

# Solar-generated Building Material from Seawater as a Sink for Carbon

The manufacture of the greater part of most conventional building materials used today is based on use of fossil fuels, thereby contributing sizeable amounts of carbon from combustion and chemical reactions in the raw material to the atmosphere. Alternative building materials and systems have to be developed in order to balance atmospheric carbon dioxide. Using electricity from renewable sources, limestone storing carbon can be precipitated from seawater with simultaneous production of hydrogen, oxygen, and chlorine gas. Existing resources for the operation of the mineral accretion process are surveyed and similarities in biogenic calcium carbonate deposition discussed. Electrolytically precipitated limestone and material consisting of artificial limestone and hard coral skeletons are proposed as a sink for carbon and for use as building materials. To assess the potential role of these materials in the carbon cycle, experimental measurements are needed.

## INTRODUCTION

With the exception of wood, sand, gravel, and natural stone, most traditional building materials like cement, lime, fired brick, steel, aluminum, and plastic are fossil-fuel intensive in their manufacture. The continued and increasing use of these materials to house the ever-growing world population and to accommodate increasingly western lifestyles ensures growing contributions of carbon (C) to the active carbon cycle through anthropogenic emissions of carbon dioxide (CO<sub>2</sub>).

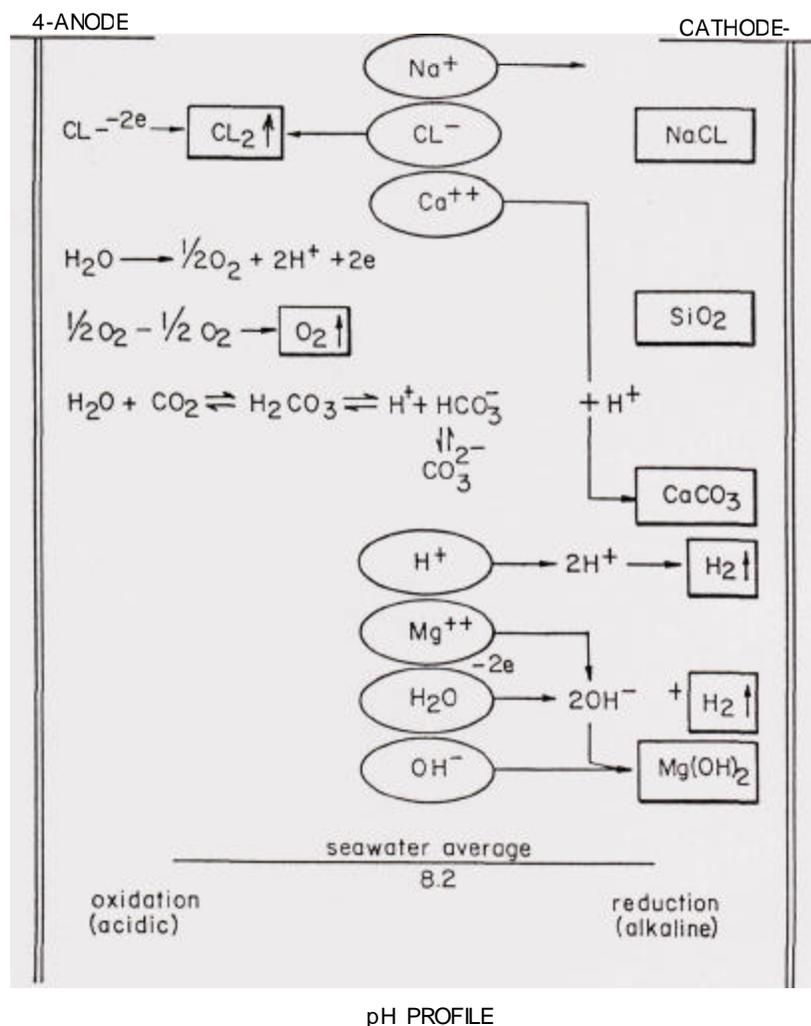
Hydraulic cement, in addition to using fossil fuel in its production, releases CO<sub>2</sub> during kilning. During calcination one molecule of calcium carbonate (CaCO<sub>3</sub>) is decomposed by heat into one molecule each of calcium oxide (CaO) and CO<sub>2</sub>. World production of hydraulic cement, the most widely used hardening agent, amounted to 0.12 10<sup>9</sup> tons in 1950, releasing 0.012 10<sup>9</sup> tons C into the environment. In 1988, production had already increased to 1.1 10<sup>9</sup> tons (1), adding 0.14 10<sup>9</sup> tons C to the atmosphere (Boden, T., CDIAC, US Dept. of Energy, pers. comm.). This alarming increase, because of its sheer volume, cannot be disregarded any longer. Although large energy efficiency improvements in the manufacture of the bulk of traditional building materials are feasible, alternative materials have to be developed as a climate defense measure.

