fib: UT/MSI 76-1

TXU-T-76-001

ELECTRODEPOSITION OF MINERALS IN SOLUTION AND ITS ENHANCEMENT BY BIOLOGICAL GROWTH FOR STRUCTURAL APPLICATIONS

Report

Seagrant No. 04-6-158-44111
Duration: July 1, 1976 - December 31, 1976

submitted to

United States Department of Commerce
National Oceanic and Atmospheric Administration
National Sea Grant Program
Washington, D.C. 20235

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December 1976

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Acknowledgements

Dr. Creighton Burk, Director, The University of Texas Marine Science Institute, Austin, Dr. Oswalt Roels, Director, The University of Texas Marine Science Institute, Port Aransas, and UT M.S.I., St. Croix, and Dr. Robert Dill, Director, West Indies Laboratory, Fairleigh Dickinson University, St. Croix, U.S.V.I., provided invaluable moral and material support.

1. Introduction.

The objectives of this program are to determine the parameters of:

1.1. The electrodeposition of minerals in solution onto large surfaces as substrate for marine growth (artificial reefs).

1.2. The electrodeposition of minerals onto large surfaces for architectural applications.

1.3. Sequencing and the interaction of biogenetic and diagenetic processes on large surfaces.

The adopted model for electrochemical reactions during electrodeposition processes of minerals in solution is shown in Figure 1. A generalized arrangement of anode and cathode for diagenetic electrodeposition is shown in Figure 2.

The term "phasing", as used throughout this report, needs clarification: an example of this process is given by a structure which undergoes electrodeposition (diagenesis) and is subsequently subjected to direct interaction with marine life which might change the properties of the previously deposited material (biogenesis). After these two phases, a third, diagenetic phase might be initiated, and so forth.

The principal investigator and two research assistants worked at Fairleigh Dickinson University's West Indies Laboratory and at the U.T. Marine Science Institute, St. Croix from July 21st until August 26, 1976.

During the remainder of the grant period the participants worked at the University of Texas Marine Science Institute at Port Aransas and at the University of Texas at Austin.

2. Test square 1, test strips 1 and 2, and test rack A.

These experiments were devised to determine the effects of spacing of electrodes, electrical cable connection location, and gas evolution upon the electrodeposition rate and the composition of electrodeposited material.

2.1.1. The test strip 1 (W.I.L. St. Croix). A steel anode was positioned 2" opposite the narrow side of a 2" x 72" galvanized 1/4" wire mesh strip with a surface area of 1 sq. ft. (Figure 3). The cathode wire was connected to the narrow end of the strip farthest from the anode. The supportive wood frame measures 2'-3' x 2'-2' x 8'-0". All bare nail heads in the wood frame were covered with silicon. The cathode was fastened with 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 next to the W.I.L. pier laboratory. Ambient water temperature was 85°F. Electrical measurements were taken with meters integrated in the power supply.

ELECTROCHEMICAL REACTIONS

- in situ -

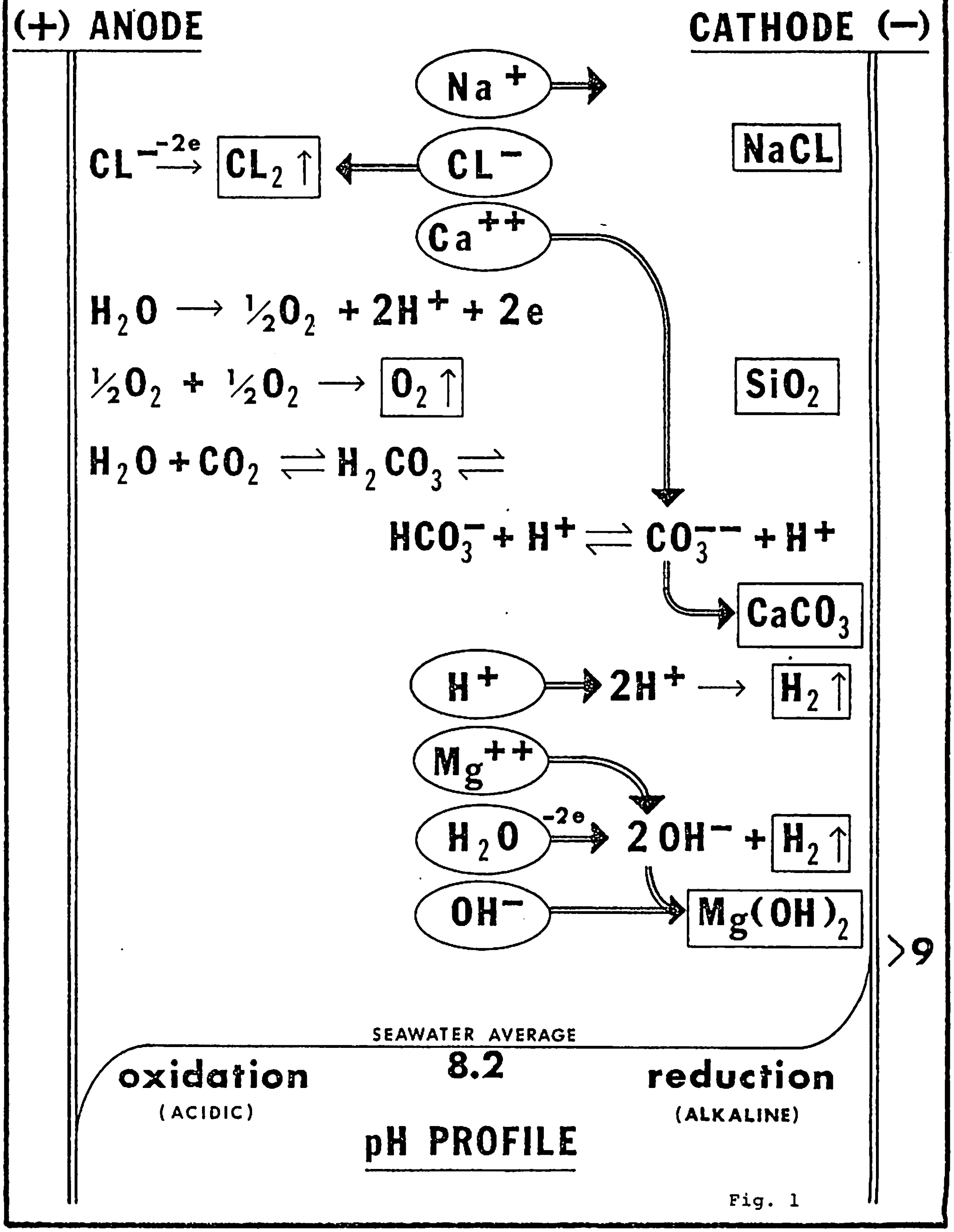
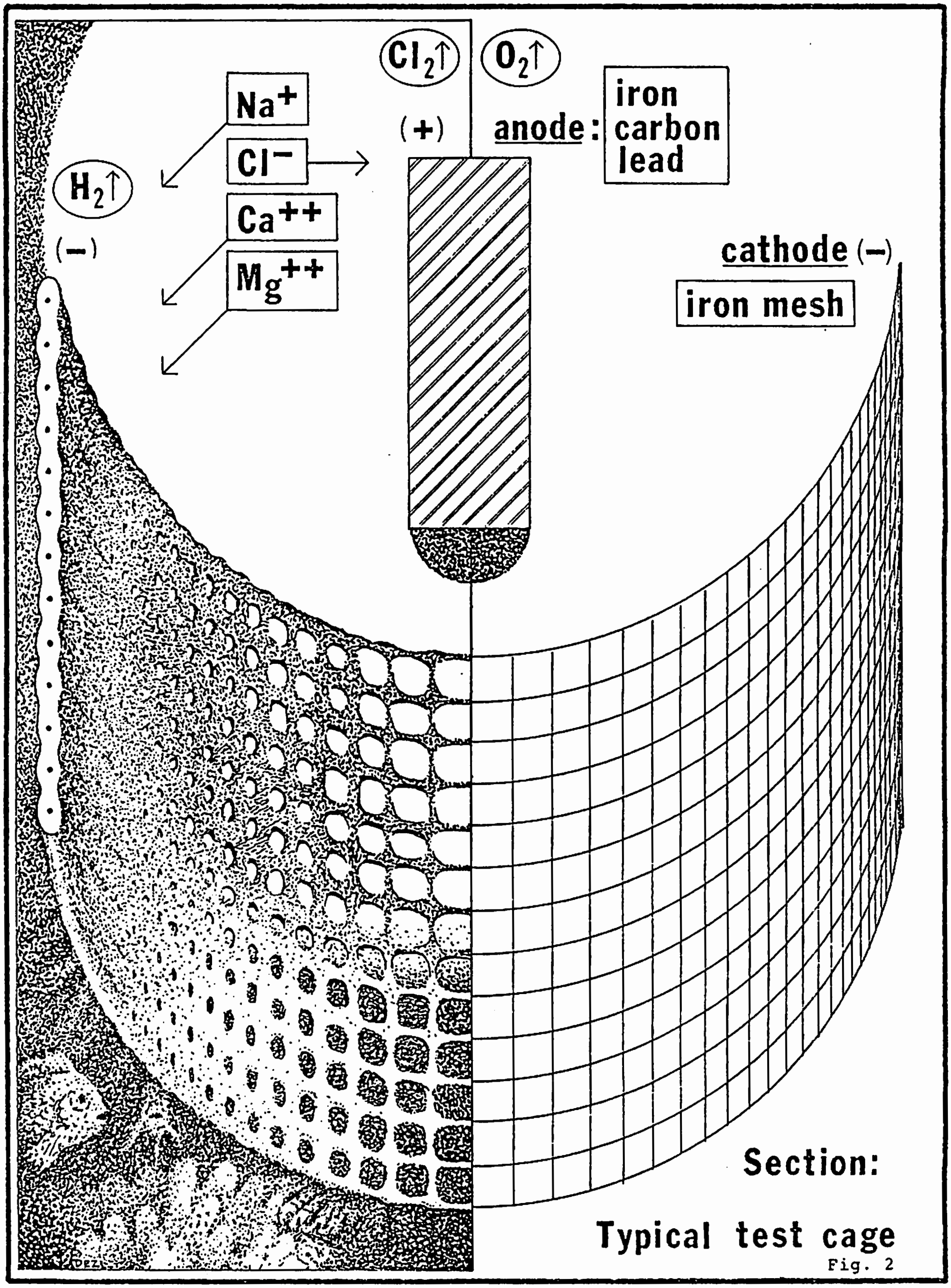


