Electrodeposition of Minerals in Sea Water: Experiments and Applications

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Abstract—By establishing a direct electrical current between electrodes in an electrolyte like sea water, calcium carbonates, magnesium hydroxides, and hydrogen are precipitated at the cathode, while the anode produces oxygen and chlorine. Recent experiments have demonstrated in part the feasibility of using the electrodeposited minerals as building materials for a wide variety of purposes, including the construction of artificial reefs. Several of these experiments are described and some implications for marine building technology are discussed.

I. INTRODUCTION

SEA WATER contains nine major elements: sodium, magnesium, calcium, potassium, strontium, chlorine, sulfur, bromine, and carbon. These elements comprise more than 99.9 percent of the total dissolved salts in the ocean [1]–[4]. The constancy of the ratios of the major elements throughout the oceans has long been well known [5]. In 1837, following the work of Davy on the protection of iron by zinc anodes, Mallet demonstrated that zinc so used became covered with a thick layer of zinc oxide and calciferous crystals which blocked the zinc surface [6], [7]. In 1940 and 1947, G. C. Cox was issued U.S. Patents No. 2 200 469 and No. 2 417 064, outlining methods of cathodic cleaning and protection of metallic surfaces submerged in sea water by means of a direct electrical current. During the cleaning process, a coating is also formed cathodically, consisting of magnesium and calcium salts [8]. If this coating is hard and continuous, it affords a considerable degree of corrosion protection to the enclosed metal [9], [10]. Lower marine organisms utilize the minerals in solution surrounding them to build structural formations. Mollusk shells, for instance, are generally composed of calcium carbonate crystals enclosed in an organic matrix. A significant proportion of the soluble protein of the matrix is composed of a repeating sequence of aspartic acid, separated by either glycine or serine [11].

This sequence, comprising regular repeating negative charges, could bind Ca^{2+} ions and thus perform an important function in mineralization of the template [11].

Although impressed current produced $CaCO_3/Mg(OH)_2$ formations were precipitated since the 1940's, these were never thought of as possible building components until recently. Consequently, only few publications outline structural testing of these materials, describe experiments and techniques using the electrodeposited material for a wide variety of structural purposes, and report on the possible suitability of the material as a substrate for biological growth in mariculture facilities and as a primary construction material for same [12]–[22].

TABLE I
ELECTROCHEMICAL REACTIONS

II. EXPERIMENTS

Large-scale studies with galvanized iron mesh cathodes and iron/lead anodes immersed in sea water have provided evidence for the role of electrochemical processes in the accretion of minerals [18]. A preliminary qualitative model for these processes has been proposed (Table I).

In order to devise methods which would allow the solid accretion of a three-dimensional cathode, the "onion" experiment was devised. This cathodic cube consisted of seven insulated layers of $\frac{1}{8}''$ galvanized hardware cloth. Immersed in sea water containing a lead anode, layer 1 was connected to the power supply. After sufficient accretion thickness was achieved, layer 2 was connected, and so forth. A solidly accreted cube was obtained [18].

Parts of beach sand volumes, between electrodes, contained in 10-gal tanks and saturated with sea water, were solidified. The results were cemented sheets of sand after flushing of loose sand particles. The water/sand mixtures were kept at a temperature ranging from 78 to 82°F. Power was supplied for 720 h at a rate of 5 V, 300 mA. During the experiments, fresh sea water was added to replace water lost through evaporation and electrolysis.

Since all previous mineral accretion experiments were performed in water depths not exceeding 15′, an experiment was devised to accrete on a 15 cm by 15 cm $\frac{1}{2}''$ galvanized hardware cloth cathode with a 1 mm × 15 mm × 30 mm lead anode at a depth of 450′ at Cane Bay, St. Croix, for 42 h. A control experiment using the same equipment, power input,
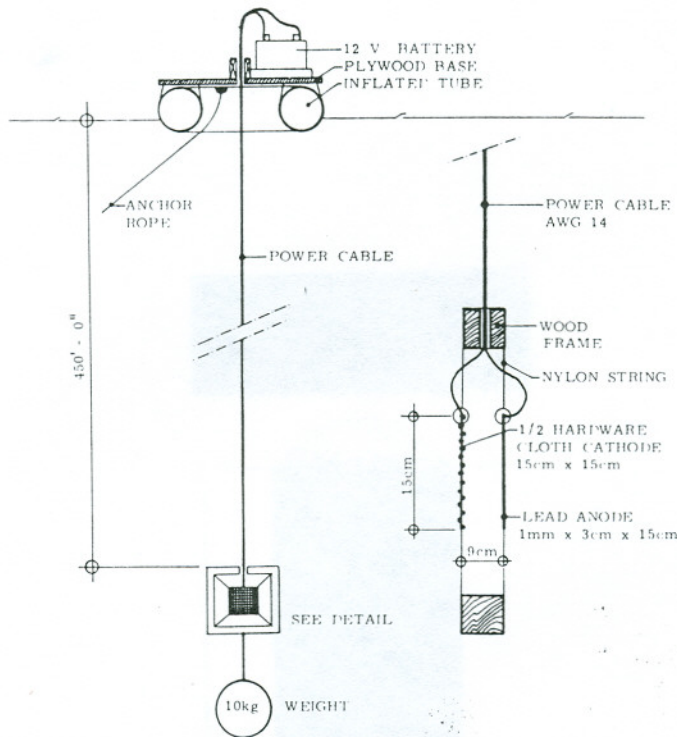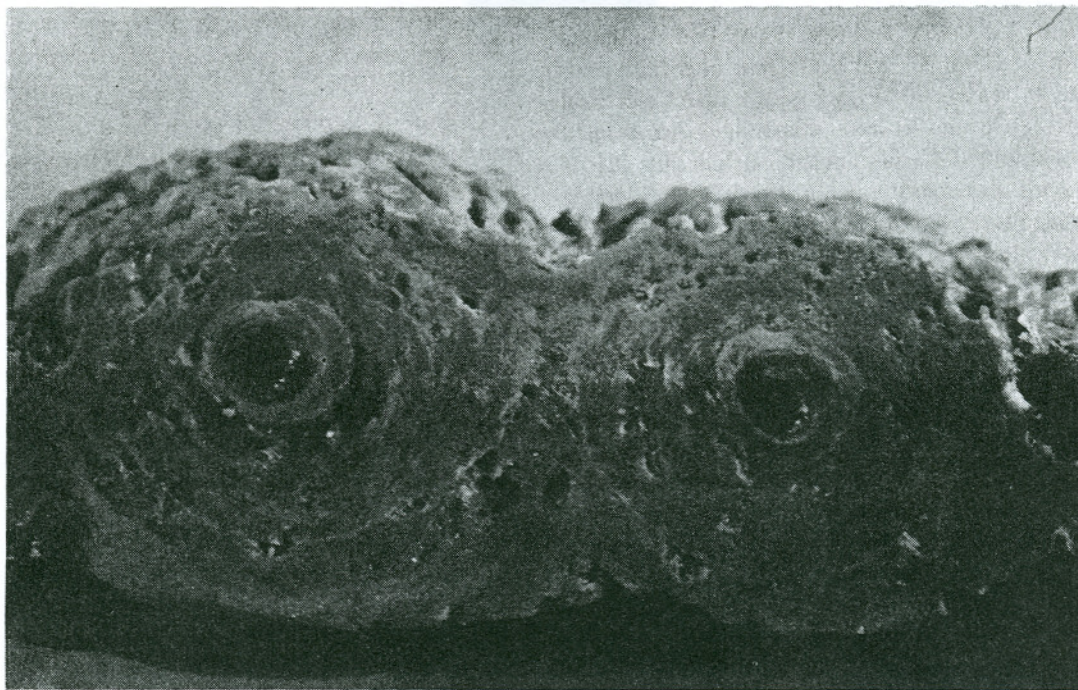
Fig. 1.   Deep water accretion experiment in St. Croix.

Fig. 2.   Accreted material on $\frac{1}{2}$" hardware cloth cathode.

and time span was performed at a depth of 1′ in Tague Bay, St. Croix. Identical accretion thickness was achieved in both experiments (Fig. 1). The current was supplied by a car battery and measured 12.25 V/1.65 A at the beginning of the experiment, and 3.8 V/170 mA at the termination.

A typical section of accreted material on a $\frac{1}{2}$" galvanized hardware cloth cathode is shown in Fig. 2. The two dark areas within the material mark the sections of the wiremesh. This

sample was obtained in the Port Aransas ship channel at a depth of ±2 m. The clearly discernable "rings" might reflect periods of time under electric power and without power. It cannot be precluded, however, that seasonal changes also might be reflected.

A neutron activation quantitative analysis of this material performed in 1976 at the Nuclear Reactor Laboratory at the University of Texas at Austin gave the results in Table II.

TABLE II
QUANTITATIVE NEUTRON ACTIVATION ANALYSIS

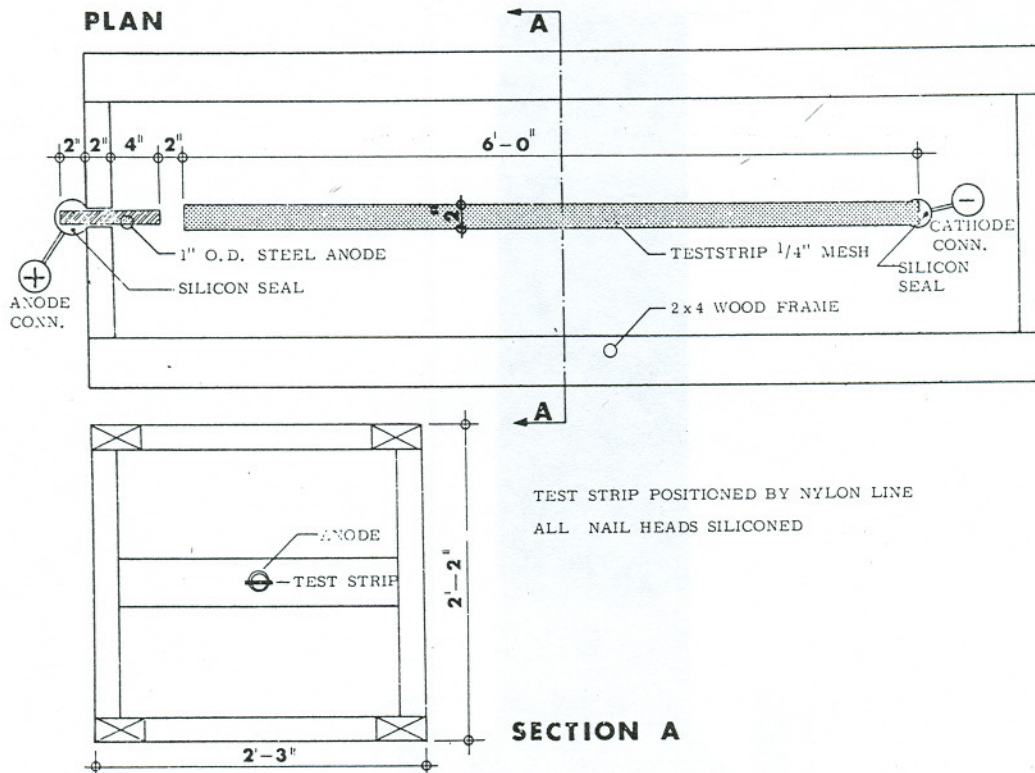| Element	%	Chemical Composition Error %
Mg	32.1	$\pm$ 4.5
V	3.4×10^{-4}	$\pm$ 6.9×10^{-5}
Al	.9	$\pm$ 1.9×10^{-3}
Ca	11.76	$\pm$ .72
Mn	.005	$\pm$ .001
Cl	.118	$\pm$ .004
Na	1.56	$\pm$ .01
Br	.53	$\pm$ .05

Fig. 3.   Test strip 1.