Solar-generated building material (SBM) from seawater or brine is such an alternative. The concept underlying the formulation and development of SBM technology is based on the availability of almost unlimited and readily accessible resources such as minerals dissolved in seawater, carbon in the atmosphere/hydrosphere system, and renewable energy.

## RESOURCES

About 1.4 10<sup>9</sup> km<sup>3</sup> of ocean water constitute the earth's largest continuous ore-carrying body, containing a total mineral reserve of 54.4 10<sup>9</sup> tons of dissolved salts, covering 70.8% of the globe's surface (2). The 10 most abundant elements in seawater, in decreasing concentrations (3), are chlorine, sodium, magnesium, sulfur, calcium, potassium, bromine, carbon, strontium and boron. Magnesium, calcium and carbon are utilized in the composition of SBM in conjunction with oxygen (O) and hydrogen (H).

Within the carbon cycle 100 10<sup>9</sup> tons yr<sup>-1</sup> of atmospheric carbon are absorbed by the sea and 98 10<sup>9</sup> tons C yr<sup>-1</sup> are returned in



pH PROFILE

Figure 1. Electrochemical pathways of mineral accretion

the form of  $\text{CO}_2$ . Only a small fraction,  $24 \cdot 10^9$  tons C  $\text{yr}^{-1}$  is incorporated in organic matter and limestone in sediments (4). In 1988,  $5.66 \cdot 10^9$  tons C from fossil-fuel combustion were added to the carbon cycle, a rise of 3.7% over the previous year. Additionally,  $1\text{--}3 \cdot 10^9$  tons C from deforestation were released in 1988 (5).

## BIOGENIC CALCIFICATION

Lower marine organisms utilize sea salts and ambient energy to grow calcareous structures with various mechanisms. For instance, a significant proportion of the soluble protein of the organic matrix of mollusc shells is composed of repeating sequences of aspartic acid with a negative potential, possibly functioning as a template to bind with calcium ions, thus understood, it can be deduced that electrical currents affect mineralization and shell formation.

Zooxanthellae, dinoflagellate algae living symbiotically with all tropical reef-building corals, seem to have a major role in depositing  $\text{CaCO}_3$ , even though they do not appear to be directly related to the calcification process (7, 8). Using photosynthesis, zooxanthellae remove carbonic acid, a limiting factor in the rate of calcification, favoring the precipitation of aragonite.

A second mechanism proposed to explain the function of zooxanthellae in the calcification process is the absorption by algae of phosphates which may act as crystal growth inhibitors of  $\text{CaCO}_3$ , (9, 10).

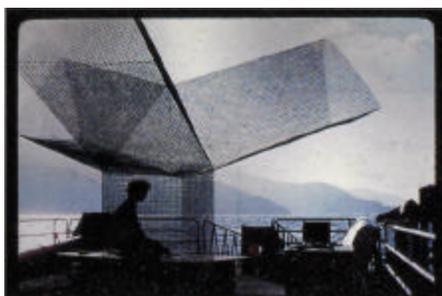
## SOLAR-GENERATED BUILDING MATERIAL

When a direct current (DC) is established between electrodes in seawater or brine, mainly magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ] and crystalline  $\text{CaCO}_3$  will be deposited at the cathode, with simultaneous gaseous evolution of hydrogen ( $\text{H}_2$ ). The anode produces oxygen ( $\text{O}_2$ ) and gaseous chlorine ( $\text{Cl}_2$ ). Chemical reactions during this process are outlined in Figure 1.

Electrolysis of seawater produces heat at the surfaces of the electrodes. Increased temperature reduces the solubility of  $\text{CO}_2$ , causing it to escape to the atmosphere. This raises the pH, converting bicarbonate to carbonate, increasing the ionic product of calcium carbonate and inducing mineral precipitation (11). As the electrolyte becomes more alkaline, at a pH greater than nine,  $\text{Mg}(\text{OH})_2$  (Brucite) as well as  $\text{CaCO}_3$  is precipitated (12). The pH of the electrolyte is determined by the current density applied between the electrodes, resulting in varying  $\text{Mg}(\text{OH})_2 / \text{CaCO}_3$  ratios in MA (mineral accretion) materials (13).