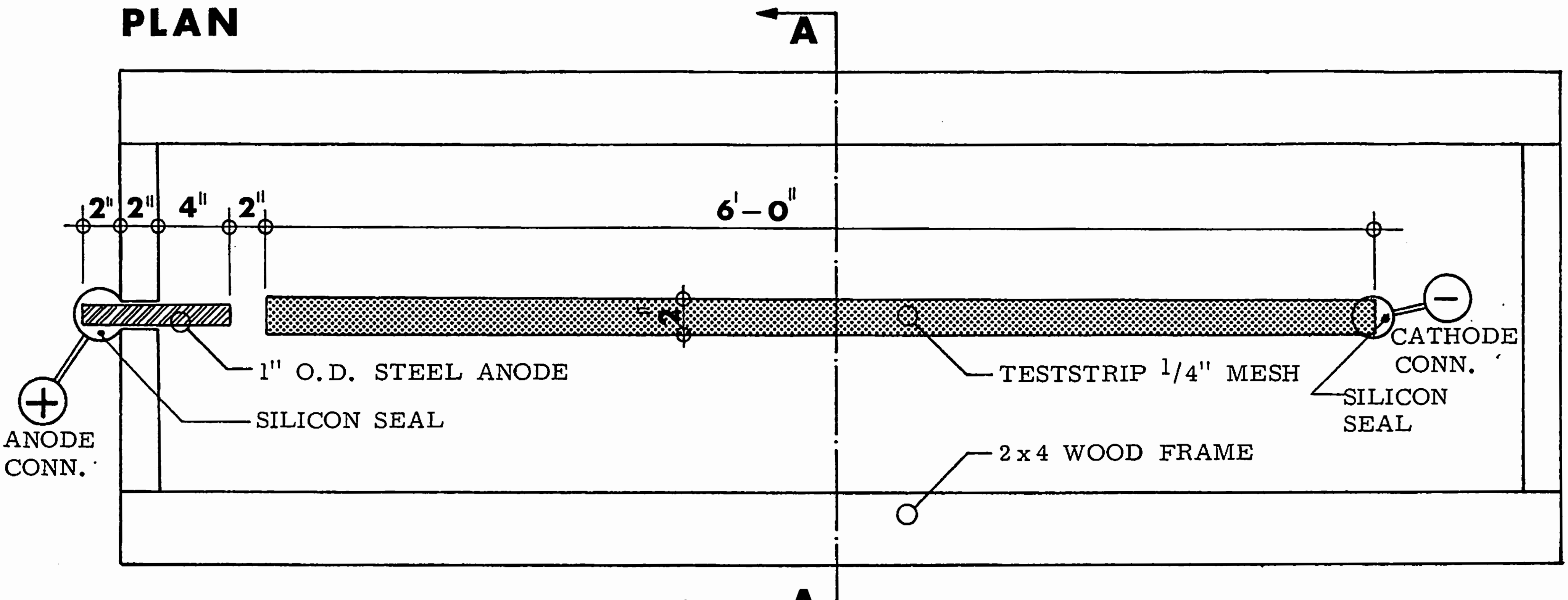
Fig. 1



Section: Typical test cage

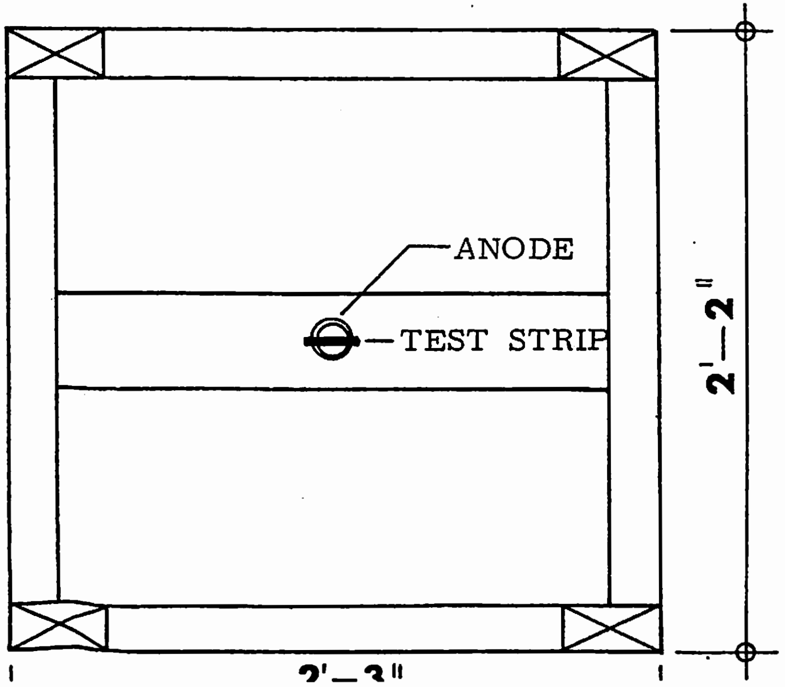
Fig. 2

PLAN



TEST STRIP POSITIONED BY NYLON LINE

ALL NAIL HEADS SILICONED



SECTION A

TEST STRIP 1

2.1.2. The test strip was submerged and under power for 52 hours. Consumption of electricity is shown in Figure 4. After submersion, the electrodeposited strip was divided into 12 sections measuring 6" each (Figure 5). At these sections, thickness of electrodeposited material was determined with a steel caliper. At every 6" section, material samples were taken (Photo 1 and Figure 5, Positions 54, 60, 66).

Table 1: X-ray Diffraction Analysis

Sample #	Description	Chemical Composition 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%

2.1.3. For discussion of comparative data see Section 2.4.3.

2.2.1. The test strip 2 (W.I.L. - St. Croix). A steel anode was positioned 2" opposite the narrow side of 2"X72" galvanized wire mesh with 1/4" spacing and a surface area of 1 sq. ft. (Figure 6, Photo 2). The cathode wire was connected to the narrow end of the strip closest to the anode. The supportive wood frame measures 2'-3" x 2'-2" x 8'-0". All bare nail heads in the wood frame were covered with silicon. The cathode was fastened with 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 next to the W.I.L. pier laboratory. Ambient water temperature was 84.5^{o}F. Electrical measurements were taken with meters integrated in the power supply.

2.2.2. The test strip was submerged and under power for 52 hours. Consumption of electricity is shown in Figure 7. After submersion the electrodeposited strip was divided into 12 sections measuring 6" each (Figure 5). At these sections, thickness of electrodeposited material was determined with a steel caliper, at every 6" section material samples were taken (Figure 5, Positions 67, 73, 79).

Table 2: X-ray Diffraction Analysis

Sample #	Description	Chemical Composition 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%

2.2.3. For discussion of comparative data, see Section 2.4.3.

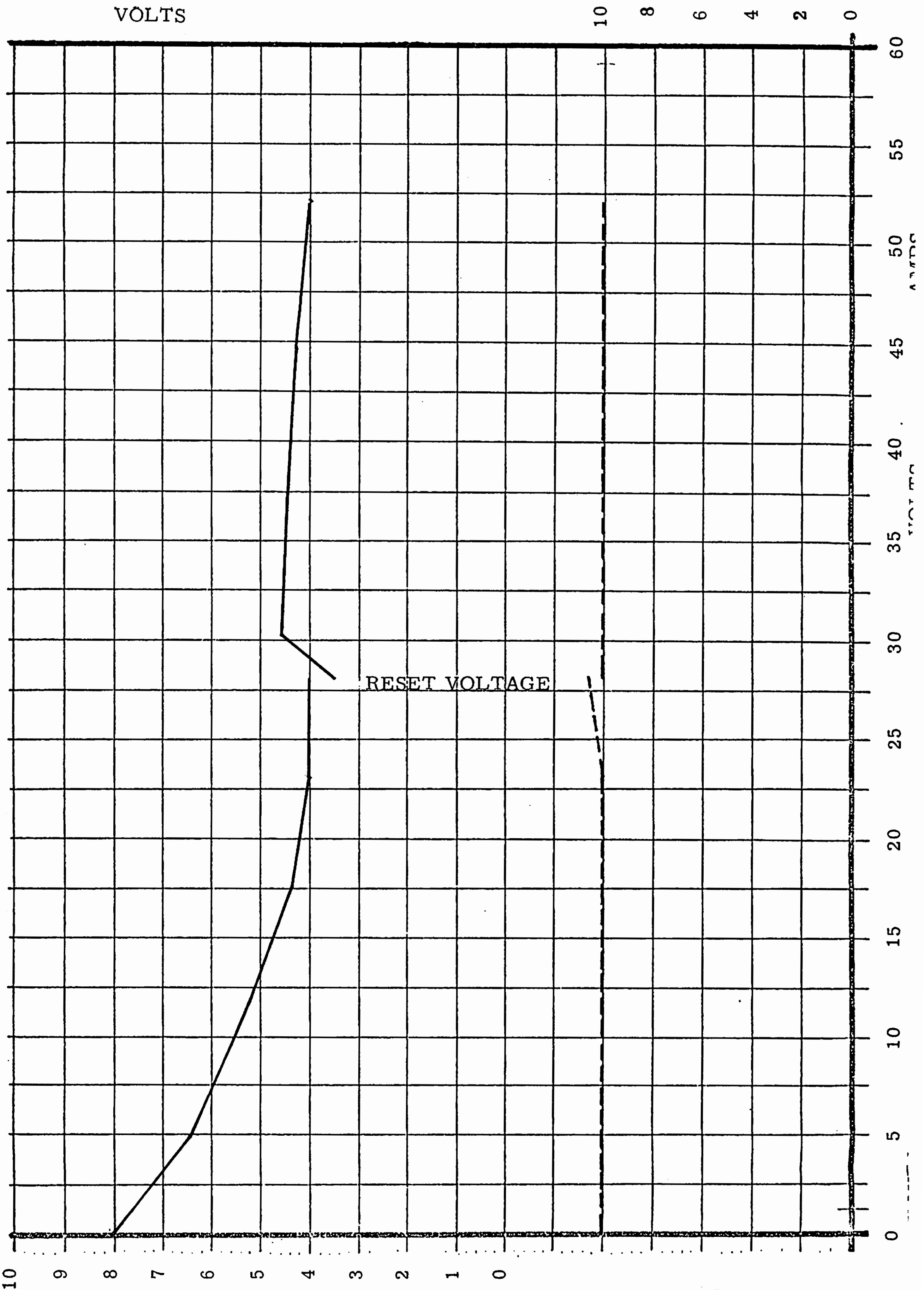
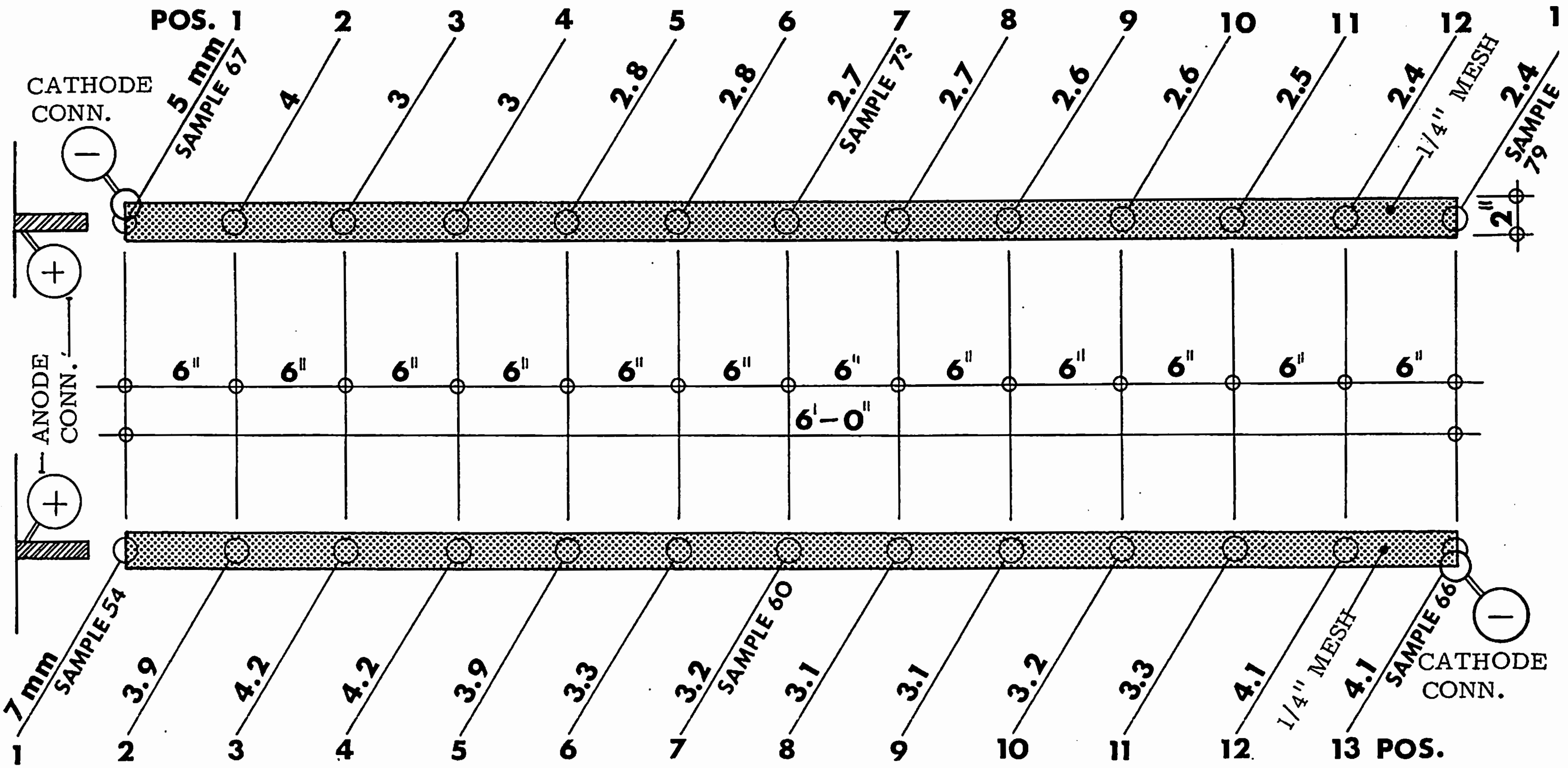


