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Marine Electrolysis for Building Materials and Environmental Restoration

Thomas J. Goreau

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1. Introduction

Within weeks after Alessandro Volta developed the battery in 1800, William Nicholson and Anthony Carlisle applied it to the electrolysis of water, producing hydrogen at the cathode and oxygen at the anode, and thereby showing that water was not an irreducible element, as had been thought, but a chemical compound made up of two elements with very different properties. It was quickly found that adding salts to the water greatly accelerated reaction rates. We now know this is caused by increased electrical conductivity and reduced resistivity, thereby increasing the electrical current flowing for a given applied battery voltage according to Ohm's Law. Humphrey Davy soon applied electrolysis to the practical problem of oxidative corrosion of copper plates used to sheath ships and protect the wood from boring organisms, founding the field of galvanic protection of metals from corrosion, now widely used to protect steel ships, oil rigs, bridges, and subsea pipes from failure.

Seawater electrolysis for galvanic protection can use sacrificial anodes, driven by the voltage potential difference between different metals, or actively impressed currents driven by a battery or a direct current power supply. In the first case the voltage differences are small, usually only tenths of a volt, according to the difference in electromotive potentials of the various metals or alloys used. The metal acting as the cathode is completely protected from rusting and corrosion as long as the electrical current flows. The metal acting as the anode usually dissolves away as the reaction proceeds, and needs to be periodically replaced in order to continue to prevent corrosion of the cathode. Increased currents accelerate reaction rates, which can cause mineral growth or scale, something most uses of cathodic protection wish to avoid. For example, if a boiler is being cathodically protected from rusting, one does not want to precipitate a mineral scale layer on it, because that is less thermally conductive than the metal, and reduces heat transfer and boiler efficiency. Therefore most uses of cathode corrosion protection use the lowest possible voltages and currents needed to prevent rusting, in order to avoid growth of scale.

There is a “natural” analog of cathode protection that is crucial for marine archaeology. A shipwreck invariably contains objects of several different metals, such as various steel alloys, copper, brass, bronze, aluminum, and others. The metal that acts as the strongest anode, according to its electromotive potential, proceeds to dissolve, releasing electrons that flow to the cathode metals, protecting them from oxidation. When the anode has completely dissolved, the next metal in the electromotive series then plays that role until there are no more anodic metals left, and at that point corrosion can take place on the last cathode metal. The process causes growth of limestone scale on the cathode, which protects and conceals it. Metal artifacts preserved in marine shipwrecks have been protected because they acted as cathodes. Despite the popular image of treasure hunters finding shiny golden coins, in fact the treasure is completely encrusted in limestone, appearing as irregular white crystalline lumps with the metal surface completely concealed. The first thing marine archaeologists do with these lumps is to throw them into an acid bath to dissolve away the limestone, in some cases speeding the process up by wiring them up as an anode of a battery, although that risks destroying the artifact if it proceeds too far. Only once the limestone has dissolved can the archaeologist see the metal artifact.

Later applications of aquatic electrolysis included making chlorine and bleach (sodium hypochlorite) from seawater and chloride brines, and purification of metals, but largely under highly controlled conditions in limited volumes, often from fused salts or acid solutions rather than from seawater. Following the First World War, the Nobel Prize winning German Jewish chemist, Fritz Haber, whose work on industrial nitrogen fixation via the Haber-Bosch process is the basis for almost all fertilizer nitrogen production, and hence for our global food supplies, sought to use electrolysis of sea water to extract traces of gold from the ocean to pay back war reparations imposed by the victors. He found that concentrations were too low to be economic, and was then hounded to death by the Nazis.

2. Physical properties of mineral production from sea water

Michael Faraday was the first to precipitate solid minerals by electrolysis of seawater. It was not until 1976 that Wolf Hilbertz recognized that these minerals, under the right conditions, could be a resource rather than a problem to be avoided. Hilbertz, an innovative architect working on self-growing construction materials, experimented with electrolysis of sea water and discovered that by varying the voltage and current applied he could grow different minerals on the cathode, ranging from soft to hard (Hilbertz, 1979). His inspiration was biological: if marine organisms could grow shells and skeletons of precisely controlled architecture from minerals dissolved in seawater, we should be able to figure out how to do so as well. Limestone does not precipitate naturally from seawater, so marine organisms must use their metabolic energy resources in order to create special internal chemical conditions that cause shell growth.

Hilbertz found that under low electrical current conditions he could grow extremely hard calcium carbonate limestone deposits, made up of crystals of the mineral aragonite, the same compound that makes up coral skeletons and the bulk of tropical white sand beaches.

Higher currents caused the growth of the mineral brucite, or magnesium hydroxide, which is soft and tends to easily break off. Through experimentation it proved possible to grow rock-hard limestone coatings of any desired thickness on steel frames of any desired shape or size, at up to 1-2 cm per year, with compressive (load-bearing) strength up to 80 Newtons per square millimeter (MegaPascals), or about three times the strength of concrete made from ordinary Portland Cement.

This material, which Hilbertz first called “Seacrete” or “Seament”, is now called “Biorock®” in order to emphasize that this is the only GROWING marine construction material that gets larger and stronger with age, and is self-repairing, like biological materials, but unlike any other marine construction material. This unique property causes any damaged or broken portion to grow back preferentially over growth of undamaged sections.