In order to determine accretion rate and composition of electrodeposited material as a function of proximity of electrodes, location of negative pole cable connections, and gas evolution, the following experiments were devised:

A. Test Strip 1 (St. Croix)

A steel anode was positioned 2″ opposite the narrow side of a 2″ × 72″ galvanized $\frac{1}{4}$″ wire mesh strip with a surface area of 1 ft^2 (Fig. 3). The cathode wire was connected to the narrow end of the strip *farthest* from the anode. The supportive wood frame measured 2′3″ × 2′2″ × 8′0″. All bare nail heads in the wood frame were covered with silicone. The cathode was fastened with $\frac{1}{16}$″ nylon string in the frame. Direct electrical current was delivered by a regulated power supply. Both anode and cathode wires were 8AWG multistrand insulated copper wire with a length of 15′0″ each. All electrical connections were insulated with clear silicon. The frame was submerged in ±2′0″ of water in Tague Bay. Ambient water temperature was 85°F.
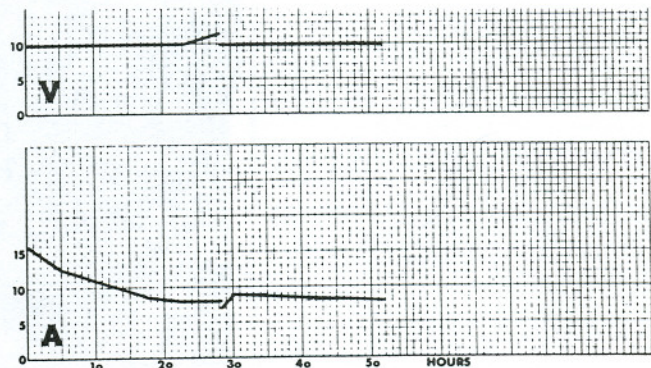

Fig. 4.   Consumption of electricity, test strip 1.

The test strip was submerged and under power for 52 h. Consumption of electricity is shown in Fig. 4. After submersion, the electrodeposited strip was divided into 12 sections measuring 6″ each. At these sections, thickness of electrodeposited material was determined with a steel caliper (Fig. 5).
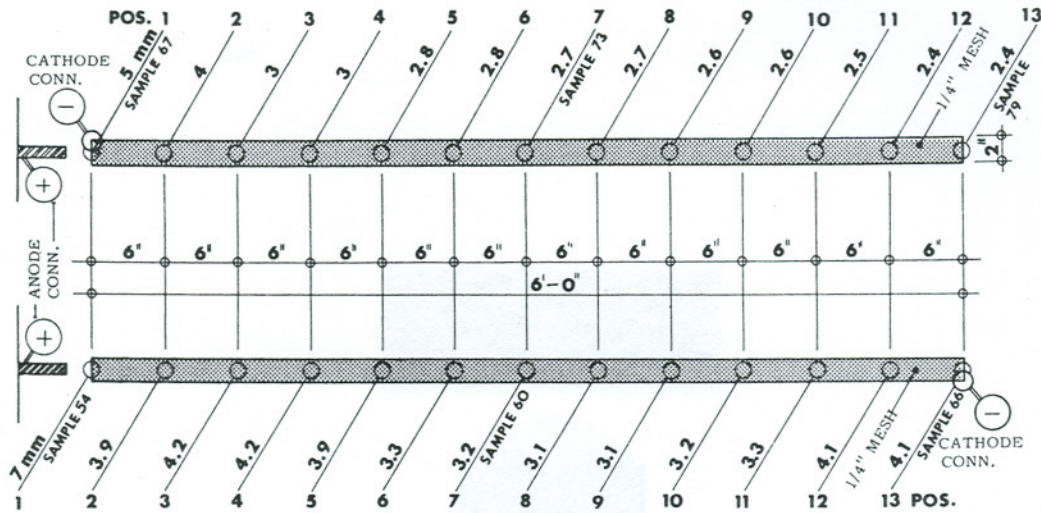
Fig. 5.   Test strip 1 (below), test strip 2 (above).

TABLE III
CHEMICAL COMPOSITION OF ACCRETED MINERALS, TEST
STRIP 1

#	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
54	0" from Anode	80%	6%	5%	2%	1%	6%
60	36" from Anode	61%	10%	2%	12%	1%	14%
66	76% from Anode	60%	4%	3%	10%	–	23%

TABLE IV
CHEMICAL COMPOSITION OF ACCRETED MINERALS, TEST
STRIP 2

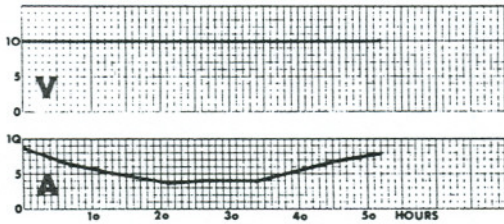| #	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
67	0" from Anode	68%	12%	5%	4%	4%	7%
73	35" from Anode	70%	25%	4%	–	–	1%
79	72" from Anode	79%	18%	3%	–	–	0%

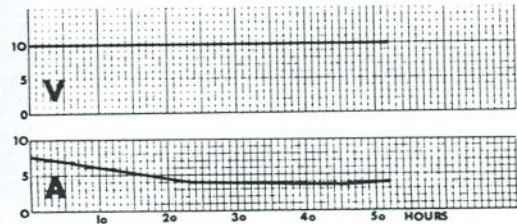Fig. 6.   Consumption of electricity, test strip 2.

Fig. 7.   Consumption of electricity, test strip 3.

At *positions 1, 7, and 13,* material samples were taken (54, 60, 66) and analyzed using a Philips X-ray diffractometer, involving an error factor of ±10 percent (Table III).

B. Test Strip 2 (St. Croix)

The arrangement was identical to that used for test strip 1, except that the cathode wire was connected to the narrow end of the strip *closest* to the anode (Fig. 5).

The test strip was submerged and under power for 52 h.

Consumption of electricity is shown in Fig. 6. After submersion the electrodeposited strip was divided into 12 sections measuring 6" each (Fig. 5). At these sections, thickness of electrodeposited material was determined with a steel caliper. At positions 1, 7, and 13 material samples were taken (67, 73, 79) and analyzed using a Philips X-ray diffractometer, involving an error factor of ±10 percent (Table IV).

C. Test Strip 3 (Port Aransas)

The arrangement was identical to that used for test strip 1. The cathode wire was connected to the narrow end of the strip *farthest* from the anode.

The frame was submerged in 2'0" of water in a concrete tank with a flow rate of $3\frac{1}{2}$ gal/min of sea water from a settling tank. Ambient water temperature was 74°F.

The test strip was submerged and under power for 52 h. Consumption of electricity is shown in Fig. 7. After submersion, the electrodeposited strip was divided into 12 sections measuring 6" each (Fig. 8). At positions 1, 7, and 13, material samples were taken (98, 99, 100) and analyzed (Table V).

D. Test Square 1 (St. Croix)

A steel anode was positioned 6'0" opposite a $\frac{1}{4}$" 1 ft^2 galvanized wire mesh anode. The supportive wood frame measured 2'3" × 2'2" × 8'0" (Fig. 9).

The cathode was fastened with $\frac{1}{16}$" nylon string in the frame. Direct electrical current was delivered by a regulated power supply. Both anode and cathode wires were 8AWG multistrand insulated copper wire with a length of 15'0" each. All electrical connections were insulated with clear silicone. The frame was submerged in ±2'0" of water in Tague Bay. Ambient water temperature was 85°F.
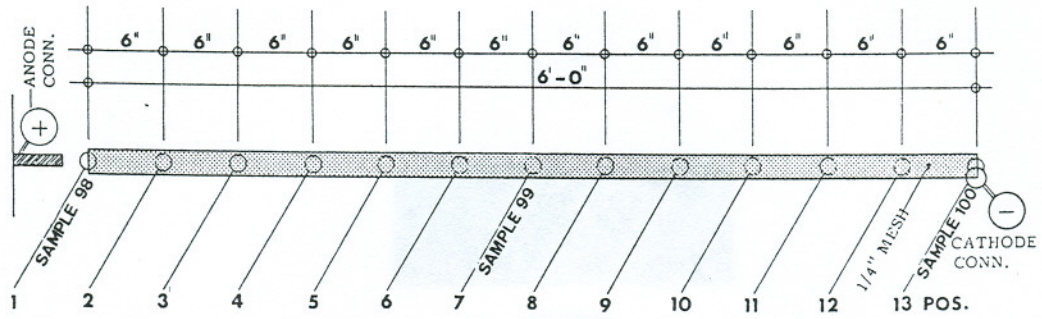
Fig. 8.   Test strip 3.

TABLE V
CHEMICAL COMPOSITION OF ACCRETED MINERALS, TEST
STRIP 3

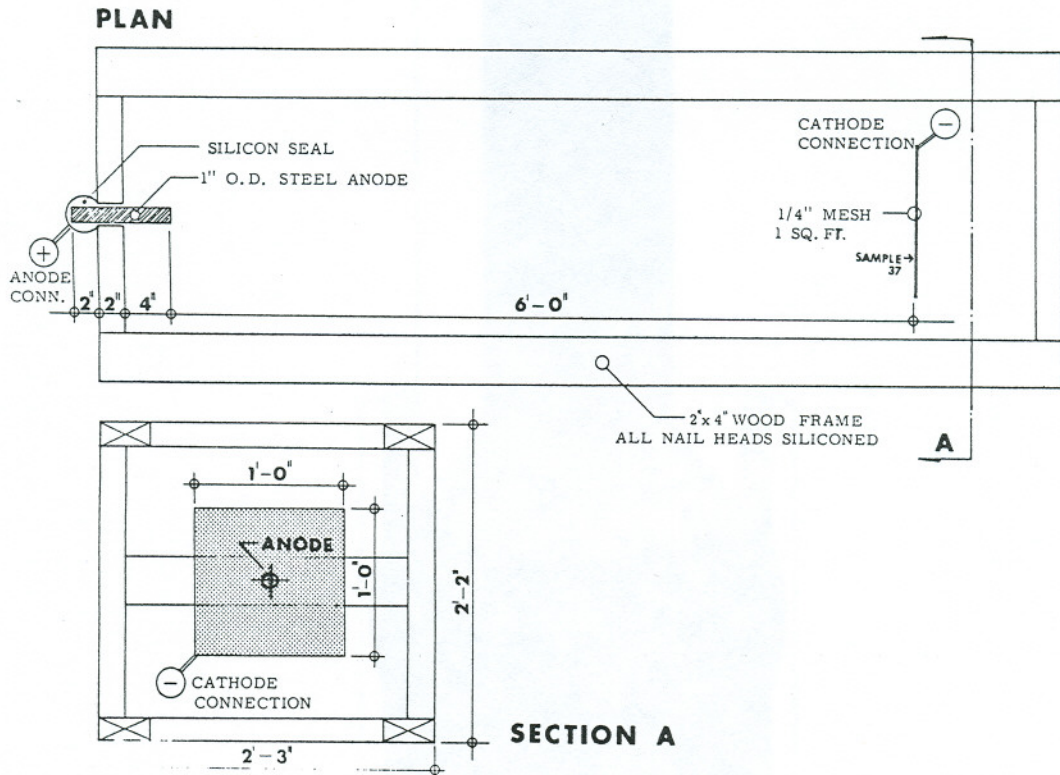| #	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
98	0" from Anode	80%	8%	1%	8%	3%	0%
99	36" from Anode	70%	22%	2%	-	-	1%
100	72" from Anode	25%	5%	trace	15%	trace	54%

Fig. 9.   Test square 1.