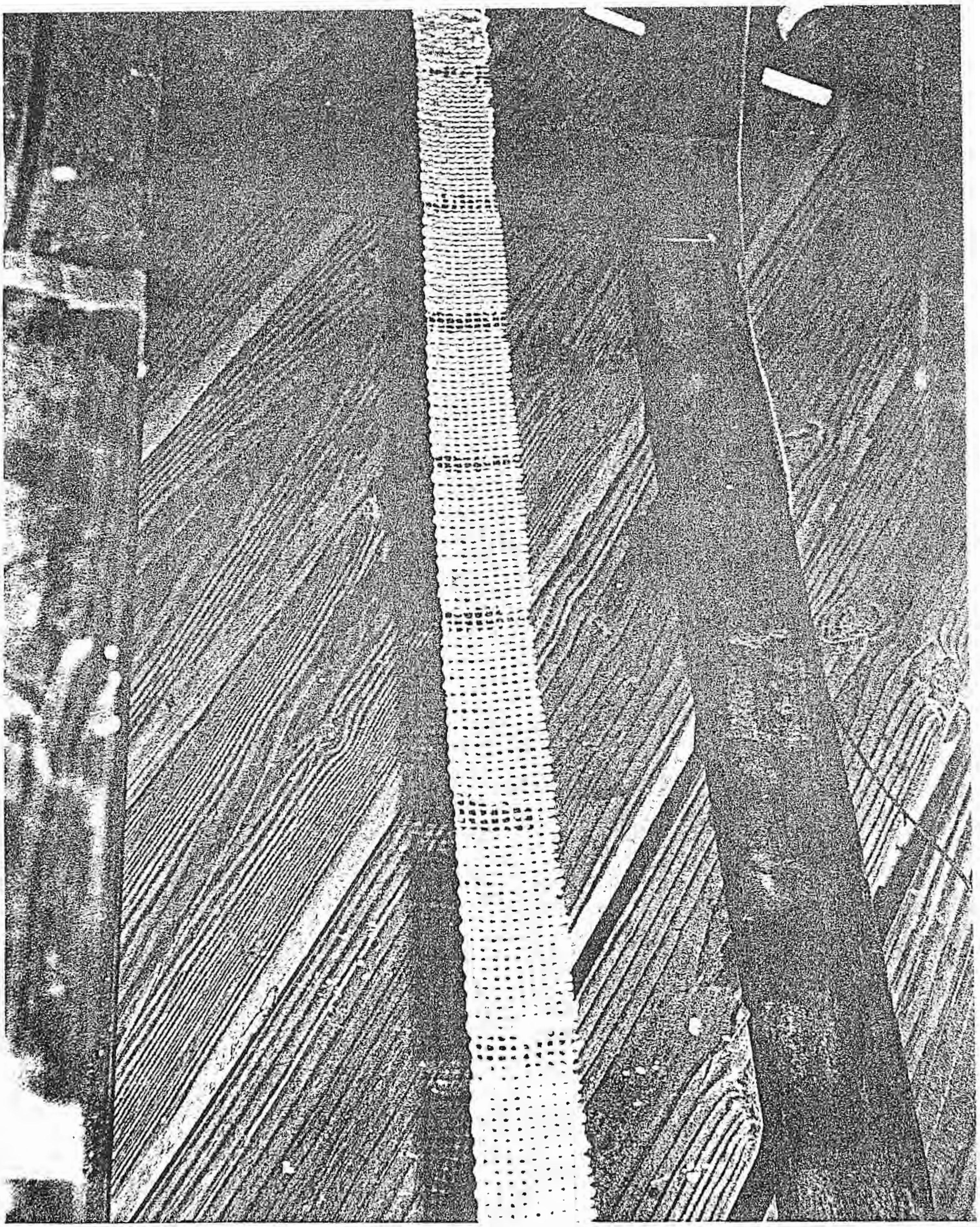
FIGURE 4 TEST STRIP 1

TEST STRIP 2



TEST STRIP 1

Fig. 5



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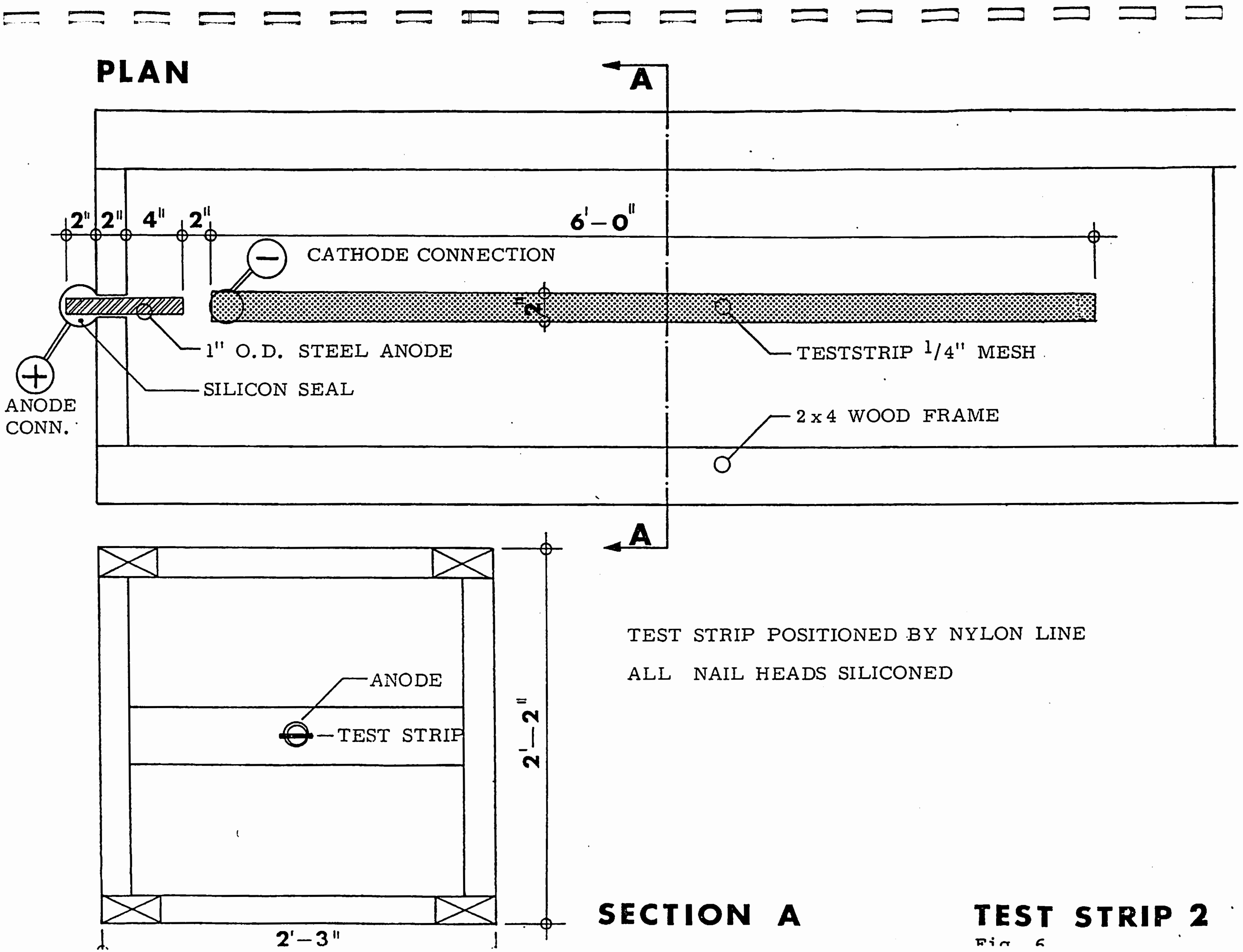
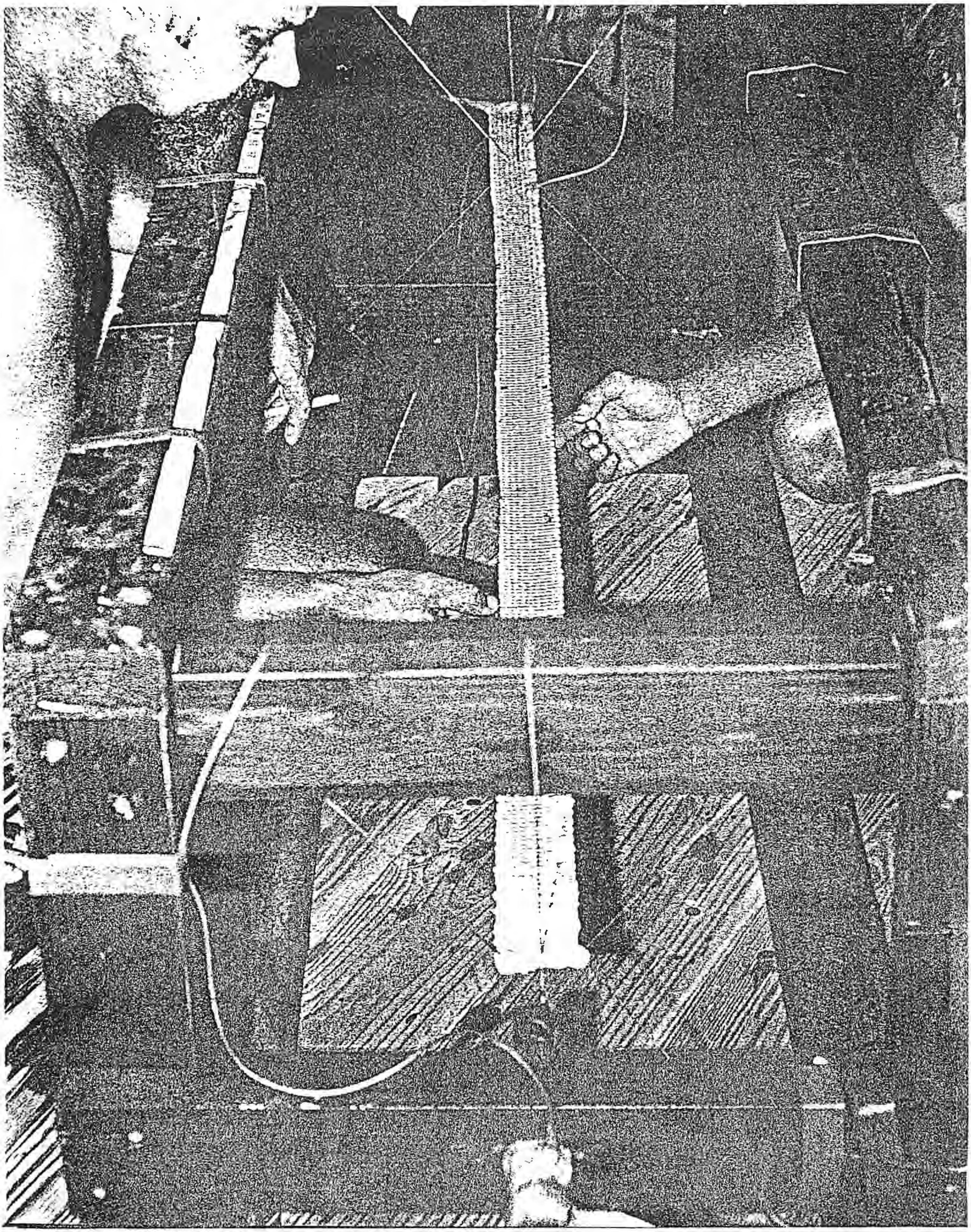