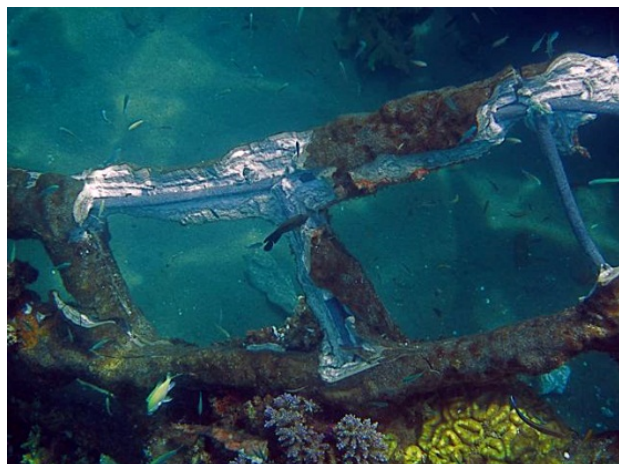
Figure 1. Biorock materials grown at Ihuru, North Male Atoll, Maldives, around a 6mm diameter steel bar in approximately one year. The darker surface color is a thin film of dried algae that migrates on the surface as it grows outward, leaving the interior bright white. The piece was hacksawed out of a growing structure. There is no corrosion at all on the steel. Photograph by Wolf H. Hilbertz.



Figure 2. Bio-rock materials from various locations. The piece at mid left is the one shown in the previous photo. The one at top left, completely overgrown with oysters, is from Louisiana, and all the rest were grown in a two and a half year period at Ihuru Island, North Male Atoll, Maldives. Samples tested from that set of samples in the Materials Testing Laboratory of the University of Graz, Austria, had compressive strength of 60-80 Mega Pascals, around three times the load bearing strength of ordinary Portland Cement concrete. Photograph Wolf W. Hilbertz.



Figure 3. This piece was cut near where two steel bars crossed. We had wedged a coral between the bars after a few months of growth. The coral skeleton is the slightly darker vertically oriented area in the center. After 2.5 years it was completely overgrown and encased by electrochemically produced minerals. Photograph Wolf H. Hilbertz.



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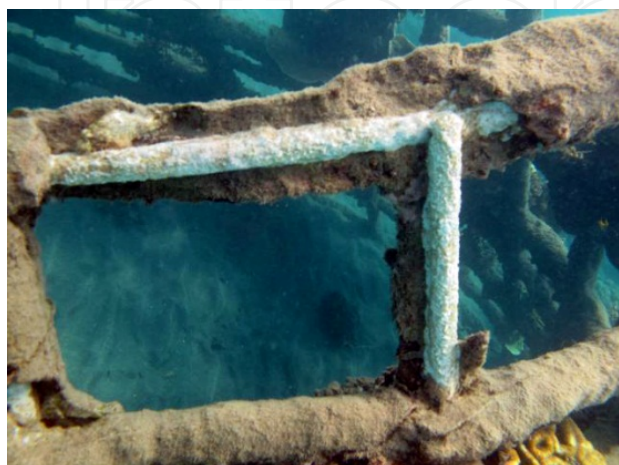
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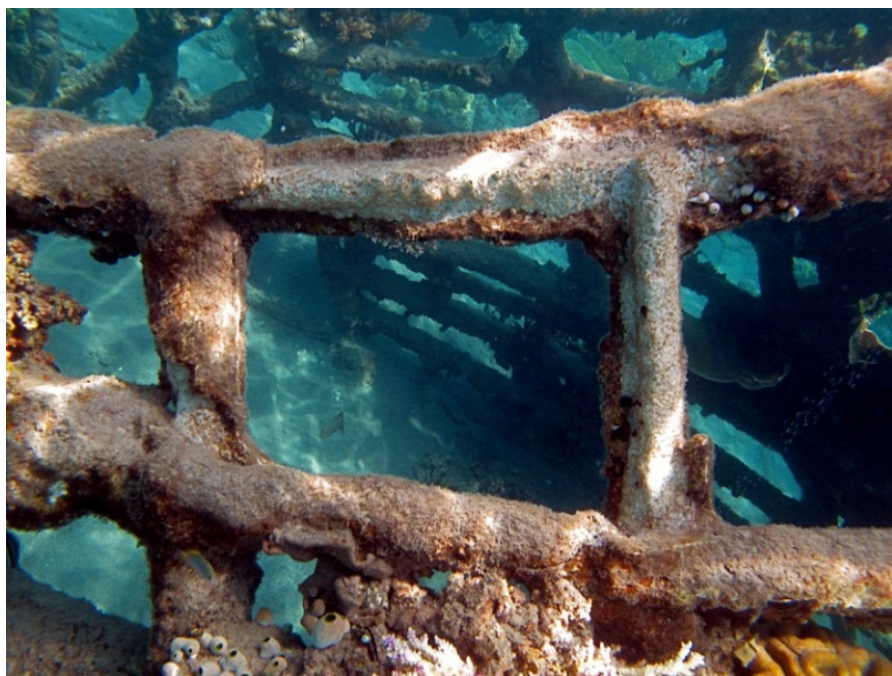
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Figure 4. Self repair of Biorock damaged by big boat impact. Time series photographs by Rani Morrow-Wuigk. This structure was installed in June 2000. Note there is no rust on the steel after nearly 11 years in seawater.

The remarkable property of self-healing structures results from the distribution of the electrical field. Initially the electrical gradient between the anode and the cathode results in growth of mineral layers all over the cathode, starting at the closest points, or at sharp extremities that focus electrical field gradients, or at sites where water currents preferentially transport electrons.

Unlike the steel, the minerals are poor electrical conductors, and act as partial insulators. Nevertheless, electrons continue to flow because of the imposed electrical gradient. Although the electrolytic reactions generate hydroxyl ions and alkalinity in the water that are neutralized by mineral deposition taking place at the surface of the metal (see next section), production of hydrogen gas at the cathode surface causes creation of tiny pores and channels from the metal surface to the seawater, out of which hydrogen bubbles emerge (such bubbling provides visible proof that the reaction is working properly). Even Biorock material with three times the load-bearing strength of ordinary concrete has around 20% porosity. While it might be thought that minerals might insulate the cathode and prevent further growth, the imposed electrical gradient ensures that growth continues, in part because electrons flow through the hydrogen escape pores. We observe no long term decrease in the rate of bubbling or the growth of minerals, even in cases where more than 30 cm of hard minerals have grown over the cathode.