Before submersion, the 1 ft^2 $\frac{1}{4}''$ wire mesh cathode weighed 96.2 g. The test frame was submerged and under power for 42 h. Consumption of electricity is shown in Fig. 10.

One material sample (37) was taken after 42 h and analyzed (Table VI). After electrodeposition, the cathode was dried for 22 h at 200°F. Weight of the cathode was 184.5 g. Thus 88.3 g of material was precipitated with an electric input of approximately 46 W, giving the approximate value of 1.9 kg of accreted mass per 1 kW expended.
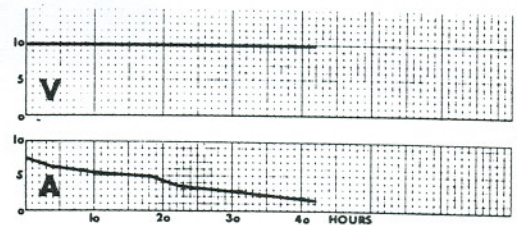

Fig. 10.   Consumption of electricity, test square 1.

TABLE VI
CHEMICAL COMPOSITION OF ACCRETED MINERALS, TEST
SQUARE 1

#	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
37	Taken at disconnect	70.	15%	1%	10%	1%	3%

The composition of the accreted material on test square 1 is very similar to the material at the center sample position of test strips 1, 2, and 3 (Tables III–V, Samples 60, 73, 99) that is, greater amounts of aragonite and less noncrystalline matter are evident.

Since the location of the cathode connection is at the top of the test square, the concentration gradient caused by different temperature/resistance factors would be less at the bottom and the accreted matter would exhibit properties like Samples 60, 73, and 99 of the test strips. It is hypothesized that, during the electrochemical process, there are three methods by which material can be accreted: 1) concentration gradient; 2) ionic attraction; and 3) electrical migration. The former is the most likely to be the cause of these findings. From comparative analyses of X-ray diffraction tests (Tables III–VI), the following preliminary conclusions can be drawn:

1) Positioning of the anode and cathode connections relative to the cathode surface area has a definite effect on the composition of material accreted in their vicinity and determines the amount of noncrystalline matter enveloped in the accretion matrix.

2) Since the position farthest from either anode or cathode cable connection reached the maximum amount of aragonite, it seems that the greatest electrochemical circuit resistance is developed near the anode and cathode cable connections. If the resistance is greater at these connections, temperature will increase and as a function of temperature, the pH will rise. Thus less favorable conditions to precipitate $CaCo_3$ exist.

3) Conversely, evolution of O_2 at the anode may decrease the pH to an unfavorable state for the precipitation of $CaCO_3$, having overcome the initial tendency for temperature/resistance to increase the pH.

4) Peak intensities and breadths from X-ray diffraction analysis reveal very few "perfect" crystals formed. Broadening of the reflections occurs due to the mosaic structure of the mineral crystals, i.e., they are composed of smaller differently oriented blocks of crystals. This broadening could also occur from lack of chemical homogeneity in the specimen. These results would support the conclusion that loosely bound crystalline structure is precipitated through physicochemical reactions of concentration gradients.

5) Considering Fig. 5, it seems that electric migration and/or ionic attraction are also significant at the anode/cathode connections. Relative thicknesses (in mm) are shown at 6″ intervals along test strip 1 and 2. Test strip 1 displayed a curve from anode end to cathode connection end: greater thicknesses at both ends and the least in the center. Test strip 2 displayed another characteristic due to the position of the cathode connection: thicknesses decreased with more distance from the electrical activity at the anode end.

6) It is evident in all cases that the greatest percentage of sample material is brucite $(Mg(OH)_2)$. It was found in two of its three distinct forms: the platy or foliate type, and massive material. Brucite, in its foliate form, is harder than talc and gypsum, and not elastic; in its massive material form it has a "soapy" appearance. It is possible that some small percentages of the composition consist of portlandite $(Ca(OH)_2)$, which is isostructural with brucite, but not as yet detected through X-ray diffraction. This is due to concentration and availability of the (OH--) and (CO3--) anions at a pH greater than 9.00 at which point brucite is known to precipitate. Fast precipitation of compounds from sea water usually results in brucite of the massive material form; slow precipitation and phasing usually result in brucite with the platy or foliate crystalline structure.

During 1977, the construction of a cathodic hull for a boat was completed [19]. The frame consists of $1\frac{1}{2}'' \times 1\frac{1}{2}''$ yellow pine to which the double-layered $\frac{1}{2}''$ galvanized hardware cloth is stapled. Spacing between layers is $\frac{3}{8}''$. The hull is being accreted at the present, consuming dc at 12 V and 1.5 A.

III. ARTIFICIAL REEFS

It has long been evident that substrates to which marine organisms can attach themselves and/or find shelter within, attract fish populations.

The oldest recorded establishment of artificial reefs dates back to the early 1800's [23]. Since the early 1950's American marine fishery interests have been investigating the possibility of using artificial reefs as management tools for manipulation of fish populations [24], [25]. Calculations of fish populations on artificial reefs as compared with control areas or before reef placement showed increases of between 3 to 16 times [26]–[28]. Since the choice of material determines to a large extent transportation, construction, and maintenance cost of artificial reefs and their design, this factor becomes very important.

Preliminary investigations indicate that the mineral accretion process produces a very suitable substrate for marine growth and, at the same time, a strong primary building material [18], [19]. Accreted wire mesh components also present a reduced profile, compared to solid components, which reduces resistance to water currents, thus increasing stability while offering open volumes and entrances for shelter to marine organisms.

Placement of steel mats or wire mesh as an artificial substrate in areas predominated by soft, fine-grained sediments has been suggested [29]. Accordingly, the use of accreted wire mesh may be particularly well suited for these areas.

Two artificial reefs were constructed and placed in Tague Bay, St. Croix, in August 1976. These constructions were built to determine the parameters of the electrodeposition process onto large surfaces as substrate for marine growth, and to support the hypothesis that wire mesh formations covered by electrodeposited minerals can support marine communities that are usually found inhabiting natural reef formations [18]. Both of these reef components were placed in shallow waters approximately 8′ deep, on relatively barren and sandy substrate with small amounts of seagrass (*Thalassia*) present.

ELEVATION
1/2" = 1'- 0"
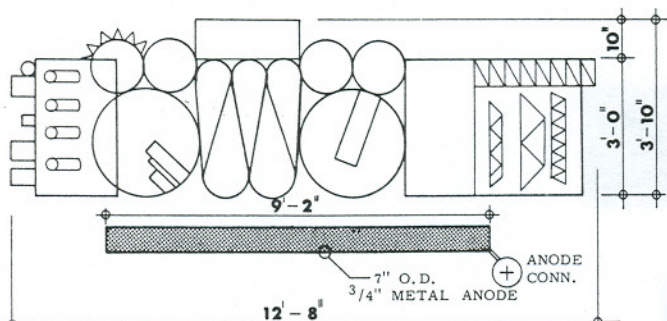
PLAN
1/2' - 1'- 0'
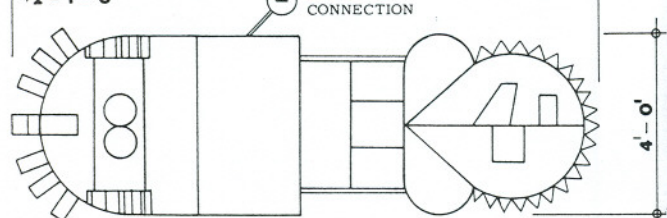
SURFACE AREA

1" x 2" MESH	141 1/4 SQ. F.
1/2" MESH	58 3/4 SQ. F.
1/4" MESH	33 1/3 SQ. F.
1/8" MESH	18 3/4 SQ. F.

Fig. 11.   Artificial Reef 1.

Direct electric current was supplied intermittantly to the reef components by an unregulated power supply in the range of 3–16 V/10–40 A.

Reef 1 consists of an assembly of regular and irregular shapes constructed with wire mesh of different gauges a total surface area of 253 ft^2 (Fig. 11). Overall dimensions of the reef are 4' × 12.67' × 3'. Average accretion thickness on the wire mesh is $\frac{3}{8}$" with thickness in some areas up to 3 in (Fig. 12). Fish censuses performed 4$\frac{1}{2}$ months and 15 months after placement indicated 127 individuals (5 species), and 483 individuals (19 species), respectively. The most dominant fishes were medium-sized grunts, parrot fish, and damsel fish.

Twenty hours after submersion white accreted material was visible on all surfaces of the structure. Seventy-two hours after submersion diatomatious and blue-green algae growth was observed on the outer surface of the structure, gradually covered all surfaces, and had reached a length of 8 cm, 280 h after inhabiting the structure. The first sample of the electrodeposited material was taken 437 h after the start of electrodeposition (Table VII, Sample 33); the second sample was taken 1991 h after the start of electrodeposition and 1508 h after the power supply was disconnected (Table VII, Sample 95). Mineral deposition thickness on 1" × 2" mesh measured 5.4 mm (diameter of metal wire = 1.75 mm) after 480 h of electrodeposition, consumption of electricity is shown in Fig. 13. The temperature of the electrolyte ranged between 82 and

88°F. The anode consisted of a cast iron 7" OD metal pipe with a length of 9'2", and was placed parallel to the cathode at a distance of 4'0" on sandy ground.

A moderate input of electrical power provided a mineral substrate that allowed rapid diatomatious and blue-green algae growth which, possibly in connection with the availability of protected spaces, attracted various fish populations. The electric field between anode and cathode did not negatively affect algae growth, as was clearly established by the observation of an electrodeposited control sample without electric field under identical conditions.

Inhabiting fish populations visibly were not affected negatively by the electric field; individual animals moved freely in and around the structure.

Preliminary conclusions from X-ray diffraction analysis show, that, after the phasing sequence, the crystalline structure of the accretion matrix becomes more apparent. Peak intensities and breadths indicate more well-ordered crystals and less non-crystalline material.

Reef 2 consists of identically folded wire mesh formations of two different gauges with a total surface area of 144 ft^2. Overall dimension are 7.5' × 7.5' × 6'.