TEST STRIP POSITIONED BY NYLON LINE

ALL NAIL HEADS SILICONED

TEST STRIP 2

Fig. 6



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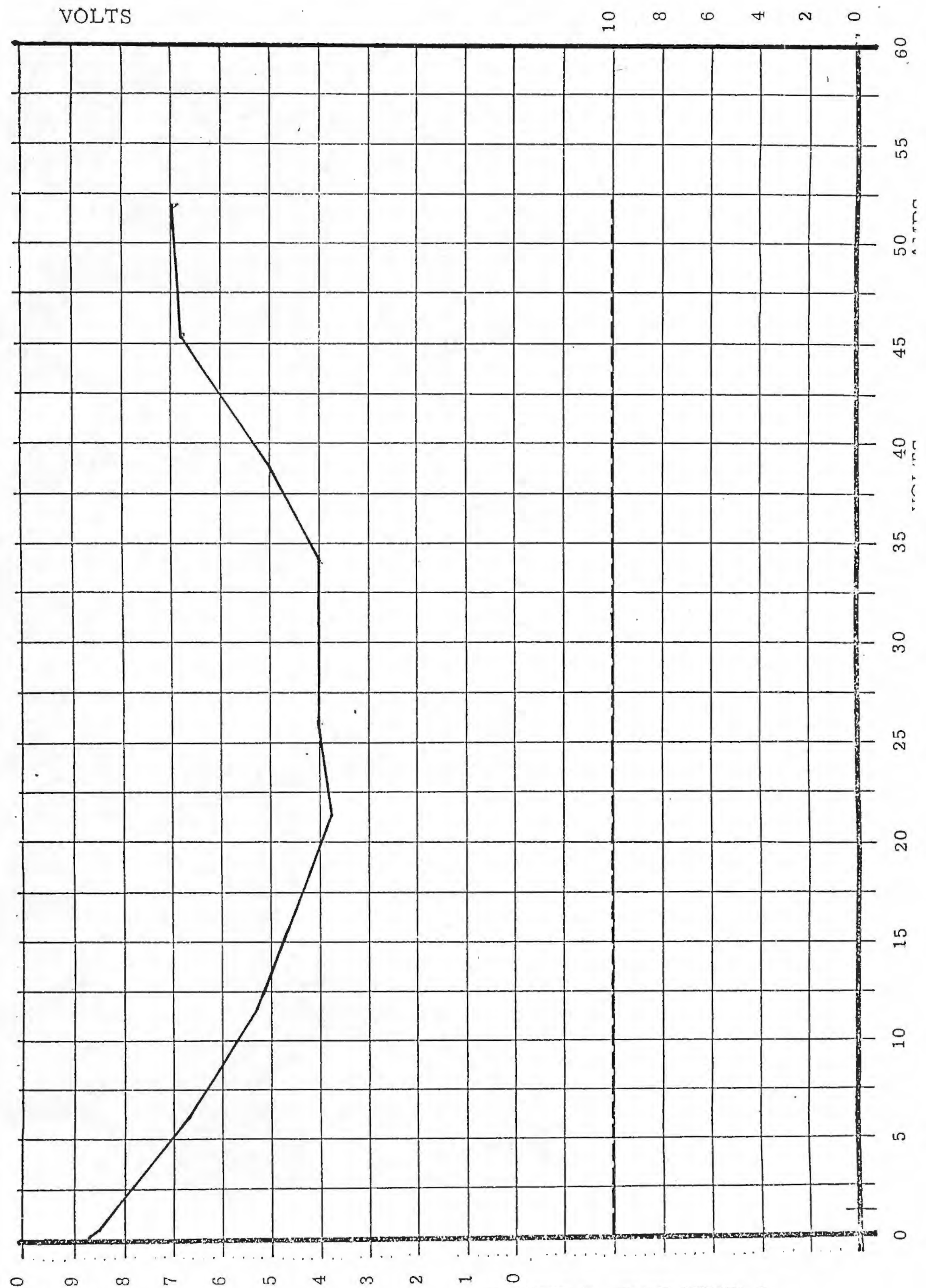


FIGURE 7 TEST STRIP 2

2.3.1. The test strip 3 (U.T. M.S.I., Port Aransas). A steel anode was positioned 2" opposite the narrow side of 2" x 72" galvanized 1/4" wire mesh strip with a surface area of 1 sq. ft. (Figure 8). The cathode wire was connected to the narrow end of the strip at the farthest side from the anode. The supportive wood frame measured 2'-3" x 2'-2" x 8'-0". All bare nail heads in the wood frame were covered with silicon. The cathode was fastened with 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 a concrete tank with a flow rate of 3 1/2 gallons per minute of sea water from a settling tank. Ambient water temperature was 74°F. Electrical measurements were taken with meters integrated in the power supply.

2.3.2. The test strip was submerged and under power for 52 hours. Consumption of electricity is shown in Figure 9. After submersion, the electrodeposited strip was divided into 12 sections measuring 6" each (Figure 10). At sections 1, 7, and 13, material samples were taken (Figure 10, Positions 98, 99, 100).

Table 3: X-ray Diffraction Analysis

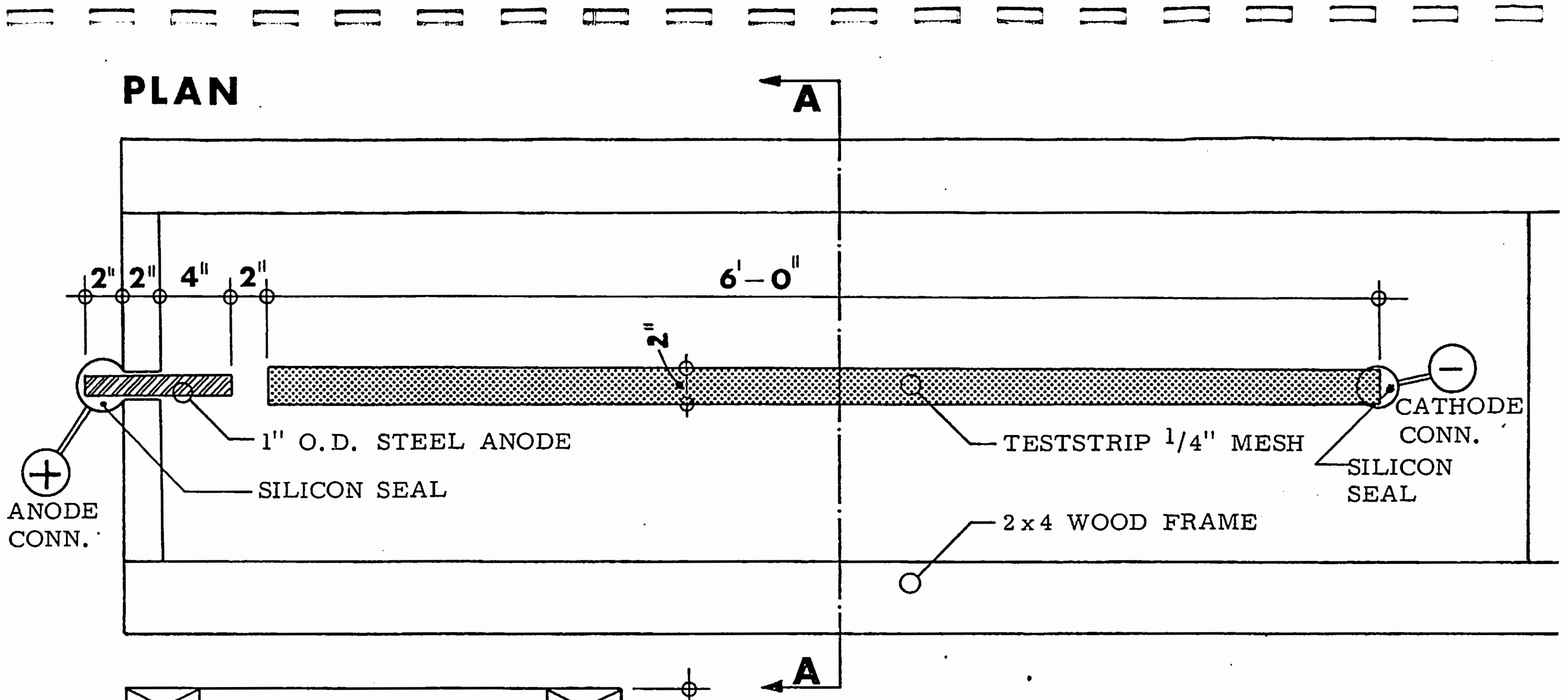
		Chemical Composition					
Sample #	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
98	0" from Anode	80%	8%	1%	8%	3%	0%
99	36" from Anode	70%	22%	2%	-	-	1%
100	72" from Anode	25%	5%	trace	15%	trace	54%

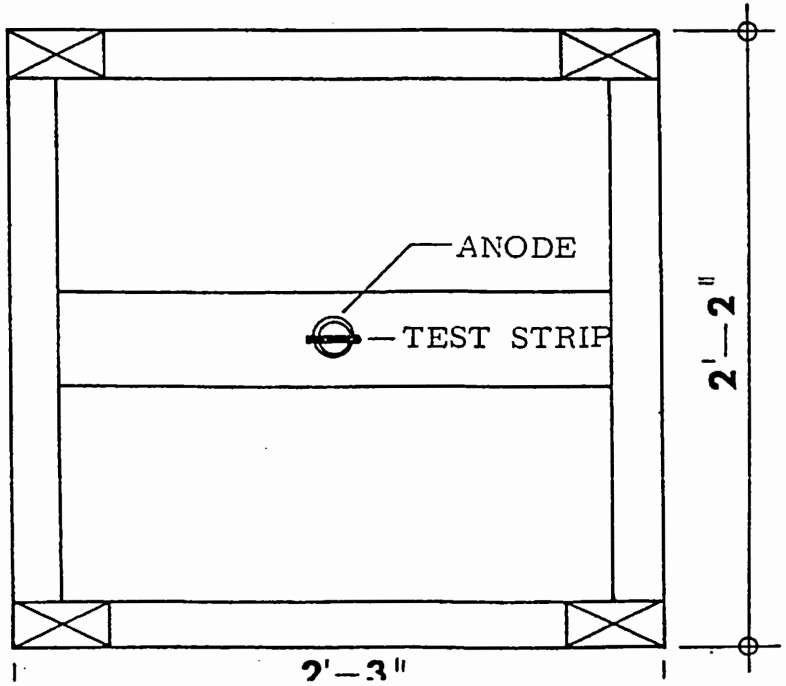
2.3.3. For discussion of comparative analysis, see Section 2.4.3.