When the mineral growth is broken off, whether by severe storm wave damage, boat impacts, or deliberately by pliers, hammers, or hacksaws, and the bare metal is exposed, there is greatly increased growth at that point, until the newly deposited minerals are as thick as adjacent unbroken material. The metal is all at the same voltage potential, but

reduced or absent mineral coatings cause the increased electrical current and mass transfer to flow through the water at that point. When the newly grown material is as resistive as the old coating the increased growth rate is self-limiting. In some cases new material is more porous due intense hydrogen bubbling, and the repaired area may grow thicker than adjacent harder and less porous material. We first recognized this focusing of current to freshly exposed surfaces in an experiment using multiple lengths of rebar as cathodes. We would periodically remove one rebar in order to measure the thickness of the material growth, replacing it with a fresh rebar, in an attempt to measure long-term growth rates and changes in chemical composition. The bare steel surface focused the current on the new rebar, which grew at the expense of all the others, stopping their growth. While the experiment did not work as intended, it provided valuable insight into the process.

3. Chemical mechanisms of mineral deposition

A minimum voltage of 1.23 Volts (at standard conditions, plus junction potentials) is needed to initiate electrolysis of water. Water is broken down at the anode to make oxygen gas and hydrogen ion, making the local environment both oxidizing and acidic:



Water is broken down at the cathode to make hydrogen gas and hydroxyl ion, making the local environment both alkaline and reducing:



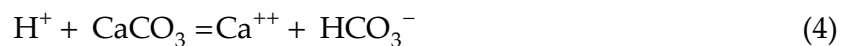
The net reaction satisfying charge and pH balance is:



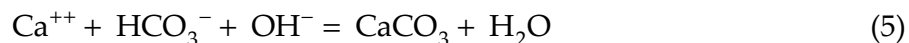
Above the threshold voltage (the sum of the half cell reactions and the junction potentials), the rate of reaction is proportional to the impressed electrical current, but the voltage determines which reactions can take place.

The hydrogen gas produced at the cathode bubbles out of the water, and could be trapped and used as a valuable side product. This is easy in an enclosed system, but practically impossible in the ocean due to currents and wave surge. The oxygen gas produced at the anode, being more soluble in water than hydrogen, tends to dissolve in the water rather than bubble out (under low to moderate current, bubbling will be greater at high current). Oxygen produced at the anode provides organisms in surrounding areas with this essential element and acts to reduce anoxia and dead zones in the ocean.

Hydrogen ions produced at the anode dissolve in the water until they react with limestone sediments in surrounding areas and are neutralized:



On the other hand the hydroxyl ions produced at the cathode are rapidly consumed by precipitation of limestone directly on the cathode surface:



The net reaction is neutral with regard to pH and alkalinity and hence to ocean CO₂ content and acidification (Hilbertz, 1992). Note however that the net effect causes limestone to be deposited in a specific and controlled location on the cathode at the expense of dissolution of limestone in sediment surrounding the anode, so this amounts to moving limestone around to a more useful location and with a controlled shape determined by the size and shape of the cathode.

Limestone deposition does not happen naturally in seawater even though the surface ocean is several times supersaturated with regard to the mineral calcite. Calcite precipitation should take place on thermodynamic grounds, but kinetic factors prevent its nucleation and growth in seawater. This occurs because magnesium ions cover the surface of calcite crystal nuclei, changing the surface free energy to make the seed crystals more soluble and preventing crystal growth (Berner, 1971; Berner et al. 1979). Seawater must be supersaturated several times over to precipitate limestone, and what precipitates is not calcite but the metastable mineral aragonite, whose chemical composition is the same but whose cell lattice is denser, and is more stable at high pressure conditions deep inside the earth than at the surface. Aragonite crystal nuclei do not adsorb a surface layer of soluble magnesium ions and hence can grow in seawater. In fresh water with low magnesium concentrations, calcite will precipitate even though it will not grow in seawater, which has 5 atoms of dissolved magnesium ions for each calcium ion. Organisms that make limestone shells and skeletons, like snails, clams, and corals, must use up metabolic energy to create internal chemical conditions that overcome these nucleation barriers, and also control the form of calcium carbonate produced.

The cathode can be made of any kind of electrically conductive metal or material, which will be completely protected against corrosion by the electrical current, with the sole exception of Aluminum. Aluminum is an amphoteric oxide and is the only common metal that readily dissolves under both alkaline and acidic conditions, so it can't be used as either an anode or a cathode. The anode, being acidic and oxidizing, creates highly corrosive conditions, so most anode metals will dissolve, usually releasing biologically toxic ions into the environment. Either the anode must be replaced as needed, or a special non-corrodible and non-toxic material must be used.

4. Effects of competing electrolytic side reactions

Overcharging the cathode with higher electrical current densities greatly increases hydroxyl ion concentrations, which causes precipitation of the mineral brucite, Mg(OH)₂ instead of aragonite. Brucite requires very high pH to precipitate, appears to have little or no kinetic barrier to precipitation, and should grow at a rate proportional to the square of the microsite pH next to the cathode. Brucite, a white mineral similar in appearance to limestone, is structurally weak and flakes off. In seawater of normal pH brucite dissolves, the hydroxyl ions