The anode consisted of a cast iron 6$\frac{3}{4}$" OD pipe with a length of 7'3" and was placed under the reef.

Fifteen hours after submersion white accreted material was visible on all surfaces of the structure. Seventy-two hours after submersion the same growth as on Reef 1 was observed covering the entire structure and reaching a length of 8 cm, 190 h after submersion. Schools of small fish were observed grazing off the growth and inhabiting the structure.

Consumption of electricity is shown in Fig. 14. One material sample was taken 413 h after submersion (Table VIII, Sample 32). Mineral deposition thickness on the 1" × 2" wire mesh measured 6.2 mm (diameter of metal wire 1.75 mm) after 485.5 h of electrodeposition.

Fish censuses performed 4$\frac{1}{2}$ months and 16$\frac{1}{2}$ months after placement indicated 92 individuals (6 species) and 142 individuals (14 species), respectively. Again, the fish population was dominated by grunts, parrot fish, and damsel fish.

Artificial Reefs 3A and 3B were built to determine to what degree the electrodeposited minerals on wire mesh formations enhance the development of marine communities, and to what degree the wire mesh formation simply acts as an attractant. Two reef components were constructed and submerged in August 1977, in Tague Bay. Both components are identical in size and construction, each consisting of folded plate $\frac{1}{2}$" galvanized wire mesh formations on a wood frame, having a total mesh surface area of 192 ft^2 and overall dimension of approximately 19.5' × 5' × 4.5' in height (Fig. 15).

Both components are situated in a water depth of ±15' on relatively barren, sandy bottom with a small amount of seagrass (*Thalassia*) present. One component (Reef 3A) is supplied with dc from an unregulated power supply in the range of 6–12 V/10–20 A; the other component, Reef 3B, is not under power, thus acting as a control since no electrodeposition occurs, and is situated 265' from Reef 3A. Floral and faunal censuses are taken every 6 weeks at both the accreting reef and

Fig. 12.   Detail of artificial Reef 1 after accretion.

TABLE VII
CHEMICAL COMPOSITION OF ACCRETED MINERALS,
ARTIFICIAL REEF 1

#	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
32	–	40%	3%	1%	2%	trace	54%

TABLE VIII
CHEMICAL COMPOSITION OF ACCRETED MINERALS,
ARTIFICIAL REEF 2

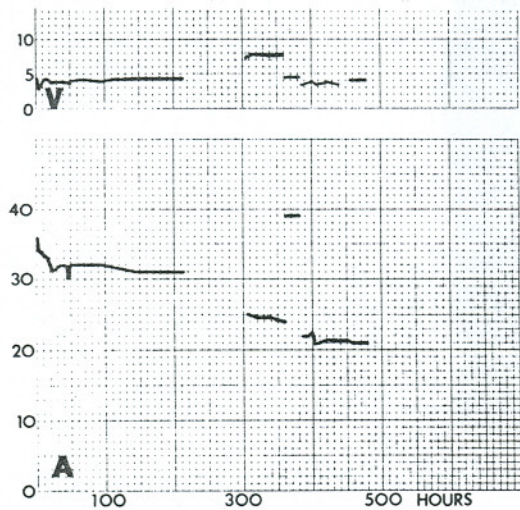| #	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
33	taken 437 hrs after power initialized	50%	10%	4%	–	1%	35%
95	1508 hrs after disconnect	98%	2%	trace	trace	trace	0%

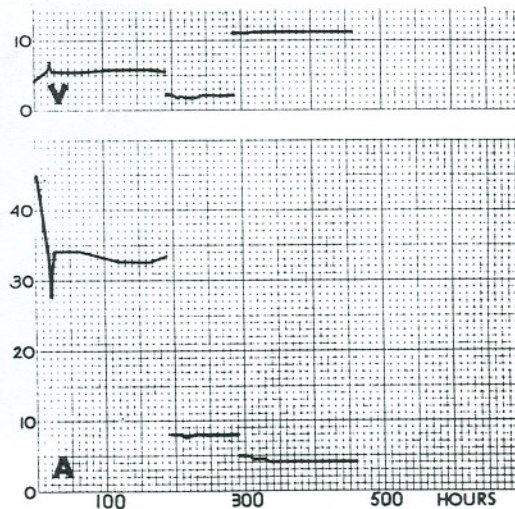Fig. 13.   Consumption of electricity, artificial Reef 1.

Fig. 14.   Consumption of electricity, artificial Reef 2.

FOLDED HARDWARE CLOTH CONSTRUCTION
NOTE: CONTROL REEF 3B IS IDENTICAL EXCEPT FOR
ANODES AND ANODE / CATHODE CABLES
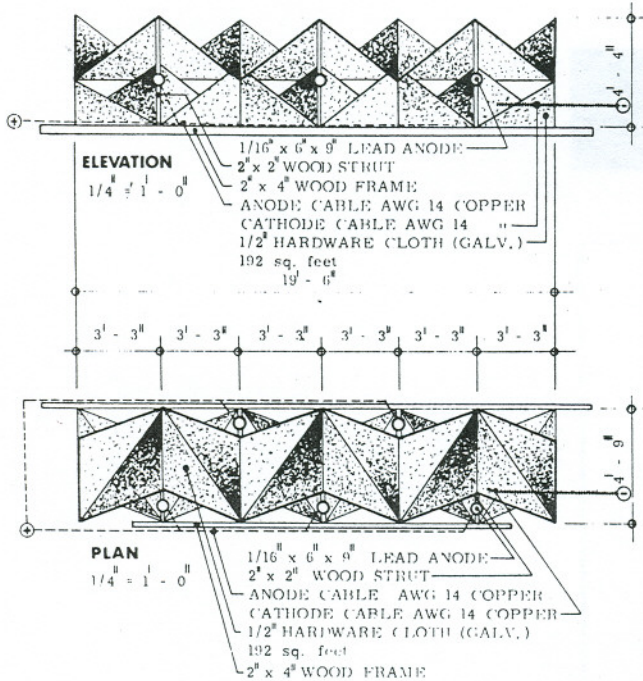WOODFRAME: 2" x 4" FIR NAILED. MESH FASTENED WITH NAILS

Fig. 15.   Artificial reef components 3A and 3B.

Fig. 16.   Artificial Reefs 4 and 5.

the control reef. Fish counts taken $6\frac{1}{2}$ months and 8 months after placement of Reef 3A indicated 17 individuals (8 species) and 33 individuals (8 species), respectively. Fish counts taken at the same time on Reef 3B indicated 33 individuals (10 species) and 16 individuals (7 species). More than 39 spiny lobsters (*Panulirus Argus*) were seen in Reef 3A, while none were seen in Reef 3B, 8 months after placement.

Reefs 4 and 5. Two larger artificial reefs, utilizing the mineral accretion process, were built and submerged in Corpus Christi Bay in water depth of $\pm12'$ on sandy bottom and 6 mi offshore Port Aransas in a water depth of $\pm60'$. The two reef assemblies are supplied with dc each by a 600-W wind-driven alternator, facilitating the utilization of locally available energy (coastal winds). The wind-driven units are located on platforms near the reefs.

Each reef assembly consists of 10 folded plate $\frac{1}{2}''$ galvanized hardware cloth components having overall dimensions of $3'0'' \times 4'0'' \times 10'0''$.

Total surface area of the hardware cloth used in each assembly is 2000 ft². The components were arranged uniformly over an area measuring $46' \times 18'$ on the sea floor (Fig. 16). Fig. 17 shows the arrangement simulated on land.

Two 8-lb lead anodes were positioned approximately 30' from the reef in Corpus Christi Bay, and approximately 90' from the reef offshore.

These reef formations, once accreted, will represent a considerable reduction in transportation and material costs when compared to concrete block or tire reefs, as the bulk of the material (substrate for marine growth and shelter) is assimilated
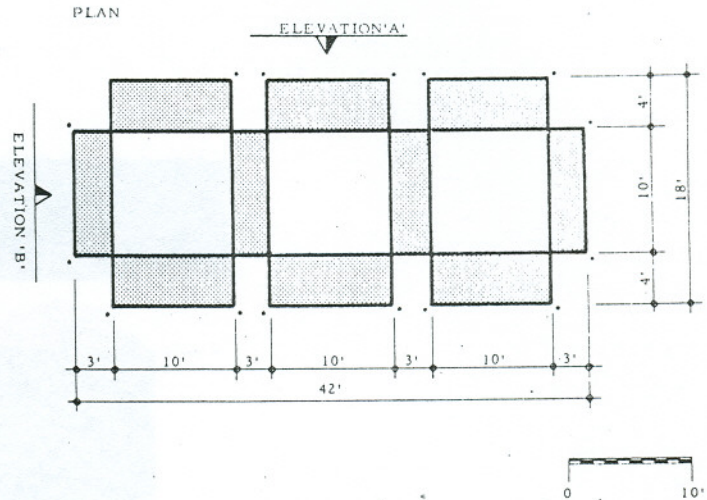
on the site. In addition, the initial layer of electrodeposited material presents corrosion of the wire mesh template.

IV. BUILDING COMPONENTS

To investigate the use of mineral electrodeposition for the construction of building components, several experiments involving large cathodic surfaces were devised.

Drum 1 consists of three layers of galvanized wire mesh with various gauges. The anode was positioned along the axis of the cylinder. The surface area of the cathode measures 81 ft². The anode consisted of a $1''$ steel rod with a length of $4'0''$. Anode and cathode wires consisted of 4AWC neoprene covered copper cable with a length of $30'0''$ each. Direct current was provided by three unregulated power supplies operating in sequence. All wire connections were insulated with clear silicone. Drum 1 was submerged for electrodeposition in $\pm5'0''$ of water in Tague Bay. Ambient water temperature ranged bwtween 82 and 88°F.

An electrodeposited layer of minerals was produced which nearly filled the entire section of the 3-layered construction. The plastic spacers did not interfere with the accretion process. The structure was under power for 714 h. Electrical power consumption is given in Fig. 18. After 714 h of electrodeposition, two material samples were taken (Table IX, Samples 35, 36). Mineral layers of the inner $\frac{1}{2}''$ mesh side of the configuration (Sample 36) were not as hard as layers on the outside of the structure (Sample 35). Accretion thickness on the inner $\frac{1}{2}''$ mesh measured 8.5 mm, 10.5 mm on the $1'' \times 2''$ mesh and 6 mm on the outside of the $\frac{1}{2}''$ mesh. Heavy marine growth was observed on the structure. After 714 h of electrodeposition, drum 1 was positioned in $37'0''$ of water north of Buck Island in order to begin phasing.

