two different types of limestone ($CaCO_3$) deposition, calcite and aragonite. These two are allotropes of each other, giving them different properties. Calcite take longer to dissolve in water and is used primarily by mollusks while aragonite is harder and used primarily in corals (Goreau 274). Calcite should theoretically deposit naturally because of thermodynamics. The Standard Gibbs Free Energies of Formation of $CaCO_3$ at 25°C and 101.3 kPa is -1127.7 J, which indicates a spontaneous reaction. Because of this, Calcite *Should* be a good material to grow on the Biorock, but magnesium ions adhering to its surface physically prevent it from depositing. However, the Biorock still accumulates minerals since aragonite can form in seawater. This is because the dissolved magnesium does not prevent its deposition (Goreau, 280). Seawater must have huge amounts of dissolved Ca^{2+} and CO_3^{2-} to precipitate limestone (in the form of aragonite) naturally, but organisms such as clams that use limestone to build structures are able to alter the chemical conditions and make deposition possible using metabolic energy (Goreau, 280).

Too much amperage to the domes can be detrimental to deposition. According to electrical engineer Rand Weeks, a substance called brucite will appear as a slime that will not build solid layers if there is too much amperage. Brucite, or magnesium hydroxide, is formed in water with a high pH, which can be caused by overcharging the cathode of the dome, thereby increases the amount of hydroxyl (Goreau, 280). In water that is a normal pH, brucite will slowly be replaced with aragonite (Goreau, 280). This means that if brucite is formed, the amperage to the domes can be lowered, which will lower the amount of hydroxyl and the pH of the water, causing the brucine to dissolve and be replaced by aragonite.

Brucite formation is also impacted by temperature. Brucite increases solubility in warmer water, so if brucite is formed in warm water, it will quickly be dissolved and replaced by limestone in tropical areas (Goreau, 282). In cold waters, the Aragonite on the Biorock will not grow as quickly or as strong because the brucite formed will not be replaced as quickly.

Organisms nearby and the shoreline can benefit from the Biorock. Submerged breakwaters can be constructed to protect the shoreline by growing artificial reefs with the Biorock system (Bozak, 3). Nearby organisms can benefit from the increased oxygen levels around the dome. Organisms that form calcium carbonate shells, like coral or oysters, can gather the free calcium ions as well and accelerate growth of shells or other external coverings (Hilbertz). Biorocks have already been used to recover coral reefs in highly endangered tropical areas (Biorock.net). Coral attached to Biorock structures in Jamaica recorded record growth rates, about a centimeter a week (Goreau. 286). The first experimental Biorock structures, near the mouth of the Mississippi, were also spontaneously overrun by oysters (Goreau. 286). One of the main purposes of this experiment is to test the effectiveness of Biorock in increasing biological productivity in non-tropical waters. Biorock could also be used to restore oyster reefs in the north Atlantic, and the systems even have a history of supporting oyster growth. Because most of the prior experimentation has taken place in the tropics, the results of our experiments will be very important to the use and success of Biorock in colder waters.

Two major differences between the tropics and the North Atlantic, salinity and temperature, cause Biorock setups in the North to require a higher voltage. Tropical ocean water is very warm and very salty, both of which increase calcium deposition. As previously mentioned, less brucite will form, and the brucite will be replaced more quickly, in warm water. In addition, calcium carbonate is not vary soluble in warm water, meaning that it will reach supersaturation faster and deposit more readily (Goreau. 281). In cold water, calcium is very soluble, so it takes much more dissolved calcium to reach the saturation needed to form aragonite crystals. Salinity also effects the growth because it effects conductivity. Deposition of all materials will occur faster in conductive, saline water, and almost not at all in fresh water (Goreau, 282).

Because of the high salinity and low temperature of the northeastern Atlantic, we would need more voltage than tropical Birocks to cause deposition. In an experiment in Jamaica, 1.5 volts of DC current were used, while in Cuba 6 volts were used (Goreau. 284). The reaction is theoretically 100% efficient at 1.23 volts, the minimum for effective deposition, but efficiency rapidly decreases with increased voltage (Goreau. 284). The minimum amount of volts possible is usually used for this reason as well as to conserve electricity. Engineer Rand Weeks suggested to us about 12 volts of voltage for our environment, twice as much as the Cuba experiment and 8 times that of the experiment in Jamaica due to the colder waters. All of this energy is needed to provide the activation energy needed for the reactions that transfer the limestone from surrounding sediments to the Biorock dome in the colder, less salty, water.