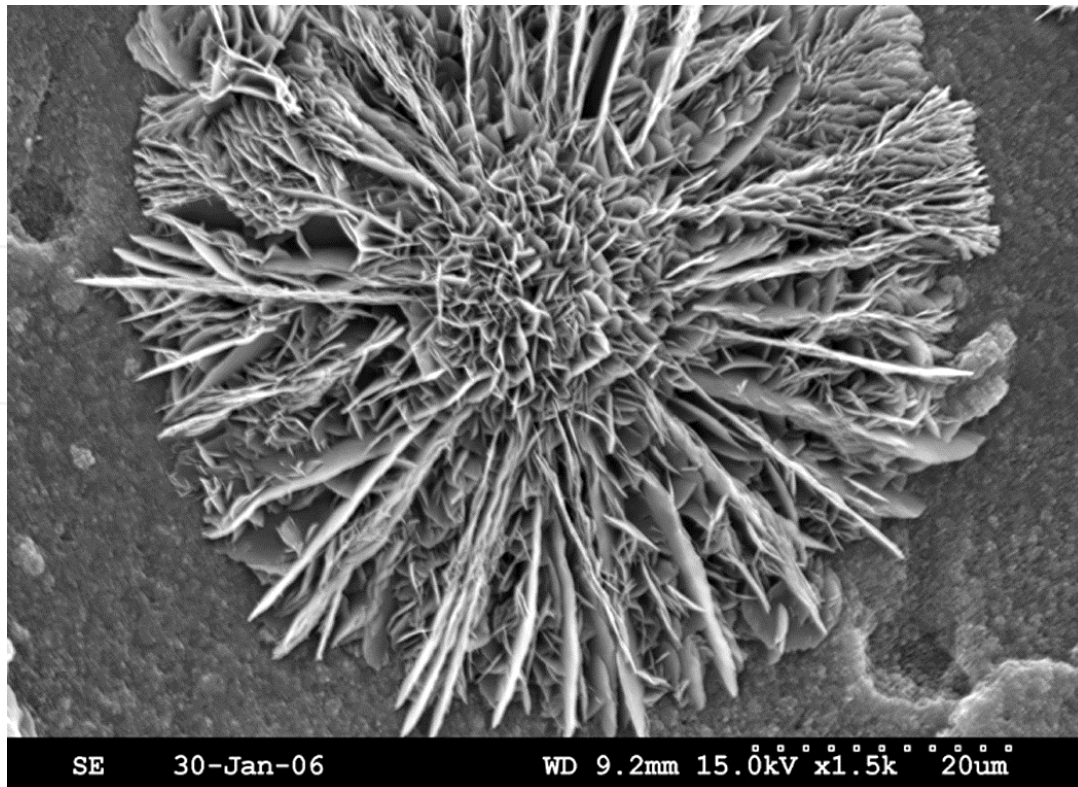


Figure 5. Brucite crystals grown on Biorock. Scanning electron micrograph by Noreen Buster, US Geological Survey.

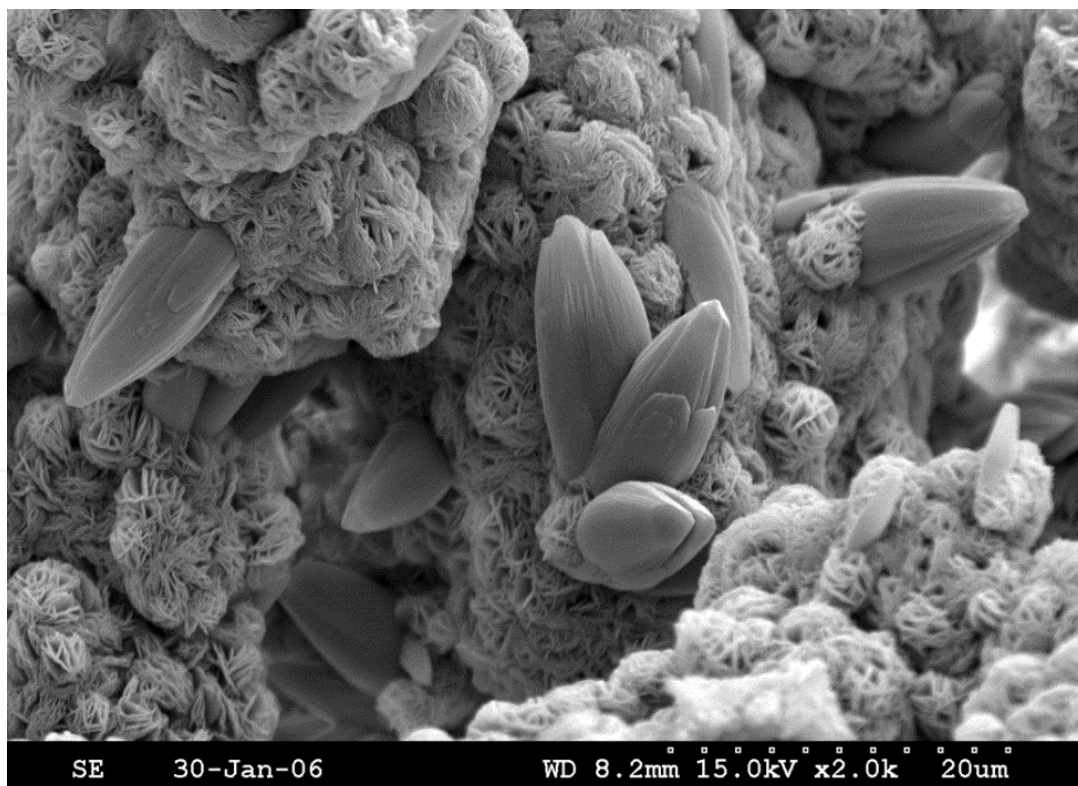
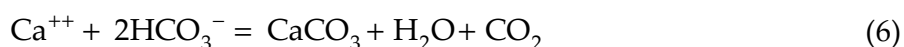


Figure 6. Mixture of Brucite crystals (rosettes) and Aragonite crystals (elongated needles). Scanning electron micrograph by Noreen Buster, US Geological Survey.

raise the pH, and convert bicarbonate ion to carbonate ion, which reacts with calcium ions. Consequently as the material grows and brucite ages it is replaced by aragonite. To optimize strength the Biorock minerals are grown at a low charging rate to produce hard limestone rather than soft brucite. We find experimentally that a growth rate of not more than 1-2 cm/per year provides maximum growth and structural strength, and above that brucite dominates.