Analyzing the results of electrodeposition rate, it is apparent that in a multilayered construction the wire mesh closest to the anode attracts the most minerals. Concerning the structural ability of the different mineral layers (Table IX, Samples 35, 36), the outer mesh provided a material superior to that found on the inner mesh, but at a slower accretion rate.
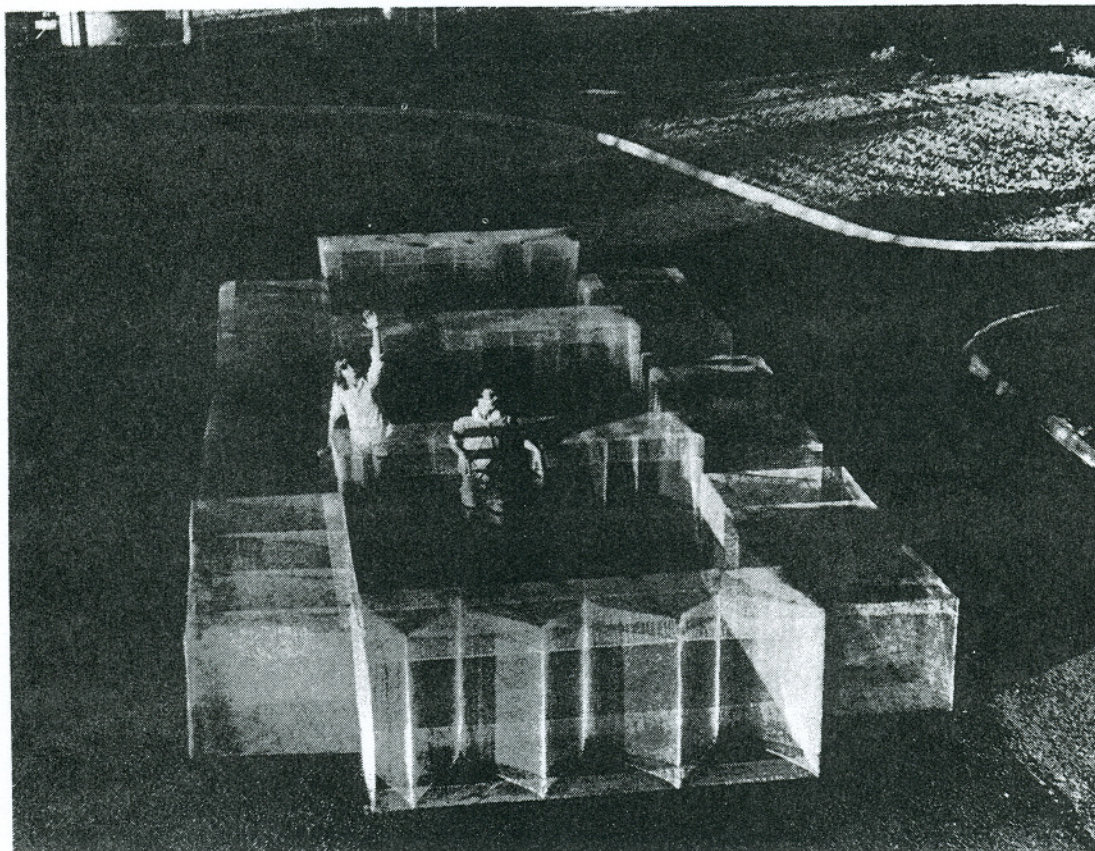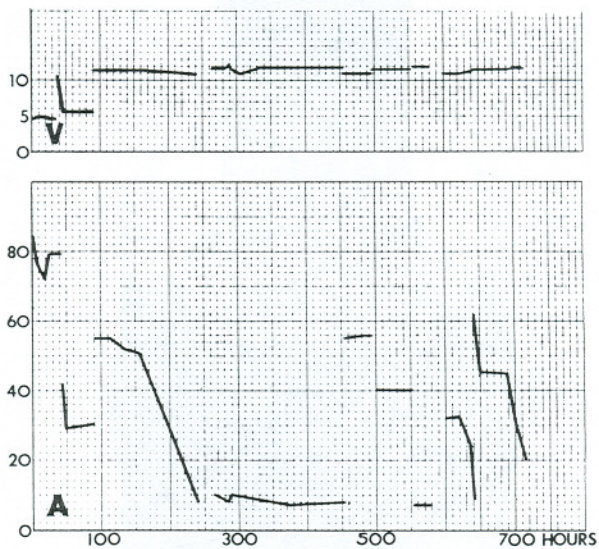
Fig. 17.   Artificial Reef 4 assembled on land.

Fig. 18.   Consumption of electricity, drum 1.

TABLE IX
CHEMICAL COMPOSITION OF ACCRETED MATERIALS, DRUM 1

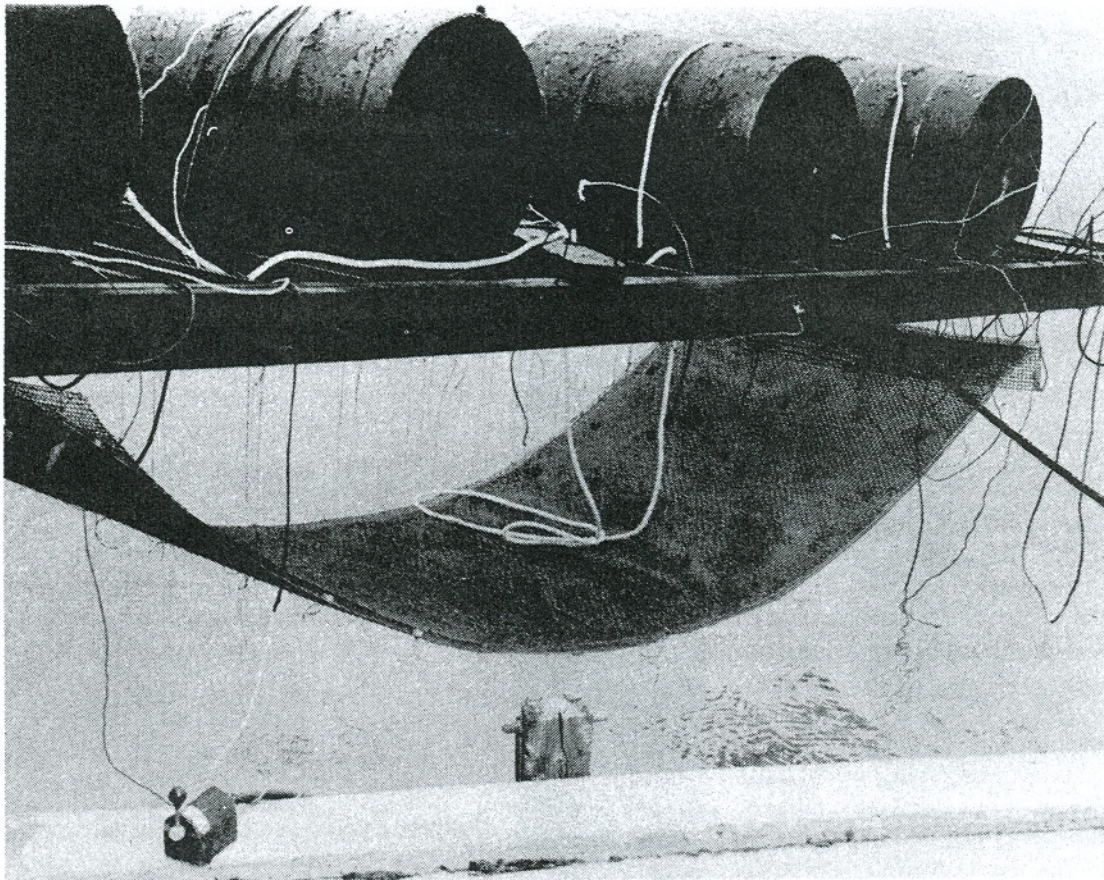| #	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
35	taken 8/24/76 hard material	35%	15%	1%	4%	2%	43%
36	taken 8/24/76 fluffy material	79%	5%	3%	2%	–	11%

Fig. 19.   Circle segment before submersion.

The circle segment (Port Aransas) consisted of a double-layered $\frac{1}{2}''$ galvanized wire mesh construction separated by $\frac{3}{4}''$ plastic spacers. It was suspended from a floating rig (Fig. 19). Total mesh area measured 112 ft². The structure was submerged for 480 h. Direct current was supplied by an unregulated power supply. The inner layer of the mesh construction performed as anode for 264 h, while the outer layer performed as cathode. Both anode and cathode cables consisted of 6 AWG multistrand insulated copper cable with a length of $30'0''$. All connections were insulated with clear silicon.

Electrical power consumption of the structure is shown in Fig. 20. After 240 h, an electrodeposited mineral layer of 4.5 mm had formed on the cathode (outer mesh). The inner mesh, performing as the anode, was significantly oxidized and collapsed over an area measuring 6.5 ft². After polarity was reversed for 216 h, an electrodeposited layer of 3 mm had formed on the cathode (inner mesh). 3.2 ft² of the anode (outer mesh) had fallen off. Sporadic marine growth was observed on both layers.

The concept of a sacrificial anode, when embedded in mineral precipitate, is an intriguing one and can offer many advantages. But, in the case of this experiment, anode corrosion data for galvanized wire mesh were not available, and the relationship between iron mass (anode) and oxidation rate was insufficient.

For an experiment with sacrificial anodes to be repeated it is proposed to treat both layers initially as cathodes until a
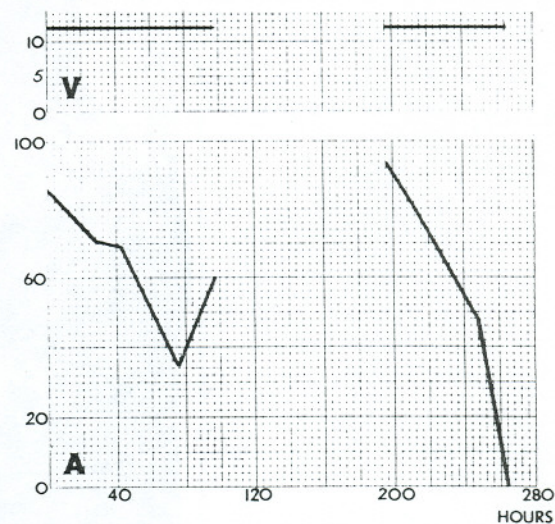

Fig. 20.   Consumption of electricity, circle segment.

mineral layer with the capability to keep the integrity of the structure has formed. Then, polarity reversal on the solidly embedded electrodes can be undertaken. Iron or steel is a rapidly oxidizing anode material; once embedded in a mineral the metal oxide will be integrated into the mineral. Thus it is hypothesized that longer lasting anode surfaces can be provided using this method. Additionally, former cathodes could be used to perform as anodes. This could be of importance
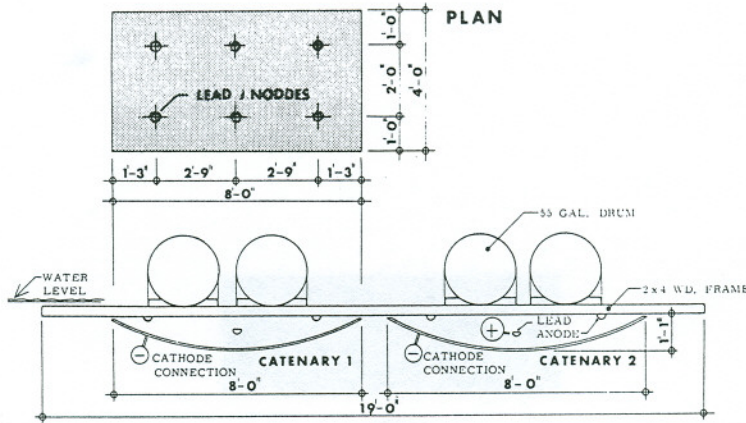
Fig. 21.   Catenaries 1 and 2.

during the mineral electrodeposition process of larger components and during the phased construction of walls or shells with very thick sections.