2.4.1. Test square 1 (W.I.L. - St. Croix). A steel anode was positioned 6'-0" opposite a 1/4" 1 sq. ft. (30 cm^2) galvanized wire mesh anode (Figure 11, Photo 3). The supportive wood frame measures 2'-3" x 2'-2" x 8'-0". All bare nail heads in the wood frame are covered with silicon.

The cathode was fastened with 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 next to the W.I.L. pier laboratory. Ambient water temperature was 85°F. Electrical measurements were taken with meters integrated into the power supply.

2.4.2. Before submersion, the 1 sq. ft. (30 cm^2) 1/4" wire mesh cathode weighed 96.2 g. The test frame was submerged and under power for 52 hours. Consumption of electricity is shown in Figure 12.





SECTION A

TEST STRIP POSITIONED BY NYLON LINE

ALL NAIL HEADS SILICONED

TEST STRIP 3

Fig. 8

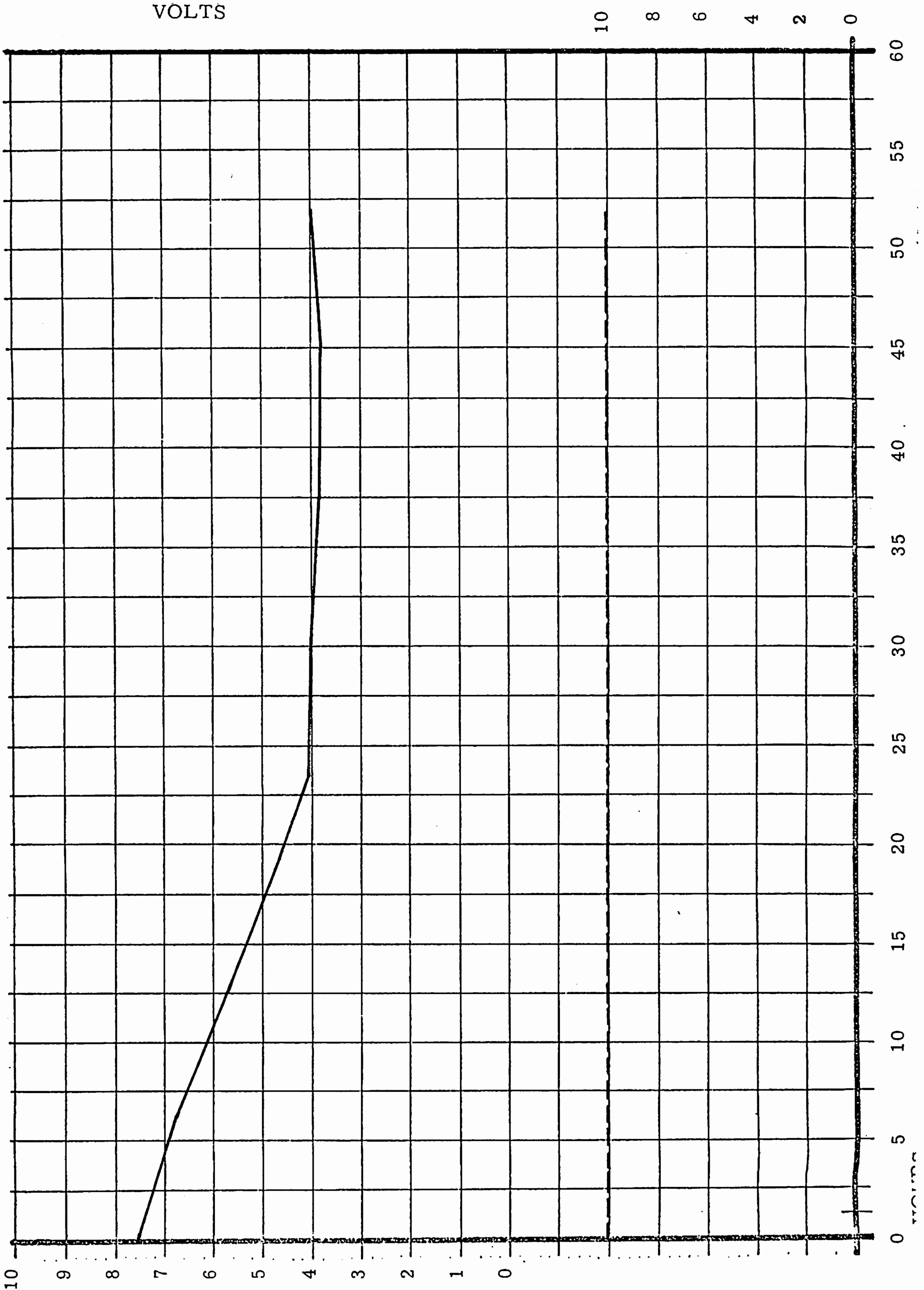
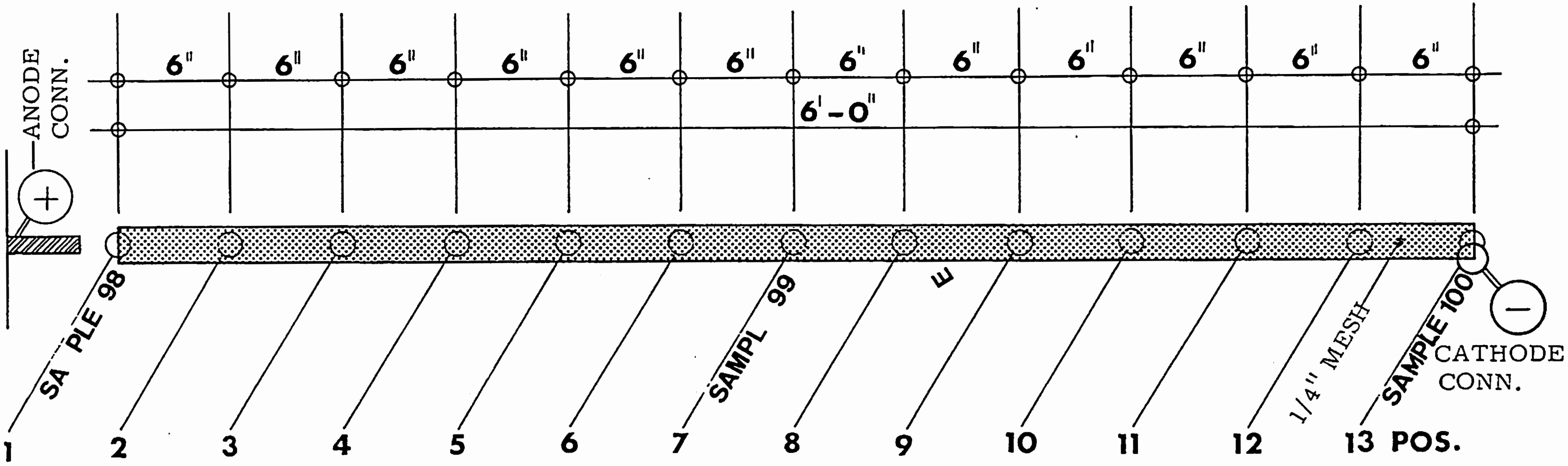
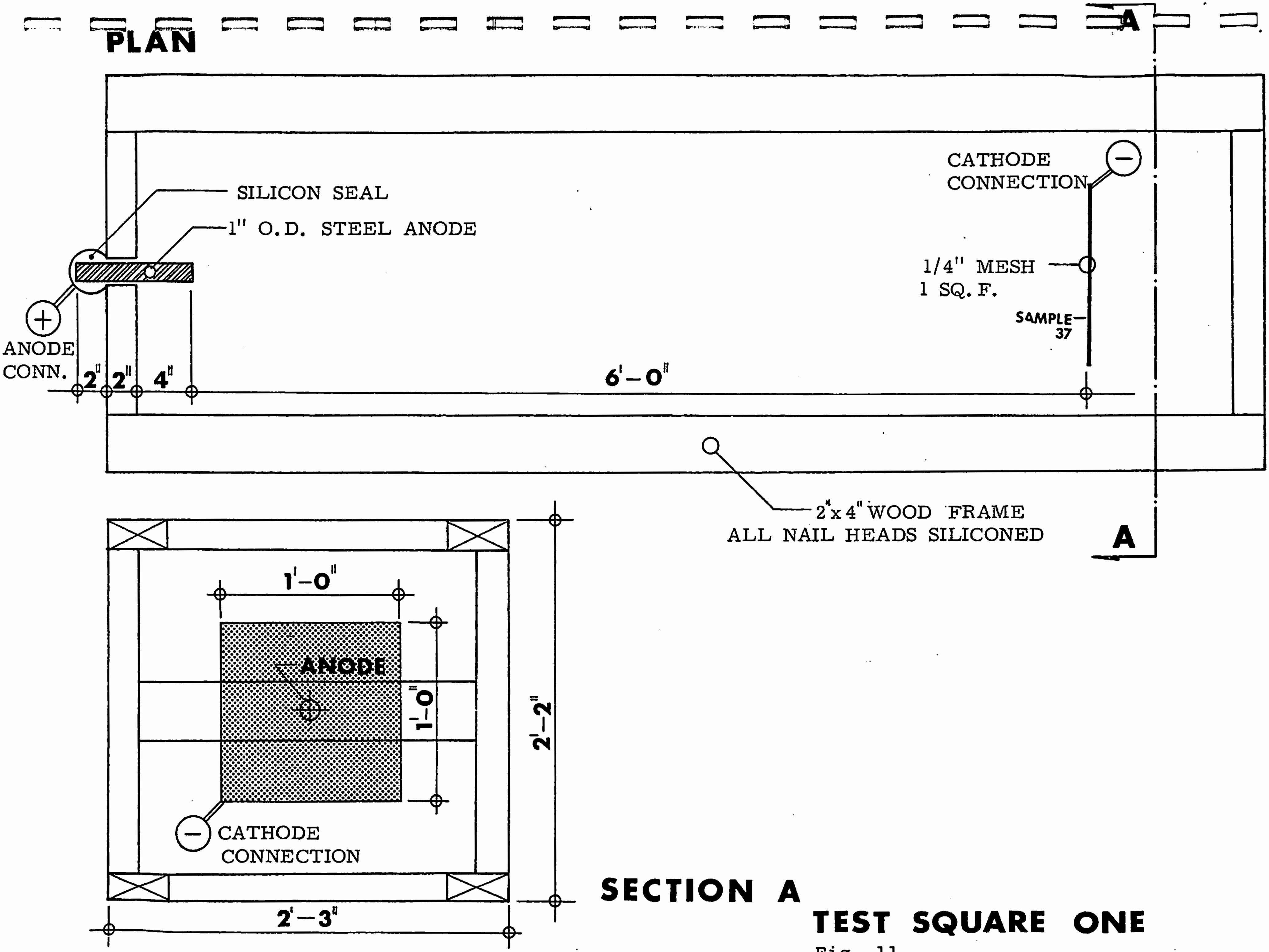