These results are strongly affected by temperature, because brucite is a normal mineral whose solubility increases with temperature, while calcium carbonate minerals are extremely unusual in having retrograde solubility, being more soluble in cold water than hot water. As a result materials grow faster and harder in warm tropical waters than in cold boreal waters. In addition the electrical conductivity is directly proportional to the salinity, so growth rates are highest in very salty waters and brines, lower in brackish waters, and very small in pure fresh water. The aragonite chemical composition, as measured by X-ray fluorescence, is indistinguishable from that of coral skeletons, being essentially pure calcium carbonate with about one percent strontium substitution in the aragonite lattice and only trace amounts of magnesium and other metals. However growth of minerals can trap sediment material suspended in the water that lands on the limestone as it grows, affecting the color of the Biorock minerals. They are pure white on remote limestone islands, but grey where there are a lot of clay minerals in the water, and can even be red where there are lots of iron oxide minerals in suspended sediments.

Because at high current densities direct brucite precipitation removes hydroxyl ion without converting bicarbonate to carbonate ion, it also reduces the amount of CO₂ produced by limestone deposition:



This is an interesting point because limestone deposition is, along with volcanic outgassing, the major source of atmospheric CO₂ on a geological time scale, while dissolution of limestone, along with weathering of aluminosilicate minerals, is the major sink. This is widely misunderstood by those not knowledgeable about the chemistry of the carbon cycle. Almost everyone seems to think that limestone deposition, which is a sink of oceanic bicarbonate, must also be a sink of atmospheric CO₂, when in fact it is a source! This common error is due to the fact that bicarbonate is the major form of inorganic carbon in the ocean, and because the ocean is a pH-buffered chemical system. In effect for each molecule of bicarbonate precipitated as limestone one molecule is released as CO₂ in order to maintain charge and pH balance. Therefore brucite formation at the expense of aragonite has a net effect of reducing the effects of ocean acidification caused by increased CO₂ in the atmosphere.

However, to put this into perspective, about half of all the net limestone burial in the ocean used to take place in coral reefs (Milliman, 1993), at least back when coral reefs were healthy and growing, before global warming, new diseases, and pollution killed most of them. About an order of magnitude more limestone was formed by planktonic organisms, but almost all of that dissolves when their microscopic skeletons fall into deep water, where they dissolve because of the lower temperature, higher pressure, and the higher acidity of

deep waters caused by decomposition of organic matter that is formed at the ocean surface by photosynthesis and falls to the deep sea where it is oxidized by decomposing organisms and bacteria. However, the rate at which we are now adding CO₂ to the atmosphere from fossil fuel combustion is about 100 times greater than the natural sources from global limestone burial (Ware et al., 1991), indicating how greatly human pollution has overwhelmed natural sources. Consequently global ocean acidification caused by fossil fuel-caused CO₂ buildup cannot be effectively countered by manipulating limestone deposition, unless fossil fuel CO₂ sources are greatly reduced and a mechanism is developed to directly remove CO₂ from the atmosphere. If allowed to build up in the atmosphere, fossil fuel CO₂ will only be very slowly neutralized over hundreds of millennia to millions of years by dissolution of terrestrial limestone rocks on land and marine limestone sediments.

Above 1.36 volts chloride, the most abundant anion in sea water, is converted to chlorine gas at the anode:



If the voltage could be maintained between 1.23 and 1.36 volts (ignoring junction potentials) then chlorine production can be avoided entirely, but this requires very precise regulation and is made more complicated by junction potentials. In practice, sufficient overvoltage to overcome junction potentials makes some chlorine production unavoidable, but the lower the voltage the less is produced.

Oxygen production is strongly favored over chlorine production because the ocean has far higher concentrations of water molecules than chloride ions (96.66% versus 1.94% by weight under standard ocean salinity of 35 parts per thousand). The ratio between oxygen production and chlorine production can be calculated from the water and chloride concentrations and the voltages applied using the Nernst Equation, but there will always be far more oxygen production than chlorine. However chlorine, as a highly reactive oxidizing agent, can build up in closed systems like aquaria or tanks, and pose problems, for example for fishes in tanks whose gills are highly sensitive to chlorine, or marine mammals whose eyes are affected. In the ocean chlorine is rapidly neutralized by reaction with dissolved organic matter and reduced compounds and elements. We have repeatedly observed that it poses no problem at all for life in the ocean, with fish and corals growing well no farther than a millimeter or two from the anode. Fish swim near the anode, and dissolution of limestone usually takes place only a very short distance away from the anode, removing the acidity produced. But in aquaria with no limestone sediments, the acidity can remain in the water.

The chlorine production side reaction competing with water at the anode also provides another side benefit in that hydrogen ion is not produced by the electron flow, so this acts to make the net reaction at both electrodes one that makes the water more alkaline, and therefore acts to locally reverse ocean acidification from increased atmospheric CO₂. However, as noted before, the effects are small on a global scale, so large-scale electrolysis in the ocean, while LOCALLY reversing ocean acidification, has only a small impact on the ocean's BULK acidity, and only abatement of fossil fuel sources and direct removal of excess atmospheric CO₂ can reverse global ocean acidification.

An interesting variant of this process has been proposed as way to mitigate ocean acidification caused by atmospheric CO₂ buildup by House et al, 2007 and by Rau and Carroll, 2011. They suggest packing the area around the anode with basic minerals, like limestone or igneous rocks high in calcium and magnesium. The acidity at the anode would then increase the dissolution and weathering of these minerals, which serves as a CO₂ sink. They suggest that the water would then turn alkaline, which would promote the dissolution of CO₂ from the atmosphere. However as noted above, the alkalinity generated at the cathode is immediately neutralized by mineral deposition and so would not build up in the water and absorb CO₂ from the air. Furthermore there would be enormous costs for transporting bulky rocks from land to the site of electrolysis, and it is likely that the benefits for reversing ocean acidification or CO₂ buildup would be small.