The Biorocks (ideally) have 10 amps flowing through them, and pose a small safety risk without proper precautions. An individual must actually touch the domes to feel any shock from this of amperage, and electricity dissipates completely within 10 feet, so the surrounding waters are safe (Weeks). The domes will be marked with buoys and the power can be shut off easily as well. We have placed the domes in a sheltered bay where there are no boats or people close by.

Experimental design (1)

- Dependent Variable – amount of calcium carbonate accumulated on the domes.
- Independent Variables – presence of DC voltage/current to the domes.
- Control – Dome with no electricity located 40 ft away from experimental domes
- Constants – size of dome, solar panels used, position of domes, angle of solar panels, bars on which deposition growth will be measured

Experimental Design (2)

- Dependent Variable –Oyster growth in length, width, and mass.
- Independent Variables – Distance of nets from the electricity source.
- Control – Net suspended 15 feet away from the dome, out of range of the domes electricity.
- Constants – size of dome, solar panels used, position of domes, angle of solar panels, bars on which deposition growth will be measured

IV. Procedure

V. Experiment 1: There will be three Biorock domes, two electrified with 12 volts and 10 amps and one non-electrified control. Each will be marked with buoys. Every one to two weeks (weather dependent), the width of the iron bars will be measured using a caliper and observations made. The data will be recorded.

VI. Experiment 2: Inside one electrified Biorock dome electrified with 12 volts and 10 amps of power, there will be a dangling net of 40 oysters. Three bags of 40 oysters apiece will be hung 5 feet, 10 feet, and 15 feet from the center of the dome. Because the electricity dissipates by about 10 feet away from the domes, the net at 15 feet will function as the control. Every one to two weeks (weather permitting), the oysters will be removed, their masses, lengths, and widths taken, and observations made.

Pertaining to all procedures:

The solar panels used were two Grape Solar 160-Watt Monocrystalline PV Solar Panels.

The dimensions of the domes are roughly 70 inches in diameter (177.8 cm) and 30 inches tall (76.2 cm)

VII. Hypothesis

VIII. Experiment 1: DC voltage/current will cause more minerals to deposit on the electrified domes than the non-electrified dome.

IX. Experiment 2: DC voltage/current will cause the oysters inside of the electrified dome to grow more than any other oyster group.

X. Data

See Attachment

XI. Conclusion

Our experiment showed that electricity increased oyster growth in all three of our tested areas, length, width, and mass. The value that we used to determine oyster growth was the difference between the initial mean or median measurements and those from the last test, more than two months later. The three groups of oysters that were exposed to electricity, at 10, 5 and 0 feet from the dome, grew more in every category than the 15-foot control group. Of all of the groups, the 5-foot group grew the most. The mean and median increases in mass, 7.07 g and 7.11 g respectively, were about twice that of the control group. The increases in length for this group (mean: 1.87 cm, median: 1.90 cm) were more than double those of the control group (mean: ,median:). The increases in width for the 5-foot group (mean 1.09 cm, median 1.05 cm) were also double the control group's increases. Once graphed, the rates of change of the mean and median values were also greater in the 5-foot group except in the category of width, where the 0 cm group was the largest. All of this indicates that electricity positively affected oyster growth. This could have been because the electricity added to the metabolic energy that oysters already use to deposit their shells, or because there was more dissolved calcium carbonate near the domes. This would suggest that the shells of our oysters grew more, but the actual visceral mass might not have. An extension of this experiment would be to mass the shells of each group of oysters tested to determine if the differences in length, width, and mass were due to shell growth or organ growth.