Electrical energy requirements to produce SBM can be minimized by applying extremely close spacing between electrodes, using highly conductive electrode materials, and working at the lowest possible voltage in tropical water or hot brine. With optimal conditions prevailing, one ton of SBM can be produced with expenditure of 1000 kWh or less.

Energy from a. intercepted solar radiation; b. geothermal; and c. tidal sources can



1. Cathodic building component before submersion. Photo: W.H. Hilbertz.



2. Cathodic building component shown in Photo 1 during accretion phase. Photo: W.H. Hilbertz.



3. Mature artificial reef. When structures like these are damaged mechanically, renewed application of electricity facilitates repair. Because of lower electrical resistivity in a broken area minerals will precipitate there preferentially. Photo: W.H. Hilbertz.



4. A growing spoil containment structure in the Gulf of Mexico. Photovoltaic panels were used as a backup to drive mineral accretion during frequent power outages. Photo: W.H. Hilbertz.



5. Autopia, ocean settlement with membrane construction. Photo: W.H. Hilbertz.



6. Light mesh cathode for fabrication of roofing components before submersion. Photo: W.H. Hilbertz.



7. Beginning colonization of accreted material by coral. St. Croix, USVI, 1976. Photo: W.H. Hilbertz.



8. Live coral (*Porites porites*) attached to active cathode. Discovery Bay, Jamaica, January 1991. Photo: W.H. Hilbertz.

## AGING OF MINERAL ACCRETION

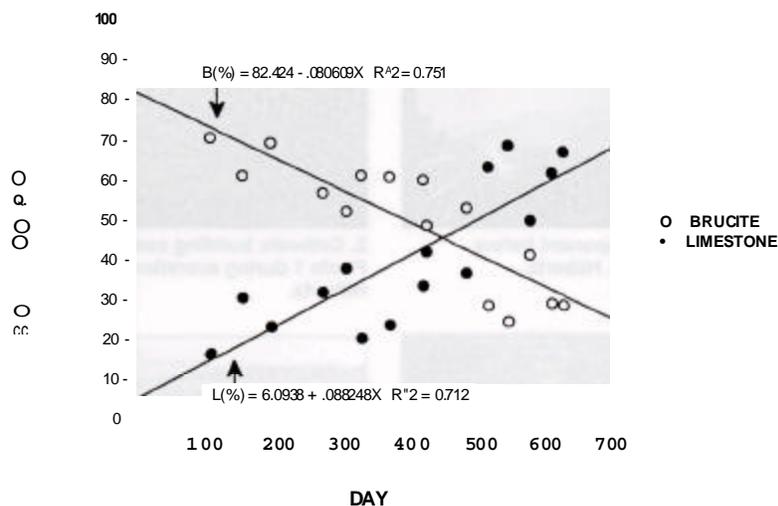


Figure 2. Change in material composition of accreted minerals. The proportions of brucite and limestone are the key determinants of the mechanical strength of the material and a measure for storage of carbon. The examined material was accreted in seasonally cold brackish water. Aging of MA should be accelerated in warm salty water. Plotted from data in Hilbertz (21). Figure by Thomas J. Goreau.

be harnessed to assemble SBM. More than 99% of these energy resources are of solar origin,  $173\,000\,10^{12}$  Watts (W), while terrestrial energy measures  $35\,10^{12}$  W, and tidal energy  $3\,10^{12}$  W(14).

Using electrolysis, numerous structures have been grown in open seawater since 1975. Photo 1 shows a building component before MA and photo 2 the same cathode during accretion. Heavy marine growth, mainly kelp, is evident.

Artificial reefs which could also double as coastal defense structures have been accreted and studied extensively (15). Generally, marine life in otherwise barren environment has increased manifold by the use of these reefs. Photo 3 shows dense marine growth, even higher plants, on an artificial and increasingly natural reef 12 months after installation in a barren sandy environment.

A coastal defense structure was grown at the Gulf of Mexico in brackish water averaging about 21 000 ppm of dissolved solids (photo 4). From this structure 15 MA samples were collected for analysis over a period of 16 months. Elemental chemistry was determined by energy dispersive X-ray fluorescence spectroscopy. Material concentrations were calculated assuming stoichiometry with oxygen. The data in Figure 2 support the hypothesis that, over time, the percentage of  $Mg(OH)_2$  diminishes while the percentage of  $CaCO_3$  increases; as it ages,  $Mg(OH)_2$  appears to be slowly replaced by  $CaCO_3$ . Results similar to those in Figure 2 are presented in Table 1. Mineral identification was determined by X-ray diffraction. The data show that amorphous (also platy or foliate)  $Mg(OH)_2$  is gradually replaced by crystalline  $CaCO_3$ , resulting in a material with higher mechanical strength, about 300 kg per  $cm^2$  break-strength in compression. This transformation of MA by dia- and biogenic processes

is of paramount importance for its utility and use. By careful control of pH during MA it is expected to achieve a break-strength of the material around 1000 kg per  $cm^2$ , using a pH of 8.7 during the MA phase.