The catenaries 1 and 2 (Port Aransas) were identical in materials and dimensions. They consisted of $\frac{1}{4}''$ galvanized wire mesh suspended from a floating rig, each with a surface area of 32 ft^2 (Fig. 21).

Both catenaries were submerged in the boat basin on The University of Texas Marine Science Institute for 2664 h, the first 1896 h under dc delivered by an unregulated power supply. Six spherical-segment lead anodes were positioned above each catenary formation. Both cathode and anode cables were 6 AWG multistrand insulated copper wire with a length of $15'0''$ each. All connections were insulated with clear silicon. Electrical power consumption is given in Fig. 22.

After 1896 h an electrodeposited mineral layer of 7.5 mm had formed on both catenaries. The first material sample was taken after 1896 h of operations (Table X, Sample 88). The second sample was taken 768 h after power cutoff (Sample 92). The electrodeposited material then was densely populated by various algae and acorn barnacies. The analysis of both samples is given in Table X.

This experiment was devised to secure data from low electric field conditions between electrodes on large architectural or engineering components to provide an economical and simple system for building the component with a uniform thickness of deposited material throughout.

It was found that accreted material on the catenary cathode 'hardened' during the no-power phase, and quantitative analysis reveals little change of the chemical composition of the samples. Therefore, a change must have occured physically between crystals, but there are insufficient data to define conclusively the nature of the problem at this point. However, some weight should be given to the fact that concentrations of elements in sea water vary from Port Aransas to St. Croix. For example, in respect to Ca^{++}, natural sea water contains 409 ppm and Texas coastal water contains only 87 ppm. With respect to Mg^{++}, natural sea water and chloride ion concentrations in Texas coastal water are one sixth of that found in natural sea water. It seems that from these figures, and comparative X-ray diffraction data, reactions that take place in sea water at Port Aransas will occur at a slower rate than in
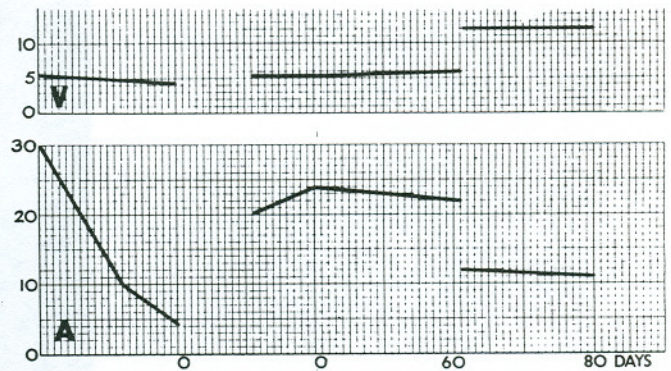

Fig. 22.   Consumption of electricity, catenaries 1 and 2.

TABLE X

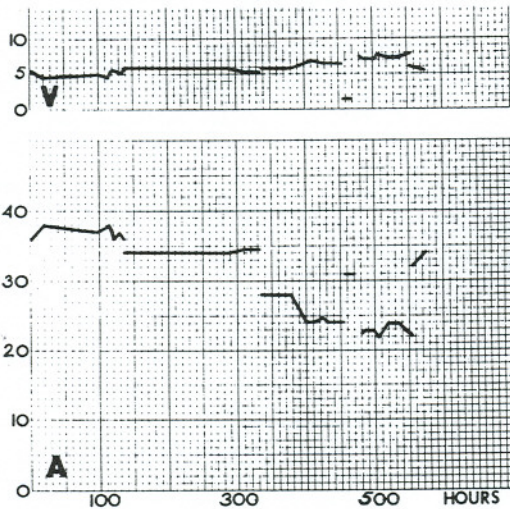CHEMICAL COMPOSITION OF ACCRETED MINERALS, CATENARIES 1 AND 2

#	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
88	taken at disconnect	89%	8%	trace	3%	–	0%
92	taken 32 days after disconnect	90%	7%	trace	trace	trace	3%

waters in which there are greater concentrations of the various ions.

The $\frac{1}{4}$ circle (St. Croix) consists of double-layered galvanized wire mesh with plastic ring spacers standing on a $2'' \times 4''$ wood frame. The total surface area measures $133\frac{1}{4}$ ft^2. A $\frac{3}{8}''$ welded steel frame was integrated into the structure to provide support. The $\frac{1}{4}$ circle was submerged in Tague Bay in $\pm 5'6''$ of water on sandy ground.

Anode and cathode wires were 6 AWG insulated multistrand copper wire. Direct electrical current was provided by an unregulated power supply. All electrical connections were insulated with clear silicone. The ambient water temperature ranged between 82 and 88°F. The anode consisted of a 7'' OD cast iron pipe with a length of $9'0''$, placed under the cathodic shell. The structure was supplied with electricity for 576 h (Fig. 23). Three material samples were taken (Table XI, Samples 30, 34, 93) and analyzed.

When conductive materials with different sections are used as a cathode, the electric field between the electrodes concentrates on the material with the larger section. Therefore, a
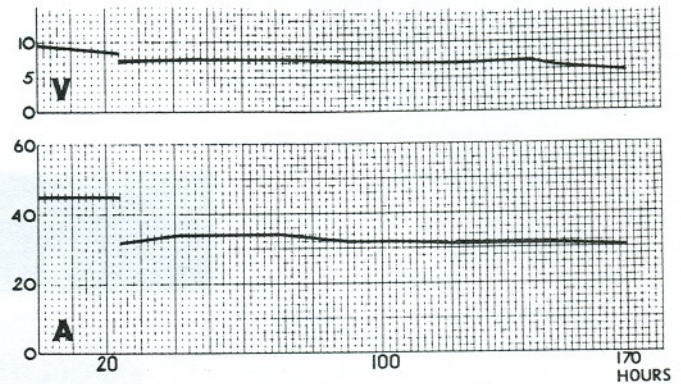
Fig. 23. Consumption of electricity, $\frac{1}{4}$ circle.

TABLE XI
CHEMICAL COMPOSITION OF ACCRETED MINERALS, $\frac{1}{4}$ CIRCLE

#	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
30	taken 2 days before #34	65%	18%	4%	11%	2%	0%
34	taken at disconnect	80%	10%	2%	2%	1%	5%
93	taken after 84 days	50%	10%	3%	5%	trace	32%

mineral layer with a thickness directly proportional to the resistance between the cathode material with the smallest section and the anode has to be formed before electrodeposition of the material with the smallest section can begin. This observation bears directly on the future design of building components as it affects dimensioning and the effectiveness of phasing. Dense algae growth similar to that observed on Reef 1 and Reef 2 appeared on the outer surface of the structure, and did not interfere with the electrodeposition process. After 576 h of continuous operation, mineral accretion thickness on the $1'' \times 2''$ wire mesh measured 5.5 mm. Mineral layers on the $\frac{3}{8}''$ steel frame measured up to 3.8 mm after 576 h.

Marine growth was observed on all parts of the structure. The $\frac{1}{2}$ circle (St. Coirx) is a double-layered construction of $\frac{1}{2}''$ galvanized wire mesh supported by a welded frame of $\frac{3}{8}''$ steel profiles. Spacing was provided by $\frac{1}{2}'' \times 8''$ OD PVC sections. The double shell was being held in tension by two marine ropes. The total surface area measured $158\frac{1}{3}$ ft^2. The component was submerged in Tague Bay in $\pm 4'$ of water on sandy bottom. Anode and cathode cables consisted of 6 AWG insulated multistranded copper wire. Direct current was supplied by an unregulated power supply. All electrical connections were insulated with clear silicon. A $7\frac{1}{2}'' \times 24''$ round aluminum tank was used as anode.

The structure was supplied with electricity for 170 h (Fig. 24). At the end of this period, a material sample was taken (Table XII, Sample 31). After 170 h, accretion thickness measured 2.7 cm on the $\frac{3}{8}''$ steel frame, and 2.3 mm on the $\frac{1}{2}''$ mesh. A sample from the steel frame showed growth of algae species *Halimeda* and *Coralina* with basal systems embedded in the accreted material. Marine growth was observed on all other

Fig. 24. Consumption of electricity, $\frac{1}{2}$ circle.

TABLE XII
CHEMICAL COMPOSITION OF ACCRETED MINERALS, $\frac{1}{2}$ CIRCLE

#	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
31	taken at disconnect	61%	5%	1%	20%	trace	13%
94	taken 2304 h after disconnect	58%	9%	2%	8%	1%	22%

parts of the structure. A second material sample was taken 2304 h after disconnection (Table XII, Sample 94).

Very slight changes occurred in the accretion matrix of samples taken from the $\frac{1}{2}$ circle component. It is interesting to note the percentage of halite; this is due perhaps to entrapment of salt crystals during rapid precipitation. Also of interest is the increasing amount of noncrystalline matter and/or less well-ordered crystals during the nonpower phase.

At a later date, the $\frac{1}{2}$ circle formation described above was attached to a flotation device and positioned near Tague reef in St. Croix. It assumed a catenary-like configuration and was supplied with dc by a wind-driven generator located on Tague reef with a peak output of 200 W.

Likewise, a $7\frac{1}{2}'$ by $15'$ circular column was supplied with dc from two wind-driven generators with a peak output of 200 W each.

The structure was of $\frac{1}{2}''$ galvanized hardware cloth double-shelled construction with approximately $1''$ spacing. Three $\frac{1}{2}'' \times 6'' \times 12''$ lead anodes were positioned along the longitudinal axis of the column. Fig. 25 shows the arrangement in elevation on Tague reef.

A small catenary form was submerged in Port Aransas. It measures $5' \times 4' \times 2'$ and is of double-shelled $\frac{1}{4}''$ galvanized hardware cloth construction with $\frac{1}{4}''$ spacing [25]. Fig. 26 shows this shell before accretion, Fig. 27 after approximately 1000 h of accretion, consuming dc typically at 6 V and 3A. The lead sheet anode is visible in the center of Fig. 26.