There were some problems with the oyster portion of the experiment. Our oyster nets broke free on two occasions. First, the 5 and 10-foot groups floated away after their ropes frayed and broke between 9/20 and 10/6. Later, the 15-foot group was lost briefly, as extreme tides broke the more reinforced tie downs between 10/26 and 11/12. There was also an extreme amount of tidal fluctuation in the sheltered cove in which we raised the oysters, and they often floated just inches above the silt and collected muck on their nets. The sheltered cove also may not have provided the oysters with optimum oxygen and food supplies.

Another issue that we encountered was oyster mortality. In the 10 ft net, 11 out of 40 oysters died over the course of the experiment. None of the other nets lost any more than two oysters. We think that more testing would needed to understand whether the electricity had any part in causing these deaths. Most likely, the detaching of the nets played the greatest par in the oyster death. The nets drifted and/or washed up on shore for an undetermined amount of time. It could be that the 10-foot net detached very soon after we tested it on 9/20, therefore leaving it exposed for longer, while the other nets broke off later in the period between tests.

We also concluded that the electrification of the domes does encourage calcium carbonate deposition. By the time we started our measurements there was an average difference of 1.32 cm between the bar diameters of the control dome and electrified domes, meaning that significant $CaCO_3$ deposition occurred before our study was approved by the Connecticut State Science Fair. The deposition is obvious in our observations and photos. There was no net growth during our test, but the deposition that occurred before we took any measurements show that the Biorock system is effective in cold waters. In addition, while no deposition was measured, we did observe that the rope that attached the oysters to the dome always had a small deposition film attaching it to the bars of the dome, so minimal deposition likely did occur.

It is likely that the weather and season of the experiment were major causes of the dropoff in deposition. In addition, cold water decreases $CaCO_3$ deposition. In addition, shortening winter days, lower sun angles, cloudy weather, and the presence of shade near the panels may have prevented them from producing sufficient and consistent voltage and amperage. It is also possible that the surrounding sediments were depleted of $CaCO_3$ by the time our experimentation started, as the system relies on environmental $CaCO_3$. After months of deposition, it is conceivable that most of the readily available calcium carbonate was used up.

It is likely that surrounding environment and irregular electricity impaired the system's efficiency in comparison to the previous warm-water experiments that showed continuous growth.

Future experiments using more controlled and reliable electricity sources will be able to fine-tune the Biorock process in cold waters, but our data shows that using the Biorock system for shoreline protections and habitat creation is feasible in cold New England waters

The data also showed that the electricity caused the oysters to grow more than the control group, especially in the category of mass. Continuing the experiment with more oysters in a more controlled environment would generate more data about the long-term effect of electricity on oyster growth.

One of the main potential uses for a Biorock system in the Northeast Atlantic and globally is protection of reefs and shorelines. Submerged or partially submerged structures, such as the Biorocks, can decrease shoreline erosion by dissipating the energy of approaching waves. Coral and oyster reefs do this naturally, but a Biorock can do the same, as our experiment shows. These oyster reefs would filter water, protect shorelines, and provide habitat. As sea levels rise and the threat of erosion increases, especially on coastal communities like Fishers Island, Biorock structures could become an important part of the attempt to limit damage to property and lives.

Bibliography

Hilbertz, W. H. (1979). Electrolysis of Minerals in Sea Water: Experiments and Applications. IEEE Journal on Oceanic Engineering, VOL. OE-4, NO.3

Goreau, T. J. (2012). Marine Electrolysis for Building Materials and Environmental Restoration, Electrolysis, Dr. Janis Kleperis (Ed.), InTech, DOI: 10.5772/48783. Available from: http://www.intechopen.com/books/electrolysis/marine-electrolysis-for-building-materials-and-environmental-restoration

Weeks, R. (2016) Minitoring Protocols for FI Biorock Experiment (unpublished experiment protocals)

Bozak, R. R. (2000). *Mineral accretion in seawater* (Order No. 9968019). Available from ProQuest Dissertations & Theses Global. (304591785). Retrieved from http://ezproxy.lib.uconn.edu/login?url=http://search.proquest.com/docview/304591785?accountid=14518

Biorock Inc. (n.d.) "Biorock[tm] Technology." Retrieved August 18, 2016 (http://Biorock.net/Technologies/index.html)