### SBM AS A SINK FOR CARBON

Assuming a final  $CaCO_3/Mg(OH)_2$  ratio of 7 to 3 by weight of MA material as indicated by Figure 1, one ton contains 0.084 ton C. With an equal percentage of calcite and aragonite in the  $CaCO_3$  part, 1  $m^3$  contains 2.664 tons MA material of which 0.2238 ton is carbon.

Assuming that one kWh derived from renewable energy costs ECU 0.01 and an accretion rate of 1 kg MA per 1 kWh, 1 ton MA costs ECU 10.00. One  $m^3$  of SBM can be produced for ECU 26.64, arresting the carbon part of 0.82 ton  $CO_2$ .

Thus, one ton of carbon can be sunk into nearly twelve tons of useful SBM at an expenditure of ECU 120. To visualize sequestering of 10% of the combined carbon emissions in 1988 from fossil-fuel combustion, deforestation, agriculture, and cement and other traditional building material production (1988 = 7-10  $10^9$  tons), a volume equal to  $3.1 \times 10^4$   $km^3$  SBM would be required, costing ECU 83-118  $10^9$ .

SBM technology could add to the earth's  $CaCO_3$  stores while being used to grow useful structures in the ocean and on land. For example, coastal defense structures against rising sea level and artificial reefs for use in protein production and energy conversion. Autopias, capable of supporting human populations, can be constructed as sinks for carbon (Photo 5). These installations could also produce SBM for use elsewhere, replacing building materials made with hydraulic cement like concrete blocks, walls, and slabs, even foundations. SBM

Table 1. Mineralogical analysis of materials accreted in spoil containment structure.

Sample	Predominant constituent	Secondary constituent
1	Brucite	Aragonite/Calcite
2	Brucite	Aragonite
3	Brucite	Aragonite
4	Brucite	Aragonite
5	Brucite	Aragonite
6	Brucite	Aragonite
7	Brucite	Aragonite
8	Brucite	Calcite/Aragonite
9	Brucite	Aragonite/Calcite
10	Brucite	Aragonite
11	Aragonite/Brucite	-
12	Aragonite/Brucite	-
13	Brucite	Aragonite
14	Brucite/Calcite	Aragonite
15	Aragonite	Calcite

can substitute for bricks made of fossil-fuel fired lime and clay, not only reducing  $CO_2$  emissions, but subtracting carbon from the carbon cycle.

In Third World countries, building materials that require fossil fuels in their fabrication are generally precious commodities and all too often not affordable. Coastal populations in these countries could produce their own SBM and an impact would probably be made on global warming. Local economic dependency on imported building materials could be reduced or eliminated. Photo 5 shows a cathodic cylinder which can easily be assembled by unskilled labor. It consists of wire mesh that is available from the local hardware store. After completed MA it can be cut lengthwise twice or three times with a handtool to yield two or three roofing elements (Photo 6). Because of their curved cross sections, with a sufficient height, these, *canaletas* can span large distances using a minimum of SBM (16).

### HYDROGEN, OXYGEN, AND CHLORINE GAS

Using SBM technology will generate vast amounts of hydrogen, about 70 kg per  $m^3$  of MA, partially offsetting production cost and contributing to the emerging hydrogen economy. Oxygen and chlorine gas originating from the manufacture of SBM can be used in industrial processes, defraying operation costs still further. Options to eliminate the precipitation of Cl<sub>2</sub> in the anolyte are being examined.

### CORAL AND SBM

Coral-reef environments have among the highest rates of photosynthesis, nitrogen fixation, and  $CaCO_3$  deposition of any environment, supporting larger numbers of

plant and animal species than any other marine habitat. Central to this high productivity is the unique biology of corals which is of vital importance to the reef community's structure, ecology, and nutrient cycles (17).