5. Efficiency and cost of mineral production

The fact that limestone minerals, harder than ordinary concrete, can be grown in the sea in any size and shape, naturally raises the question whether doing so is cost-effective. Hilbertz and Goreau did an experiment in the 1980s at the Discovery Bay Marine Laboratory in Jamaica in which a new battery of known voltage and amp hours was completely discharged through electrodes and the amount of minerals grown on the anode was weighed. The yield was 1.07 Kilograms/Kilowatt hour, very close to the theoretically expected value. A field experiment done in the sea at the Marina Hemingway, near Havana, Cuba measured values of around 0.4-0.5 Kg/KWh (Amat et al., 1994). At this site there were many large steel structures in the water nearby, which attracted stray currents and reduced measured efficiency of mineral production on the cathode.

When one balances the chemical and charge equations, and assuming that all the hydroxyl ions produced by electrolysis of water are neutralized by limestone deposition, one gets 3.7 grams of calcium carbonate per amp hour of electricity.

To calculate the efficiency as yield per watt one must assume a voltage. The Jamaica experiments were done at 1.5 volts, and the Cuban ones at 6 volts. The lower the voltage is (as long as it is above the minimum voltage of 1.23V for electrolysis of water and ignoring junction potentials) the more efficient the process is (Table 1). For standard solar panels at 17 volts, only around 7% of the potential energy is used, and nearly 93% is wasted.

VOLTAGE (VOLTS)	EFFICIENCY (PERCENT)
1.23	100
1.5	82
3	41
6	20.5
12	10.25
17	7.24

Table 1.

Using 6 volts we get a limestone yield of 0.62 Kilograms of calcium carbonate per Kilowatt-hour, which is close to what the Cuban researchers found in the field despite stray current losses!

For high charge rates producing brucite, one produces half as many molecules of brucite for the same charge, because only one hydroxyl ion is needed for each calcium carbonate molecule, but two are needed for each brucite. As brucite molecules weigh 68% as much as limestone, the efficiency in weight produced per kilowatt should be one third that of limestone.

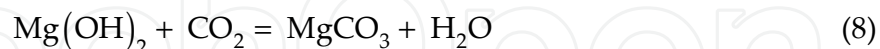
In addition for every two molecules of calcium carbonate (or one molecule of brucite) produced one also produces one molecule of hydrogen gas, which can be used as a fuel in fuel cells. And one would also be producing oxygen and chlorine at the other terminal in a ratio that depends on the voltage and can be calculated from the Nernst Equations.

The energy efficiency of production is inversely related to the voltage above the minimal value for seawater electrolysis because higher voltages produce electrons with much more energy than is needed to break down water, so the excess is wasted as heat. We have never felt or measured significant increases in temperature, so the effect seems to be very small in practice. This decrease of efficiency at higher voltages is equally true of efficiency of hydrogen production using photovoltaic panels. This fact was completely missed in a major review of the subject (Blankenship et al. 2011), which consequently greatly overestimated efficiency of the photovoltaic hydrogen production process. The previous generation of 17 volt photovoltaic panels cause nearly 93% of the potential energy to be wasted when applied to electrolysis for hydrogen production. Such 17 volt panels are now no longer being manufactured, while the new panels, with 24, 48, 60 volts or higher will be even more inefficient for Biorock materials or hydrogen production end uses, so it is clear that efficient use of power requires voltages matched to the minimum end use requirements.

If we assume that the yield is 1 Kg/KWh and that electricity costs from \$.03 to \$.30 per KWh, the electrical cost of the materials produced ranges from \$.03-.30/Kg. This would be highly competitive with cement in many places where transport of cement affects the local cost, especially in small islands surrounded by the sea where cement is expensive because of transport costs.

The materials that are produced, if grown slowly, have a load bearing strength of around 80 MegaPascals, about 3 times stronger than concrete from ordinary Portland Cement, and can be grown in any size or shape. Wolf Hilbertz's original vision was to grow prefabricated construction materials, like roofs, walls, arches, blocks, etc. in the sea and then use them on land for construction. The most effective use would be in what architects call "shells", structures that are thin with regard to their other dimensions like domes, and whose strength in large part comes from tensile forces. Unfortunately the construction market wants buildings immediately, and is rarely willing to wait years for the material to be grown slowly and hard, when concrete will set in days. In addition, in the late 1980s our Biorock work switched away from building material applications to focus on coral reef restoration, and we never had a chance to get back into the construction aspects that Wolf had intended. However the principle is still valid, and such structures would be cost effective in many places far from cement plants.

By applying higher current densities, mineral production can be readily switched from calcium carbonate to magnesium hydroxide. While this material is soft, flaky and not useful for load bearing uses, it has many other applications. This material can be cast in molds to form bricks and blocks or other shapes, and we have done so successfully. Brucite can be readily converted into magnesium carbonate cements by absorbing CO₂ and these are even harder than calcium carbonate.



The manufacture of Biorock cements therefore removes CO₂ from the atmosphere as they set. In contrast cement manufacture, which combusts limestone to make quicklime, releasing CO₂, is a major global source of greenhouse gases, about 5-10% as much as fossil fuel combustion. Therefore Biorock cements can be readily produced on a large scale that are far harder than contemporary cements and help to reduce global warming instead of causing it like conventional cements do.

Use of Biorock cements can therefore help undo the global warming that cement manufacture contributes to, and hence are truly “green” cements as long as sustainable energy resources like solar, wind, wave, biomass, or tidal current energy are used to make the electricity for its manufacture. We have used all of these energy sources, and currently work with top pioneering groups in the development of all of these energy technologies for growing Biorock materials.