FIGURE 9 TEST STRIP 3



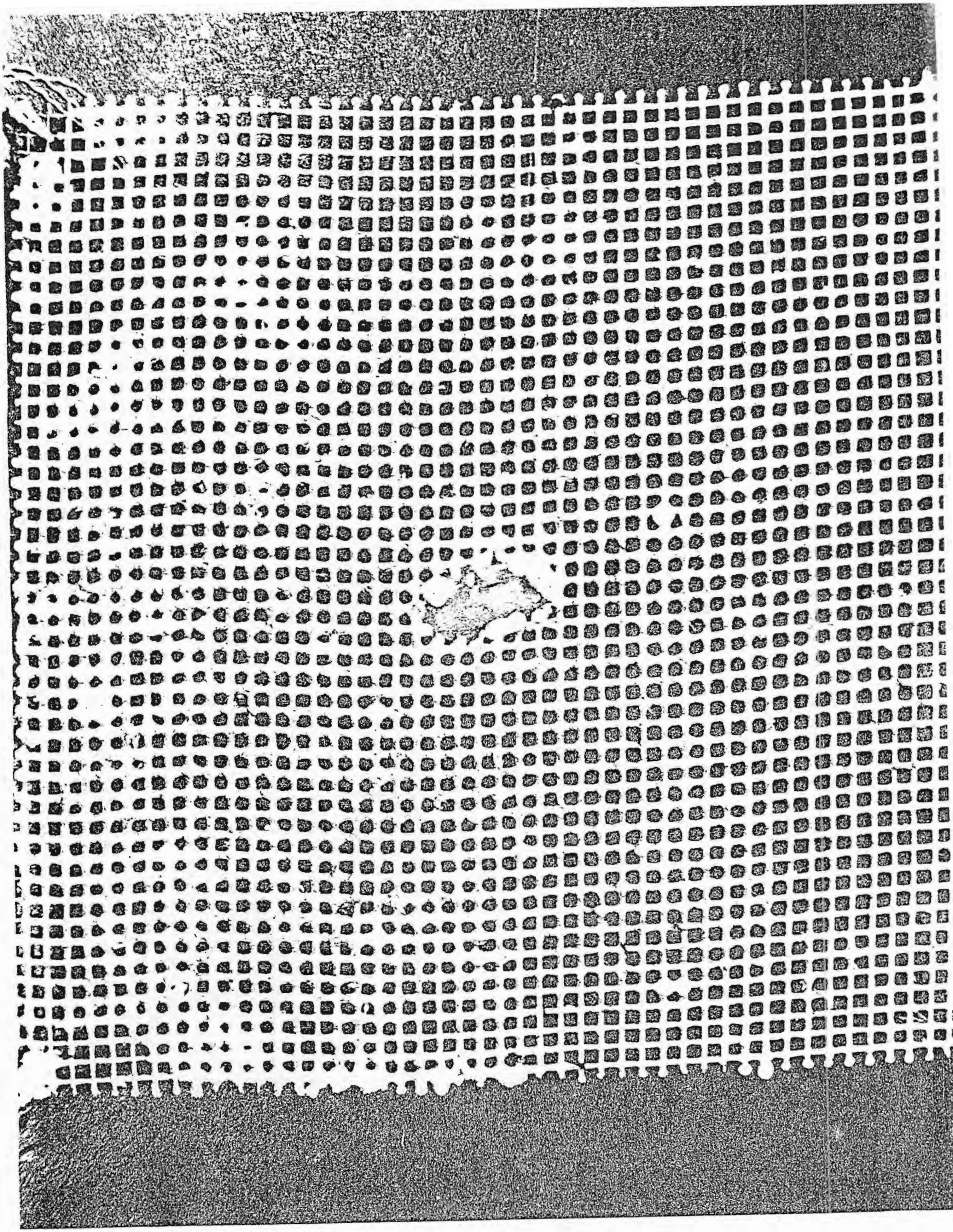
TEST STRIP 3

Fig. 10



TEST SQUARE ONE

Fig. 11



Photo

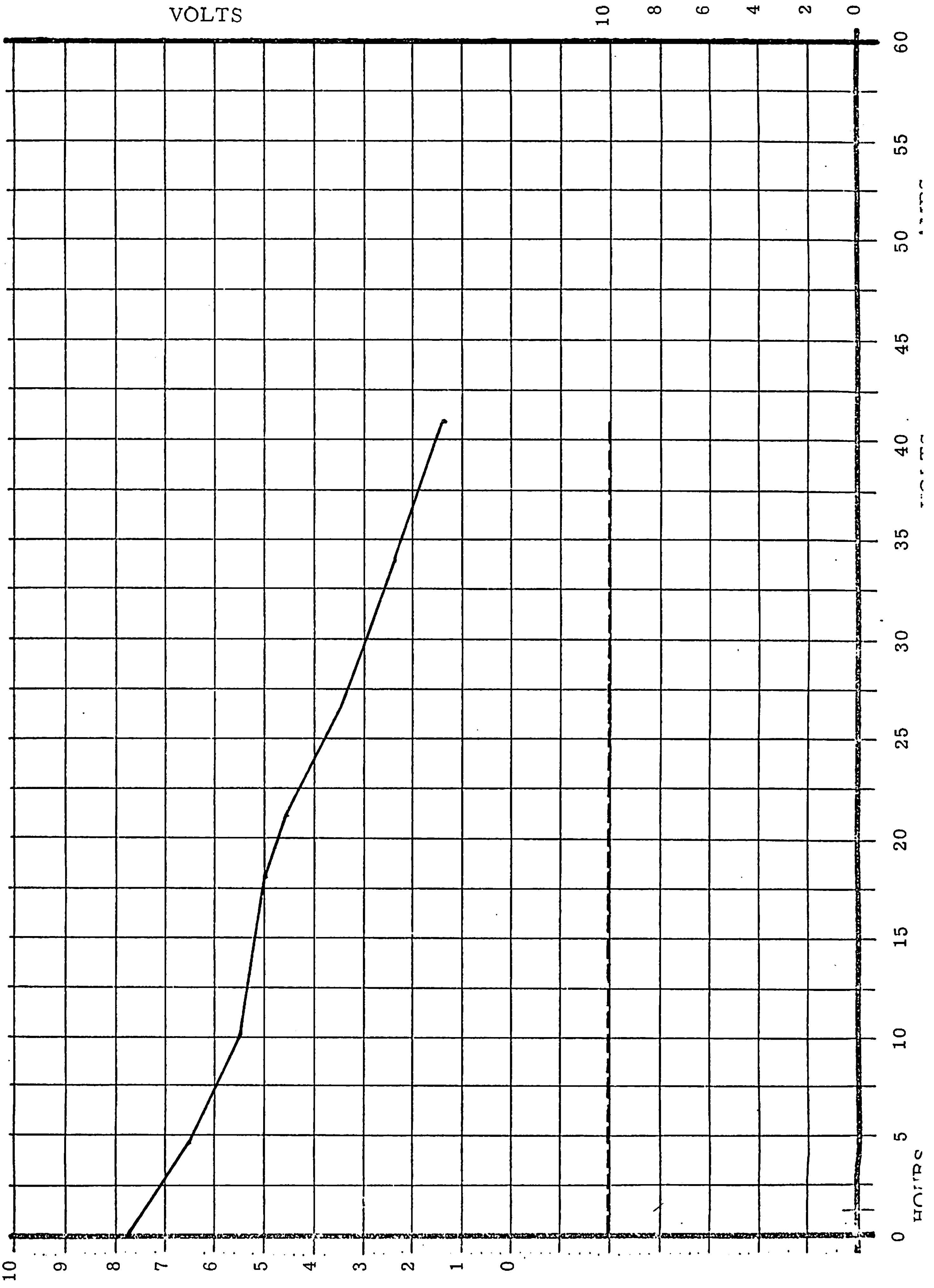


FIGURE 12 TEST SQUARE

One material sample (Figure 11, Position 37) was taken after 52 hours. After electrodeposition, the cathode was dried for 22 hours at 200°F. Weight of the cathode was 184.5 g. Thus, 88.3 g. of material was precipitated.

Table 4: X-ray Diffraction Analysis

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

2.4.3. Analysis of test square 1 (Table 4, Sample 37): the composition of the accreted material is very similar to that exhibited at the center (36") sample site of test strip 1, 2, and 3 (Table 1, 2, 3, samples 60, 73, 99) that is, greater amounts of aragonite and less non-crystalline matter. 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. This seems to be a viable hypothesis from conversation with Dr. Allen J. Bard, U.T. Chemistry Department. 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 1, 2, 3, 4), we can draw the following preliminary conclusions:

- Position of the anode and cathode connections relative to cathode surface area has a definite effect on the material accreted in their vicinity as well as the amount of non-crystalline matter enveloped in the accretion matrix.

- Since the position farthest from either anode or cathode (36") reached the maximum amount of Aragonite, it seems that the greatest electrochemical circuit resistance is developed at the anode and cathode connections. If the resistance is greater at these connections, the temperatures will also increase and as a function of temperature, the H will also rise. The more alkaline H becomes, the less favorable conditions will be to precipitate $CaCo_3$.

- 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.

- 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 conclusions of a loosely bound crystalline structure precipitated through the physicochemical reaction of concentration gradients.

- Looking at Figure 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 became less with more distance from the electrical activity at the anode end.

- It is evident in all cases that the greatest percentage of sample material is Brucite ($Mg(OH)_2$). We have found it 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 consists of portlandite ($Ca(OH)_2$), which is isostructural with brucite[2], but not as yet detected through x-ray diffraction. This is due to concentration and availability of the (OH^{--}) and (CO_3^{--}) anions at a pH greater than 9.00 at which point brucite is known to precipitate [3 4 5]. Fast precipitation of compounds from seawater usually results in brucite of the massive material form; slow precipitation and no-power phasing usually results in brucite with the platy or foliate crystalline structure.

2.5.1. The Test Rack A, (U.T. M.S.I., Port Aransas). This construction was devised to determine the effects of gas evolution both from the anode and the cathodes on electrodeposition rate and composition of electrodeposited materials, (Figure 13). It was hypothesized and observed that all produced gases will take a vertical path upwards when released. Thus, layer 4 would not be affected by gases other than those generated on its own surface. Layer 3 would be affected by hydrogen gas precipitated by layer 4. Layer 2 would be affected by hydrogen gas precipitated by layers 4 and 3, as well as oxygen and chlorine gases produced by layers 4, 3, and 2, and oxygen and chlorine gases evolved by the anode.