Accepting the estimate of an existing worldwide reef area of 617 000 km<sup>2</sup> (18) and using specific measurements, coral reefs are estimated to act as a sink for 111 10<sup>6</sup> tons C per year (19). Considering that vast reef habitats are increasingly damaged by bleaching, hurricanes, excessive over-fishing, and tourism, the feasibility of re-pairing and even extending existing reefs has to be examined. SBM can be used to stimulate reef and shell-building organisms, creating artificial reef communities. Deployment of steel mats or wire mesh as artificial substrate for coral growth in areas predominated by soft, fine-grained sediments has been suggested (20). The use of accreted wire mesh is particularly suited for areas and sites with muddy bottoms (21). Productive artificial reefs, breakwaters, and other coastal defense structures can be grown in muddy waters where corals cannot grow (T.J. Goreau, pers. comm.).

Photo 7 illustrates an early experiment to graft hard coral onto SBM. A branch of elkhorn coral (*Acropora palmata*) was covered by a cathode of galvanized wire mesh. A single anode was placed nearby. Both electrodes were connected to a small photovoltaic cell above sea level, causing MA to envelop the coral branch. After completed accretion (15 days later) coral began to colonize the SBM, starting at the coral-sided fringe of the cathode covered with MA. Similar investigations are in progress involving multiple specimens of several live coral species which were attached to MA surfaces without electricity and cathodes producing MA (Photo 8). The coral specimens are monitored to determine the effects of electric fields, hydrogen evolution at the cathode, pH of the surrounding electrolyte, ion density in the vicinity of the cathode, and other factors.

Using SBM substrate to expand existing coral reefs and establishing new coral habitats in hitherto barren environments, the mass of living coral can be increased. Shallow oceanic regions, too cold now to support coral growth, could possibly warm sufficiently in the future to sustain coral habitats which might be initiated on SBM substrate. While coral reefs might slowly recede from locations in the tropics due to rising water temperatures, habitats might be established at the outer fringes of the tropics which might warm in the course of greenhouse events.

It has been pointed out that under heightened greenhouse conditions existing reefs could double CaCO<sub>3</sub> deposition (19). Thus, significant amounts of carbon could be sequestered by SBM substrate for coral growth and newly growing coral stock.

The Environmental Protection Agency (EPA), Washington, has identified 25 major deltas and 39 major marshes and lagoonal areas, globally, which are highly vulnerable to rising sea levels (22). Providing for protection of these and marginal low-lying areas worldwide against a

sealevel rise of one meter will require an SBM volume equal to 800-120 km<sup>2</sup> fomed into land defense structures of various designs. This volume of SBM could remove 180-270 10<sup>6</sup> tons of carbon. Thus, harnessing minerals and CO<sub>2</sub> dissolved in the increasing volume of seawater can provide bulk material for coastal defense while, simultaneously, the single most important factor causing sea-level rise is reduced.

## CALCIUM CARBONATE AS A BUILDING MATERIAL

Nature uses controlled and uncontrolled biomineralization processes to build a variety of structures. At least 55 phyla mineralize. They produce about 60 different minerals (23). CaCO<sub>3</sub> is one of the more abundant minerals involved in these processes which are often on such a scale that they affect ocean/atmosphere chemistry and form major parts of sedimentary rocks.

Several millenia ago man began to learn how to use limestone and marble to build structures. Wherever available, hard coral species have been utilized for centuries as a dependable and lasting building material for structures and roads. A good estimation is that more than half of the bulk of the construction material used in the ancient city of Cartagena de las Indias in Colombia con-

sists of coral blocks. Similar observations can be made in nearly all settlements around the world which have access to coral reefs. Until recently, natural coral quarries have yielded vast amounts of limestone for building.

Expanded artificial/natural reefs using MA could be used to produce large amounts of proven building material. At the same time, as a result, global warming would be mitigated.

A note of caution needs to be taken (T.J. Goreau pers. comm) in equating carbon removal from the ocean with carbon removal from the atmosphere. When one molecule CaCO<sub>3</sub> is precipitated from seawater, charge balance requires the formation of one molecule of carbonic acid and supersaturation of carbonic dioxide. If this escapes to the atmosphere, carbon is removed from the hydrosphere, but CO<sub>2</sub> added to the atmosphere. Therefore, deposition of CaCO<sub>3</sub> is often seen as a source of atmospheric CO<sub>2</sub>, ignoring all other reactions which could produce or consume acidity or CO<sub>2</sub>. SBM is a sink for carbon although its direct effect on the atmosphere has to be treated as controversial. To fully assess the role of SBM in the global atmospheric balance the net effect of all electrolytic and biogenic reactions needs to be measured experimentally.

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