Magnesium carbonate cements are far harder than either calcium carbonate or concrete, and were widely used by the Romans. Roman ruins in Italy built of limestone or marble blocks cemented with magnesium carbonate cements reveal that the limestone is dissolving with acid rain, while the cements are much more resistant. The cements stick out while the building blocks are caved in from dissolution by rain, the opposite effect of bricks whose mortar is crumbling. Using Biorock technology it is now possible to produce such cements in any desired quantity from seawater and hypersaline lakes and lagoons.

6. Biological responses

The biological effects of the electrical fields produced by seawater electrolysis result in astonishing increases in the settlement, growth, survival, and resistance to environmental stress of almost all marine organisms (Hilbertz & Goreau, 1996). Commercial divers on cathodically protected oil rigs, who spend much of their time replacing sacrificial anodes, have to spend a great deal of time scraping off the prolific growth of corals, oysters, and other marine organisms, which are far less abundant on rusting oil rigs that lack cathodic protection. Wolf Hilbertz's first Biorock structures, built at Grand Isle, Louisiana, near the mouth of the Mississippi River, were completely overgrown with oysters that spontaneously settled on them and grew very rapidly. The first experiments with corals done at the Discovery Bay Marine Laboratory in Jamaica in the late 1980s used small pieces of corals attached to Biorock structures. They grew at record rates, up to nearly a centimeter a week (Goreau & Hilbertz, 2005). The results were so dramatic that after 1987 we

immediately focused all of our efforts on coral reef restoration, as this is the most sensitive of all ecosystems to increases in temperature, sedimentation, and pollution.

Subsequent work by us and our students on hundreds of Biorock projects across the Atlantic, Pacific, Indian Ocean, and Southeast Asia showed that corals, oysters, seagrasses, saltmarsh, and apparently almost all marine organisms, had much higher settlement, growth, survival, and resistance to environmental stresses, including high temperatures, than genetically identical controls in the same habitat. For example coral growth rates are typically 2-6 times faster than controls, depending on species and conditions, and survival of corals from severe high temperature bleaching stress were 16-50 times higher (Goreau & Hilbertz, 2005). The data are presented in a 2012 book in press, *Innovative Methods of Ecosystem Restoration*, so the details will not be repeated here. Abstracts of most of the papers in that volume were presented at the Symposium on Innovative Methods of Marine Ecosystem Restoration at the 2011 World Conference on Ecological Restoration, Merida, Yucatan, Mexico, and can be found at: http://www.globalcoral.org/world_conference_on_ecological_r.htm

Initially it was thought that the benefits were due to the higher pH around the Biorock structure, but direct pH measurements showed that the hydroxyl ions generated at the cathode were immediately neutralized by mineral deposition, and very little pH change could be measured in the water even very close by, unless the limestone was broken off to expose the bare shiny metal surface. In addition it was noted that organisms without limestone skeletons also had extraordinary growth rates, that the organisms on the structure had much faster budding and branching, brighter colors, and that there was greater coral settlement and growth in the areas AROUND the structures, not just on them. These benefits were observed to disappear when the power was turned off and growth decreased to levels similar to the controls, but immediately resumed when the power was turned back on. For much more detailed data on biological benefits of electrical fields and their interpretation, please see the forthcoming book, *Innovative Methods of Ecosystem Restoration*.

Applications of electrolysis to biological phenomena precede even the invention of the battery. In 1791 Luigi Galvani published his book on "Animal Electricity", based on experiments with static electrical discharges that caused the limbs of dead frogs to twitch. This led to the discovery of electrical propagation in nerves, and a long series of experiments on the effects of electrical currents on limb healing and regeneration in frogs and salamanders, followed by work on electrical stimulation of brains (Becker & Selden, 1985). Much of this work used high voltages or alternating current, and so are fundamentally different phenomena than the low voltage direct currents used in our work. The use of electroshock therapy gave the entire field a bad name, and a reputation for quackery, so that the legitimate scientific applications of low voltage electrical fields were ridiculed and neglected, to the detriment of scientific understanding (Oschman, 2000, 2003). The "snake oil" or "Frankenstein" reputation has unfairly tarnished the serious science of biological/electrical interactions due to the bogus claims of charlatans or deluded people.

While full explanation of the effects of electrical fields at the biophysical and biochemical level requires further work, the empirical results show enormous benefits for biological health when

they are in the right range. Electrical fields that are too low will have little impact, and those that are too high might well have negative impacts, with maximum benefits at some intermediate value. It is long known that organisms maintain a voltage gradient across their cell membrane of around a tenth of a volt, and that they must expend energy to maintain this gradient by enzymatically pumping cations and anions. The resulting voltage gradient drives flows of electrons and protons that are tapped by enzymes to form the high energy biochemical metabolites that serve as the cell's "energy currency", driving synthesis of compounds whose formation would otherwise be thermodynamically prohibited.

Thus electrical gradients of the right magnitude effectively provide living cells with available biological energy at lower cost, leaving them with extra energy for growth, reproduction, healing, and resisting environmental stress. Optimizing these benefits will take much further work on mechanisms. When these are fully explored, the benefits in terms of higher growth and better health will certainly prove revolutionary in many fields of biology, and result in more productive forms of mariculture, aquaculture, and agriculture.

7. Applications

To date electrolysis has largely been used to develop chemical processes in closed systems with controlled chemical composition. The only large-scale environmental application, corrosion control, is operated at the lowest possible level in order to prevent or minimize the applications described in this article. The work we have done since the mid 1970s opens the door to large-scale environmental applications of many novel kinds. These include:

1. protecting coral reefs against global warming, sedimentation, and pollution
2. restoring coral reefs where they have died or been degraded
3. restoring oyster reefs where they have died or been degraded
4. restoring fish habitat
5. restoring shellfish habitat
6. restoring seagrasses
7. restoring saltmarshes
8. mariculture
9. shore protection from erosion and global sea level rise
10. construction materials
11. hydrogen production
12. agricultural applications

Biorock applications involve low voltage and low current densities, and so do not use much electricity, in fact they usually cannot be felt even when one short circuits the system by grabbing the anode and cathode simultaneously with bare hands, since the electrons flow through much more conductive seawater. Using Biorock technology, coral reefs can be grown in front of hotels, which grow the beaches back using about as much electricity as the beach lights, or one or two air conditioners. This is a negligible amount of electricity for places that may be running hundreds of air conditioners at a time, and so the benefits far outweigh the costs. Biorock structures cost a small fraction of the cost of concrete or rock

structures with the same dimensions. Reinforced concrete construction first assembles a framework of reinforcing bar, which is a negligible portion of the total structure cost. The concrete poured around it, and the labor, cost many times more than the steel. Biorock construction assembles a steel framework, but instead of purchasing concrete simply wires it to a power source and grows the material over the steel.