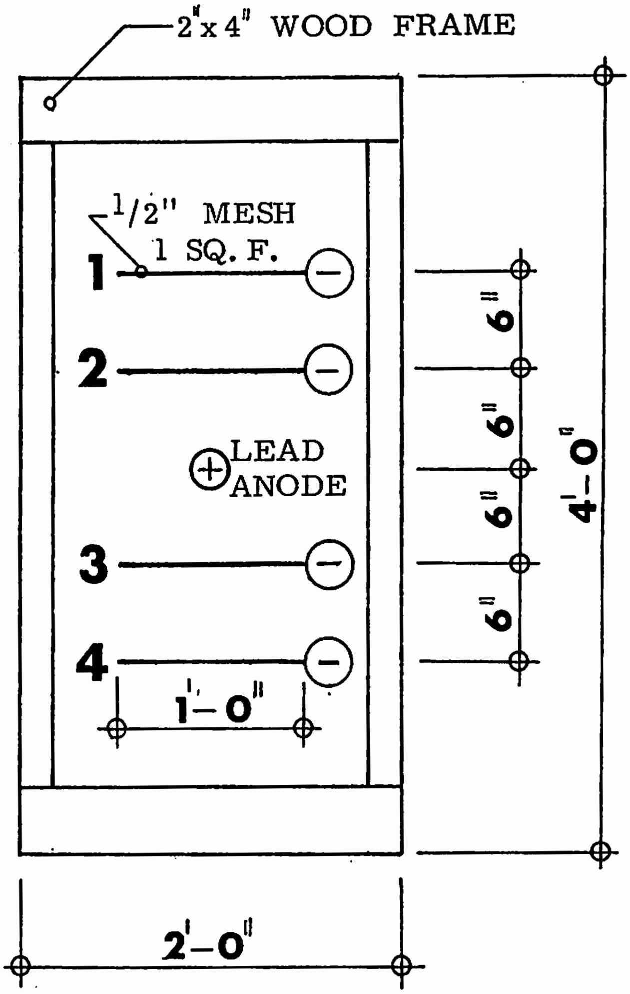
Direct current was provided by a regulated power supply. Both anode and cathode wires are 8AWG multistrand insulated copper wire. All electrical connections are insulated with clear silicon. The test rack was submerged in 3'-6" of water in a concrete tank at the U.T. M.S.I. Port Aransas. Flow rate of seawater from a settling tank is 3 1/2 gallons per minute. Ambient water temperature ranges between 68° and 74°F.

2.5.2. No results are available at this time.

2.5.3. No discussion is possible at this time.

3. Artificial Reefs.

These constructions were built to determine the parameters of the electrodeposition of minerals in solution onto large surface as substrate for marine growth and to prove the hypothesis that wire-mesh formations covered by electrodeposited minerals can support marine communities usually found inhabiting natural reef formations.



TEST RACK A

Fig. 13

3.1.1. Reef 1. This construction consists of an assembly of regular and irregular shapes. The material used was galvanized wire mesh with various gauges and a total area of 252 1/3 sq. ft. (Figure 14). Direct electrical current was provided by an unregulated power supply. The anode and cathode wires consist of 6AWG type THW multistrand insulated copperwire with a length of 250'-0" each. All wire connections were insulated with clear silicon. The structure was submerged 200'-0" north of the W.I.L. pier laboratory in 7'-0" of water on sandy ground (Figure 15, Position 1). Electrical readings were taken with a Micronta double range 22-204A meter.

3.1.2. Twenty hours after submersion white accreted material was visible on all surfaces of the structure. Power supply to the structure was irregular due to circuit overloading (Figure 16). Seventy two hours after submersion diatomatious and blue-green algae growth was observed on the outer surface of the structure (Photo 4). This growth gradually covered all surfaces of the structure (Photos 5, 6), and had reached a length of 8 cm, 280 hours after submersion. Schools of small fish were observed grazing off the algae and inhabiting the structure (Photo 8). The first sample of the electrodeposited material was taken 437 hours after the start of electrodeposition (Table 5, Sample 33); the second sample was taken 1991 hours after the start of electrodeposition and 1508 hours after the power supply was disconnected (Table 5, Sample 95). Mineral deposition thickness on 1" x 2" mesh measured 5.4 mm (diameter of metal wire = 1.75 mm) after 480 hours of electrodeposition. The structure was under power for 483 hours. The temperature of the electrolyte ranged between 82°F and 88°F.

Table 5: X-ray Diffraction Analysis

		Chemical Composition					
Sample #	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%

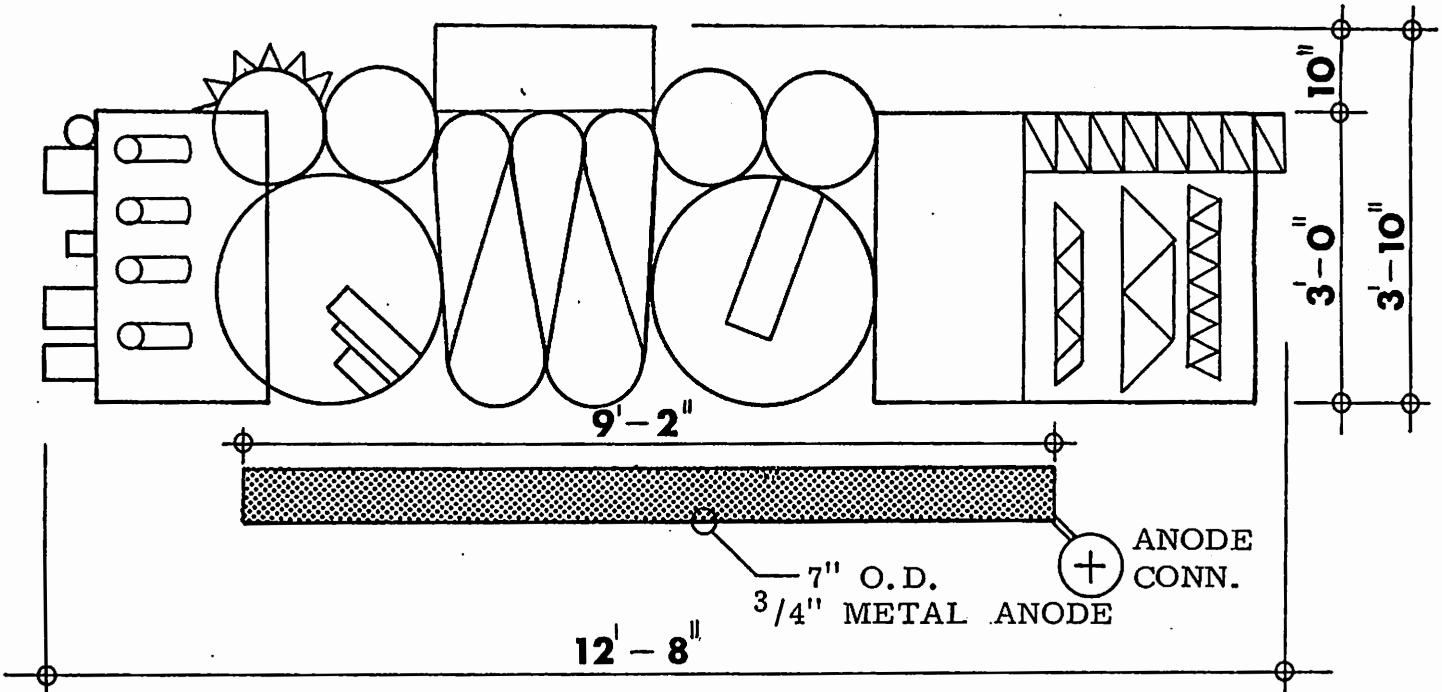
3.1.3. A moderate input of electrical power provided a mineral substrate that allowed rapid diatomatious and blue-green algae growth which, possibly in connection with the availability of protected spaces, attracted various fish populations. The electric field between anode and cathode did not affect 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 by the electric field; individual animals moved freely in and around the structure. Detailed data on observed diatomatious and blue-green algae growth as well as observed fish population, species, and behaviour will be given in the forthcoming addendum to this report.

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.[1]

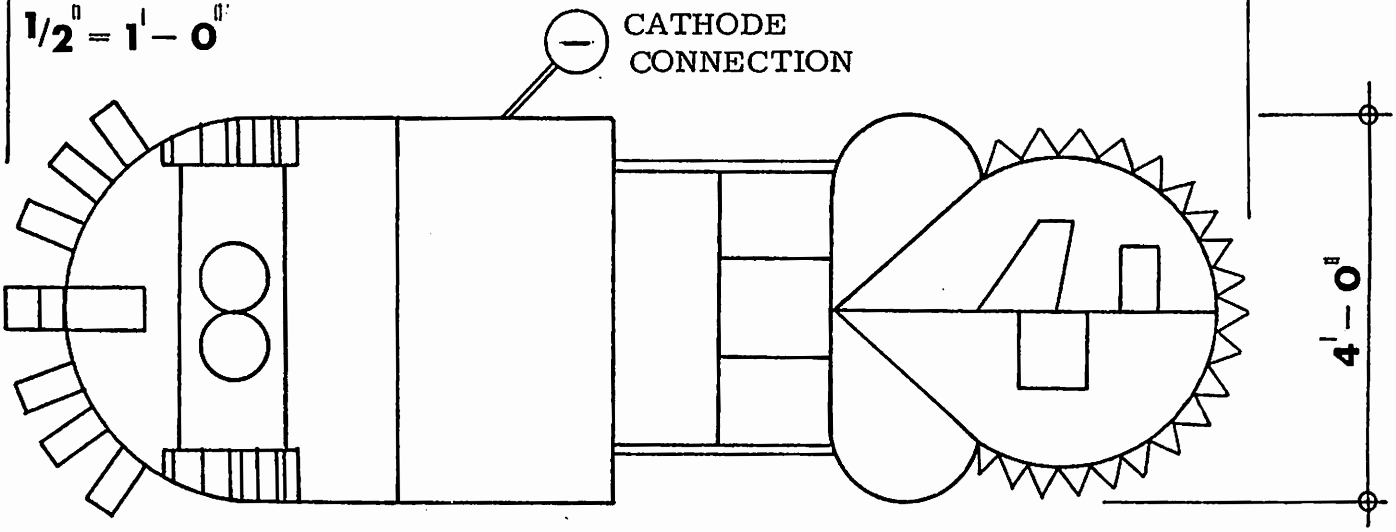
ELEVATION

1/2" = 1'-0"



PLAN

1/2" = 1'-0"