V. PHASING OF ELECTRODEPOSITED MATERIALS

An example of the phasing process is given by a structure which undergoes electrodeposition (diagensis) and is subsequently subjected to direct interaction with marine life without being supplied with dc (biogenesis). This interaction, combined with the effect of the surrounding sea water, might change the properties of the previously deposited material. After these two phases, a third, diagenetic phase might be initiated, and so forth.
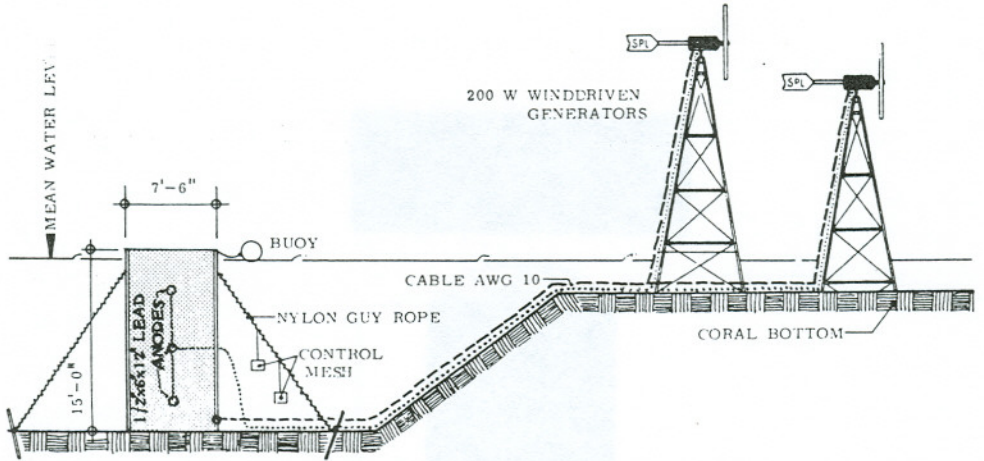
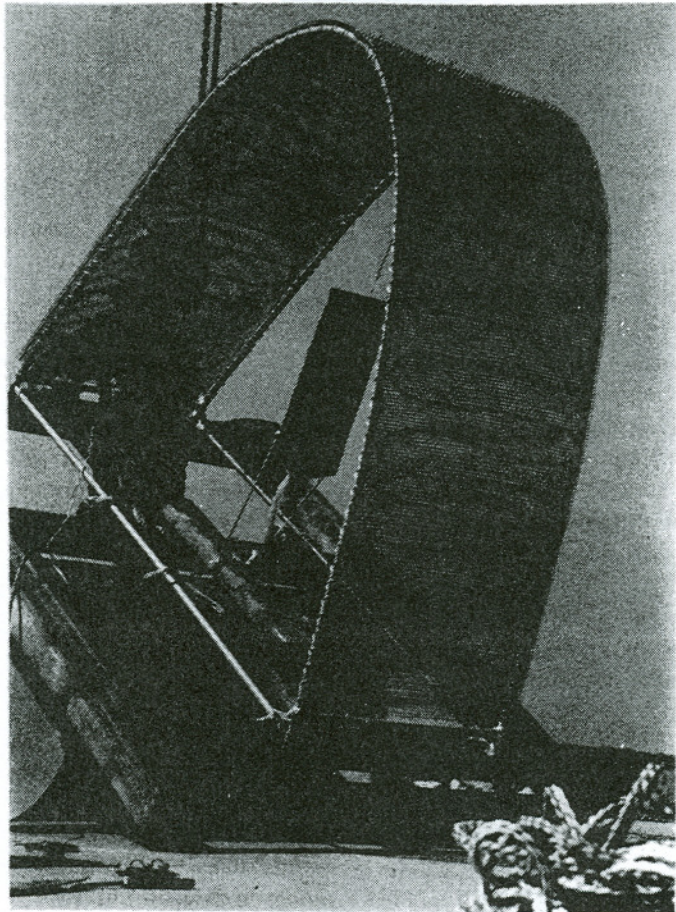Fig. 25.   Circular column and wind driven generators.
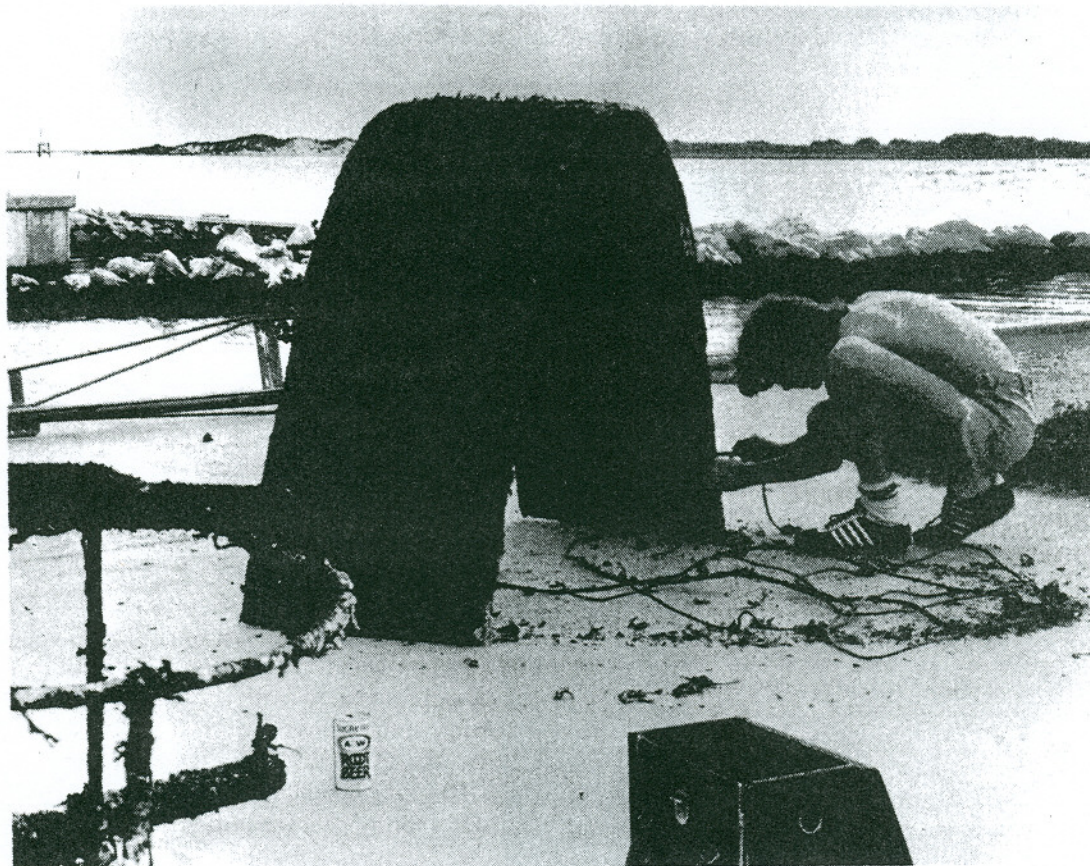

Fig. 26.   Catenary formation before accretion.

Fig. 27.   Catenary formation after accretion.

Observations made on previous test components showed that phasing appeared to alter the properties of the electrodeposited material. Therefore, controlled series of phasing tests were performed in St. Croix in order to verify these observations.

The first phase of the test was conducted in 15-gal aquaria supplied with raw sea water at a rate of 4.5 gal/min. Cylindrical cathodes of $\frac{1}{4}''$ hardware cloth were used, with a circumference of $18''$, a height of $8''$, and a total surface area of 144 in². A $5'' \times \frac{3}{4}'' \times \frac{1}{8}''$ lead anode was placed in the center of each cathode.

Nine test cages were accreted, 2–4 at a time, powered by direct electrical current with an average power input of 0.5–1.5 A/3.5–8.0 V. All cages were supplied with dc for 8–11 days at which time a white, fairly structural material of approximately 0.5-cm thickness had been deposited. Material samples (Table XIII) were taken at this time for X-ray diffraction analysis.

After this first phase, the anodes were removed and the accreted cages were placed in the following locations:

1) Two cages on the barrier reef at Tague Bay, at a depth of $15'$ and $18'$ (*Position 1*).

2) Four cages on a reef patch north of Buck Island at depths varying from 20–30′ (*Position 2*).

3) Two cages on the inner reef north of Buck Island, at depths of $12'$ and $14'$ (*Position 3*).

Water temperature at all locations varied between 82–86°F.

TABLE XIII
CHEMICAL COMPOSITION OF PHASED ACCRETED MINERALS

#	Description	Brucite	Aragonite	Calcite	Halite	Other
17	Typical test cage before phasing	79%	15%	1%	5%	0%
38	After 7 days of phasing	64%	25%	3%	8%	0%
42	After 10 days of phasing	50%	25%	1%	trace	24%
44	After 19 days of phasing	40%	17%	4%	1%	38%

Material samples were again taken from all test cages at *Position 1* after 19 days (Sample 44), *Position 2* after 10 days (Sample 42), and *Position 3* after 7 days (Sample 38).

Small amounts of organic growth; including blue-green algae, diatoms, juvenile anemones, and coralline algae, were observed several days after the test cages were placed at their inner and outer surfaces. X-ray diffraction analyses of the material samples are given in Table XIII.

In Sample 17, a general decrease in brucite appears over time while phasing. At the same time, an increase in material undetected by X-ray diffraction occurs; this might consist of either poorly crystallized compounds or noncrystalline matter. Considering the percentage shifts, two conclusions are offered: organic matter may be increasing within the accreted material, which would alter total percentages of the compounds themselves; also, as the electrodeposition process is discontinued, the chemical equilibrium appears to shift to the left and allows brucite to dissolve back into the sea water. A possible mechanism for the dissolution of brucite is the decrease of the pH

Fig. 28. Compressive strength of accrete obtained in Port Aransas and St. Croix waters.

Fig. 29. Proposed cold water pipe for OTEC plant, horizontal section.

at the cathode surface, occurring when electrical current is discontinued. These two situations may be occurring simultaneously, or one may be entirely responsible. Further data must be collected to be conclusive.

VI. TESTING OF MECHANCIAL PROPERTIES

Twenty samples of electrodeposited minerals obtained on $\frac{1}{2}''$ galvanized hardware cloth in Port Aransas and St. Croix, were prepared and tested at The University of Texas Structural Testing Laboratory. Following standard procedures for concrete testing, compression forces were recorded at the point of breakage [25]. Individual and averaged test results reflecting psi strength are shown in Fig. 28. For comparison, concrete that is typically used for stairs and steps, sidewalks, driveways, slabs on grade, and basement wall construction (probable 28th day strength, normal Portland cement Type 1, 15 percent less than recommended by ACI Joint Committee) breaks at about 3500 psi [30].

VII. OTEC FACILITY PROPOSAL

The mineral accretion process potentially can contribute significantly to the solution of formidable engineering tasks which will be undertaken in the oceans, like the construction of Ocean Thermal Energy Conversion (OTEC) plants. It is evident, for example, that the use of traditional engineering materials like steel or fiber reinforced concrete, tubular steel or reinforced plastics for the construction of OTEC systems cold water supply pipes will produce enormous costs because the system will have to be overdesigned in respect to unknown or only vaguely defined parameters. Quite to the contrary, a relatively light aquadynamic cathodic tube configuration (Fig. 29), which permits assembly on the plant on-site, can be ac-
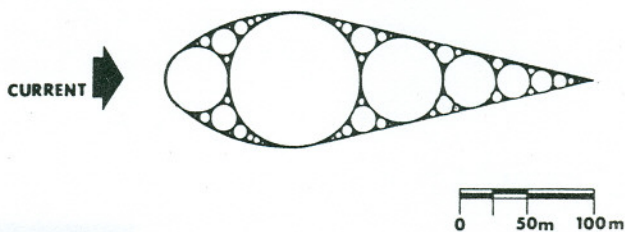
creted selectively in order to effectively withstand changing and unpredictably occurring forces (e.g., changing current patterns).