Since steel is the cheapest and most available construction material, Biorock costs are largely dependent on the price of electricity. Since most electricity is produced from fossil fuels like coal, oil, and natural gas, it is the largest source of greenhouse gases causing the global warming that is now the major killer of corals worldwide. For this reason we work very closely with the pioneers in sustainable energy systems, in particular wave, tidal, wind, and solar power, so that untapped renewable local energy sources can be used that do not generate CO₂. We are especially focused on use of the development of new wave energy generators that work in waves of less than 10 cm amplitude, which will allow energy to be made along almost any coastline most of the time.

Generation of electricity on-site from renewable energy also avoids power losses in transmission, and will allow much larger structures to be grown with less energy. This will open the possibilities of very large environmental electrolysis projects to save entire coastlines from the effects of global sea level rise and restore their collapsing coral reefs, oyster reefs, and fisheries, while at the same time promoting the development of sustainable energy sources that do not produce CO₂ and cause global warming and sea level rise.

Biorock reefs grown in front of severely eroding beaches, with trees and buildings collapsing into the sea, have grown back up to 15 meters (50 feet) of new beach back in a few years, by reducing wave impacts at the shoreline. Therefore they will have major applications as global sea level rise accelerates in the future. Artificial islands can be grown that keep pace with sea level rise, if Biorock technology was used on a large scale.

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This paper is dedicated to the memory of the late Wolf Hilbertz (1938 – 2007), the inventor of the Biorock Process and an innovator in new applications of electrolysis. This paper is based on 25 years of close work with him in developing the Biorock technology that emerged from his pioneering vision.

8. References

Enrique Amat Balbosa, Juan Carlos Prada, Frank Moore Wedderborn, & Eumelia Reyes Reyes, 1994, Estudio preliminar de la acrecion marina, Revista Arquitectura y Urbanismo, Vol XV, No. 243:1-16

- Robert O. Becker & Gary Selden, 1985, *The Body Electric: Electromagnetism and the Foundation of Life*, William Morrow, New York
- Robert A. Berner, 1971, *Principles of Chemical Sedimentology*, McGraw Hill, New York
- Robert A. Berner, J. T. Westrich, R. Graber, J. Smith, & C. S. Martens, 1978, Inhibition of aragonite precipitation from supersaturated seawater: a laboratory and field study, *American Journal of Science*, 278:816-837
- Robert E. Blankenship, David M. Tiede, James Barber, Gary W. Brudvig, Graham Fleming, Marina Ghirardi, M. R. Gunner, Wolfgang Junge, David M. Kramer, Anastasios Melis, Thomas A. Moore, Christopher C. Moser, Daniel C. Nocera, Arthur J. Nozik, Donald R. Ort, William W. Parson, Roger C. Prince, & Richard T. Sayre, 2011, Comparing photosynthetic and photovoltaic efficiencies and recognizing the potential for improvement, *Science*, 332:805-809
- N. A. Buster, C. W. Holmes, T. J. Goreau, & W. Hilbertz, 2006, Crystal habits of the Magnesium Hydroxide mineral Brucite within Coral Skeletons, *American Geophysical Union Annual Meeting, Abstract and Poster*
- T. J. Goreau & W. Hilbertz, 2005, Marine ecosystem restoration: costs and benefits for coral reefs, *WORLD RESOURCE REVIEW*, 17: 375-409
- Wolf H. Hilbertz, 1979, Electrodeposition of minerals in sea water: Experiments and applications, *IEEE Journal on Oceanic Engineering*, 4:1-19
- Wolf H. Hilbertz, 1992, Solar-generated building material from seawater as a sink for carbon, *Ambio*, 21, 126-129
- W. H. Hilbertz & T. J. Goreau, 1996, Method of enhancing the growth of aquatic organisms, and structures created thereby, United States Patent Number 5,543,034, U. S. PATENT OFFICE (14pp.).
- Kurt Zenz House, Christopher H. House, Daniel P. Schrag, & Michael J. Aziz, 2007, Electrochemical acceleration of chemical weathering as an energetically feasible approach to mitigating anthropogenic climate change, *Environmental Science and Technology*, 41:8464-8470
- John D. Milliman, 1993, Production and accumulation of calcium carbonate in the ocean: Budget of a nonsteady state, *Global Biogeochemical Cycles*, 7:927-957
- James L. Oschman, 2000, *Energy Medicine: The Scientific Basis*, Churchill Livingstone, Edinburgh
- James L. Oschman, 2003, *Energy Medicine in Therapeutics and Human Performance*, Butterworth Heinemann, Edinburgh
- Greg H. Rau & Susan A. Carroll, 2011, Electrochemical enhancement of carbonate and silicate weathering for CO₂ mitigation, *Goldschmidt Conference Abstracts, Mineralogical Magazine*, p. 1698
- John R. Ware, Stephen V. Smith, & Marjorie L. Reaka-Kudla, 1991, Coral reefs: Sources or sinks of atmospheric CO₂?, *Coral Reefs*, 11:127-130
- World Conference on Ecological Restoration, 2011, Abstracts:
http://www.globalcoral.org/world_conference_on_ecological_r.htm