In case of slowly or suddenly occurring damage to the wall section, the tube can be repaired by placing an anode in the vicinity of the damaged portion, thus facilitating, for instance, cementation of cracks, replacement of lost materials, and reinforcement of previously deposited mineral layers. The OTEC plant could be moured at an accreted gravity anchor block and could move with prevailing currents (Fig. 30).

Aside from converting ocean thermal energy into electricity, the plant can also produce hydrogen, ammonia, and $Mg(OH)_2$ as a byproduct of the electrolysis process used to provide uplift of cold water in the deep water pipes (Fig. 31).

Through the application of heat, brucite can be directly reduced to the mineral periclase (MgO). Thus the plant can produce refractory magnesia, the raw material for magnesium production. The Cl_2 gas, resulting from electrolysis, can also be utilized. While building a considerable, but not yet calculated head, the upwelled water/gas mixture can drive turbines. The nutrient rich deep water can be utilized at the ocean surface as a mariculture medium.

VIII. SUMMARY AND CONCLUSIONS

Electrochemical accretion of minerals in sea water and other media (e.g., blood serum = internalized ocean in mammals) appears to be as old as life itself and seems to have proven its worth during evolutionary time. Construction, maintenance, and destruction technologies as used at the present, are mainly brain children of the first industrial revolution with built-in limits [12]. Example given: A concrete or steel element in sea water, once broken or decayed, is useless because it cannot meet its design specifications unless it is repaired. In most cases repair necessitates removal from the site and repositioning, thus incurring unreasonably high cost.

An element produced by electrodeposition, however, can be repaired or reconditioned in situ after failure. With renewed electrical power input the same conditions and resources which formed the element initially can be utilized again. This characteristic is not found in any commonly used construction method or material. Conversely, when, for instance, a reinforced concrete volume is cured and has left the form, its structural and formal characteristics can be altered only by major operations. Thus strict limits concerning the element's adaptability to changing conditions in situ are enforced.
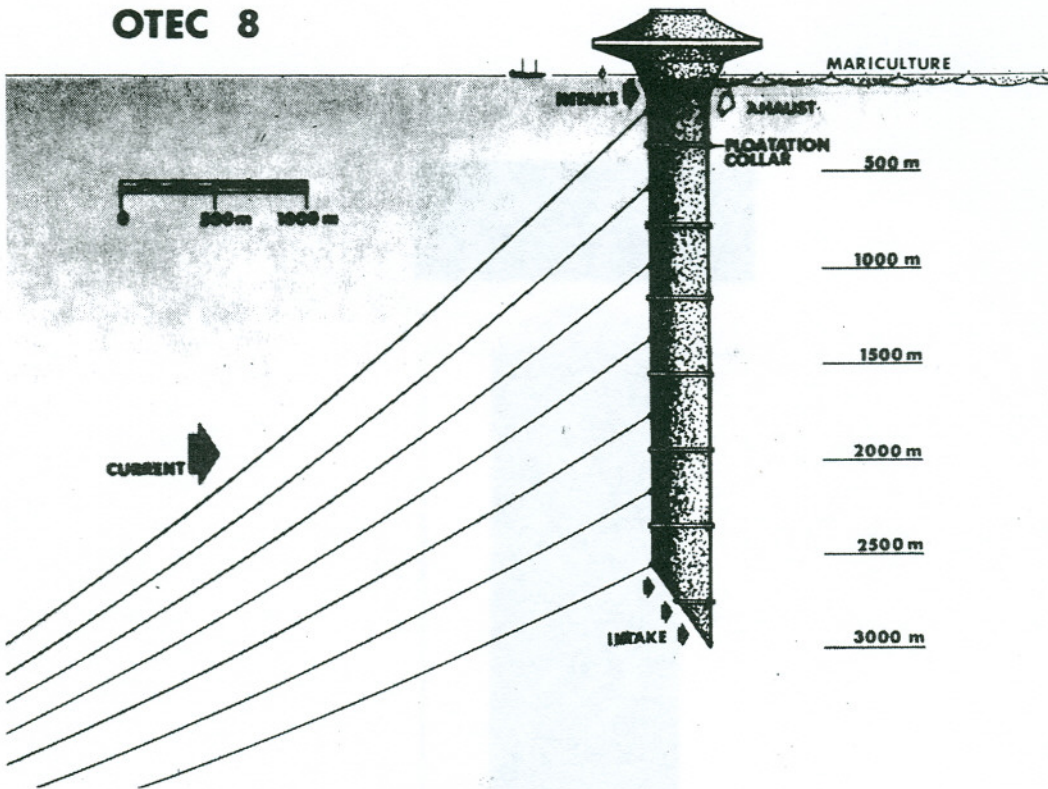
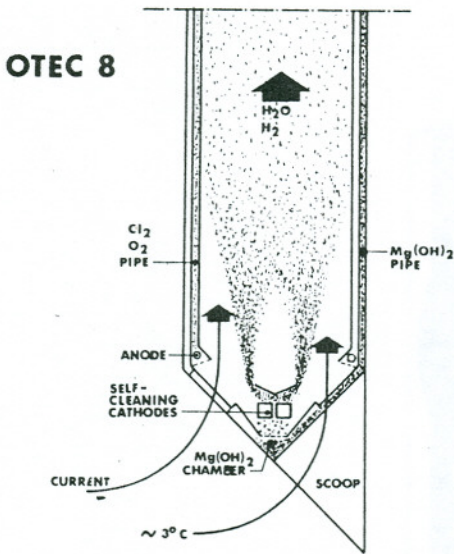Fig. 30. Proposed multifunctional OTEC plant.

Fig. 31. Functions of proposed OTEC plant.

Other applications for the electrochemical accretion process can be seen readily: floating habitats and industrial islands, settlements on banks, shoals, and the continental shelves (Fig. 32), mariculture facilities, breakwaters, storage tanks, dams and jetties, pipelines, bridges, tunnels, airports, beach solidifications and accretions, current diverters, building components for use on land, sea walls, marinas, atoll closures, and power as well as sedimentation generating facilities.

Structures, while accreting, can double as artificial reefs. Thus a combination of aquaculture facilities and building component plants is envisioned.

Building components can be accreted at greater depths and be designed and calibrated in such a way, that, when surfaces are closed by the electrodeposited materials, accumulated hydrogen, oxygen, or chlorine gas provides uplift and "mature" components can be harvested at the water surface. In a similar way building processes can be designed that allow structures to "grow" out of the electrolyte (Fig. 33).

Moveable articulated form generators can be designed to produce a variety of configurations continuously by unspooling or weaving of cathodic material formations. These devices can "ride" on the generated profiles of pipes (Fig. 34). Anodes can be integrated in the generator or positioned independently in the vicinity of the form to be accreted. Energy requirements for the electrodeposition of minerals in sea water generally vary between 0.4 and 2 kW for 1 kg of accreted mass, depending on various parameters. Solar energy in its various forms can be harnessed everywhere to meet these requirements. The medium for construction, maintenance, repair, and reclamation of structures produced by the mineral accretion process covers 70.8 percent of the earth and thus represents a major resource for building in the oceans.

Furthermore, plasticity, a major principle in organic evolution, has to be maintained and augmented in order to ensure valid developments within the context of a continuously evolving world [13]. To this the process described above can contribute.
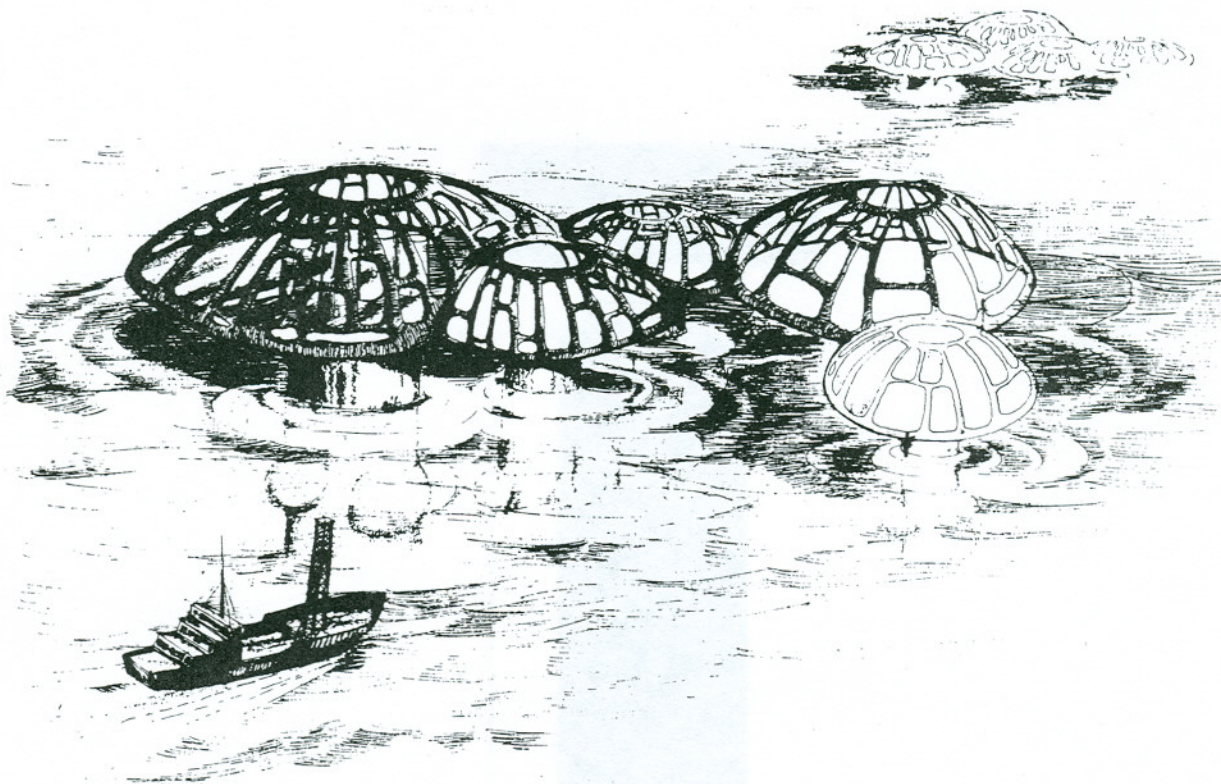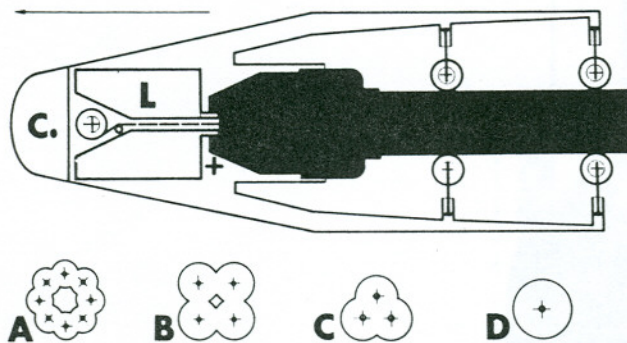
Fig. 33. Structures "growing" out of the ocean.

Fig. 34. Mobile form generator and reclamation device designed to ride on accreted sections.

ACKNOWLEDGMENT

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