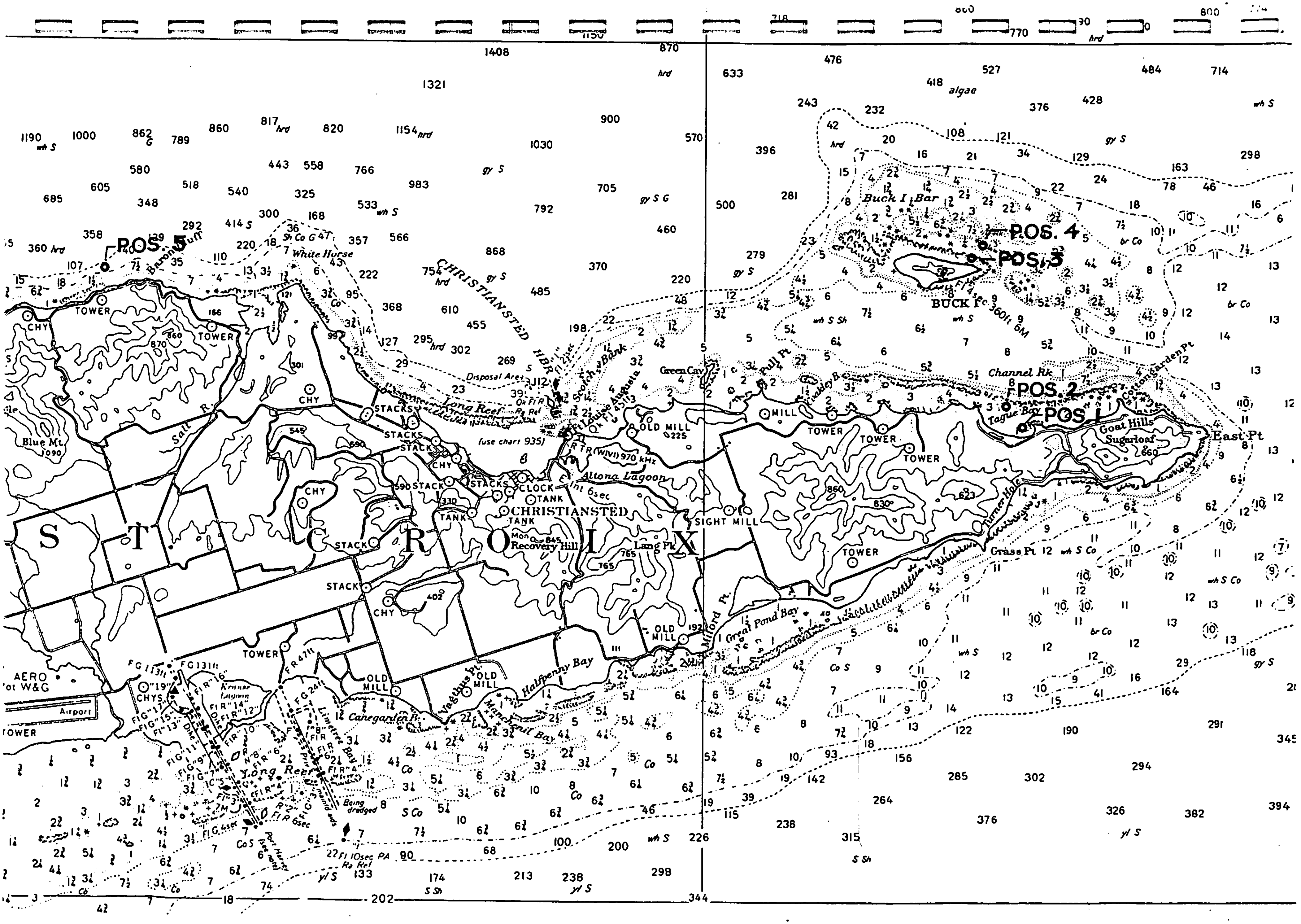


SURFACE AREA

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.

ARTIFICIAL REEF 1

Fig. 14



POS. 5
POS. 4
POS. 3
POS. 2
POS. 1
ST CROIX
CHRISTIANSTED
CHRISTIANSTED HBR
Buck I Bar
BUCK I
Channel Rk
Tague Bay
Coakley B
Goat Hills
Sugarloaf
East Pt
Cottongarden Pt
Grass Pt
Turner Hole
Great Pond Bay
Milford Pt
Halfpenny Bay
Manchenil Bay
Vagthus Pt
Canegarden B
Limetree Bay
Long Reef
Krause Lagoon
Airport
AERO
Blue Mt
Salt R
Baron Bluff
White Horse
Long Reef
Scotch Bank
Ft Louise Augusta
Green Cay
Pull Pt
Altona Lagoon
Recovery Hill
Lang Pk
Disposal Area
(use chart 935)
TOWER
CHY
STACK
STACKS
OLD MILL
SIGHT MILL
MILL
CLOCK
TANK

LOCATIONS

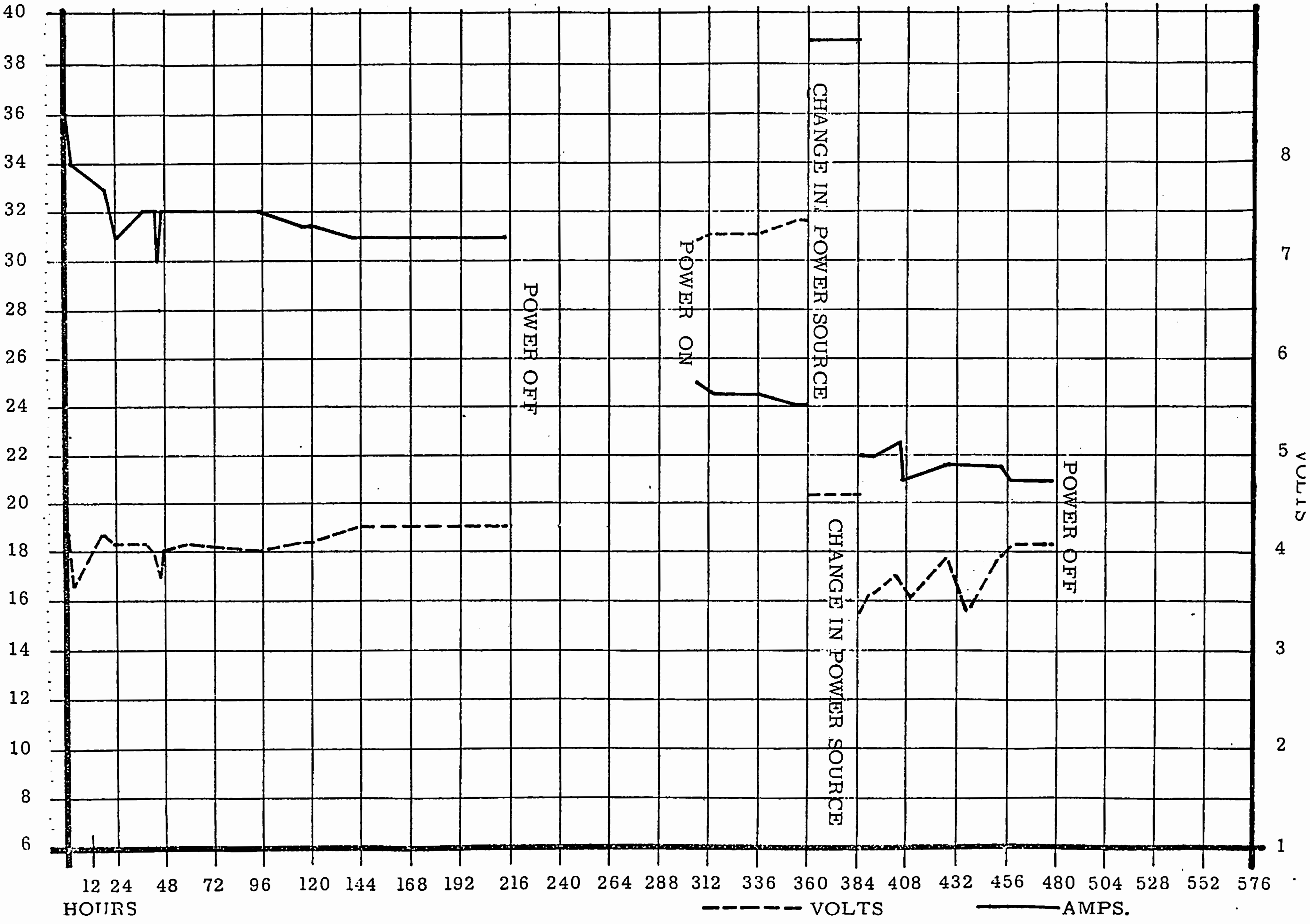
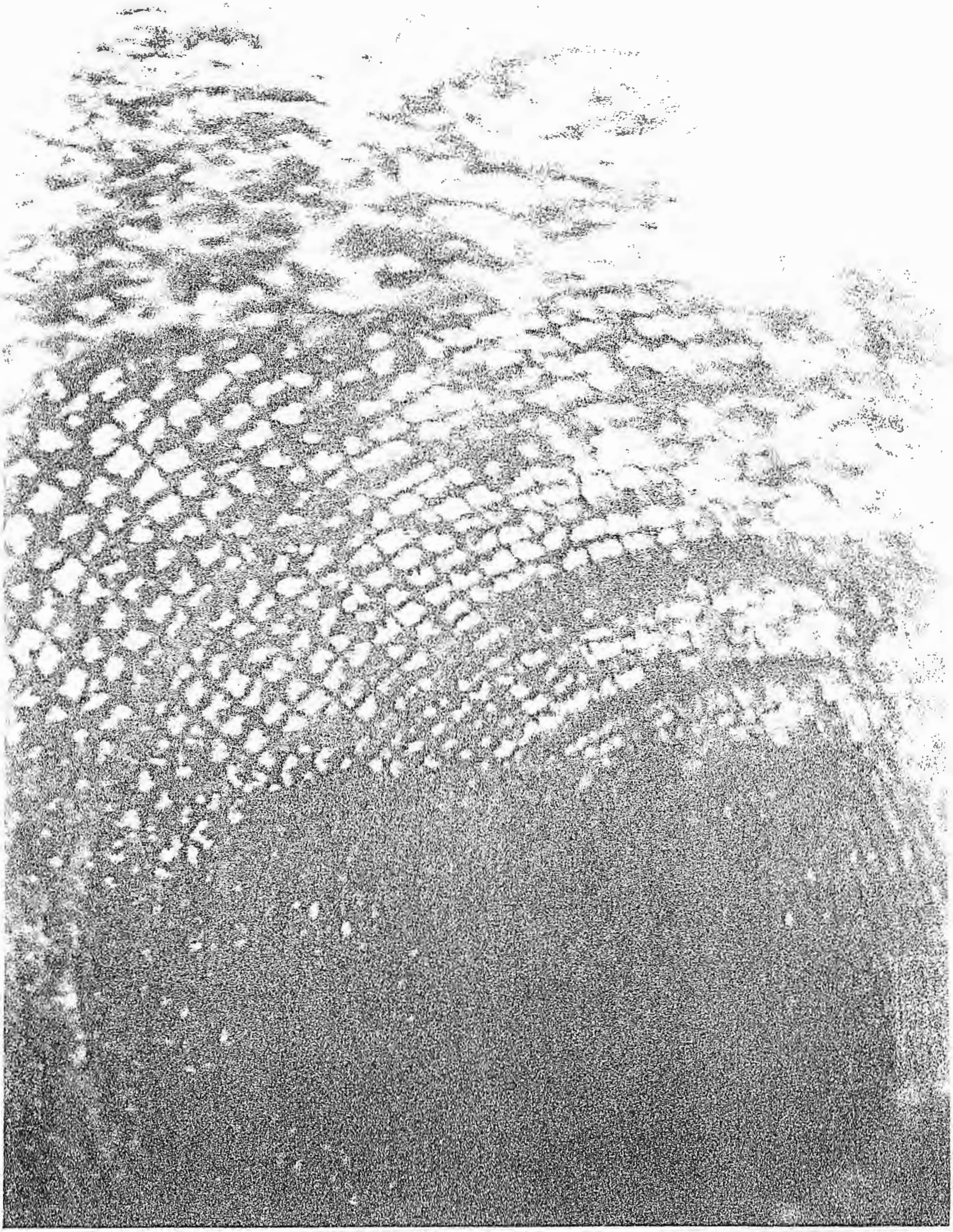
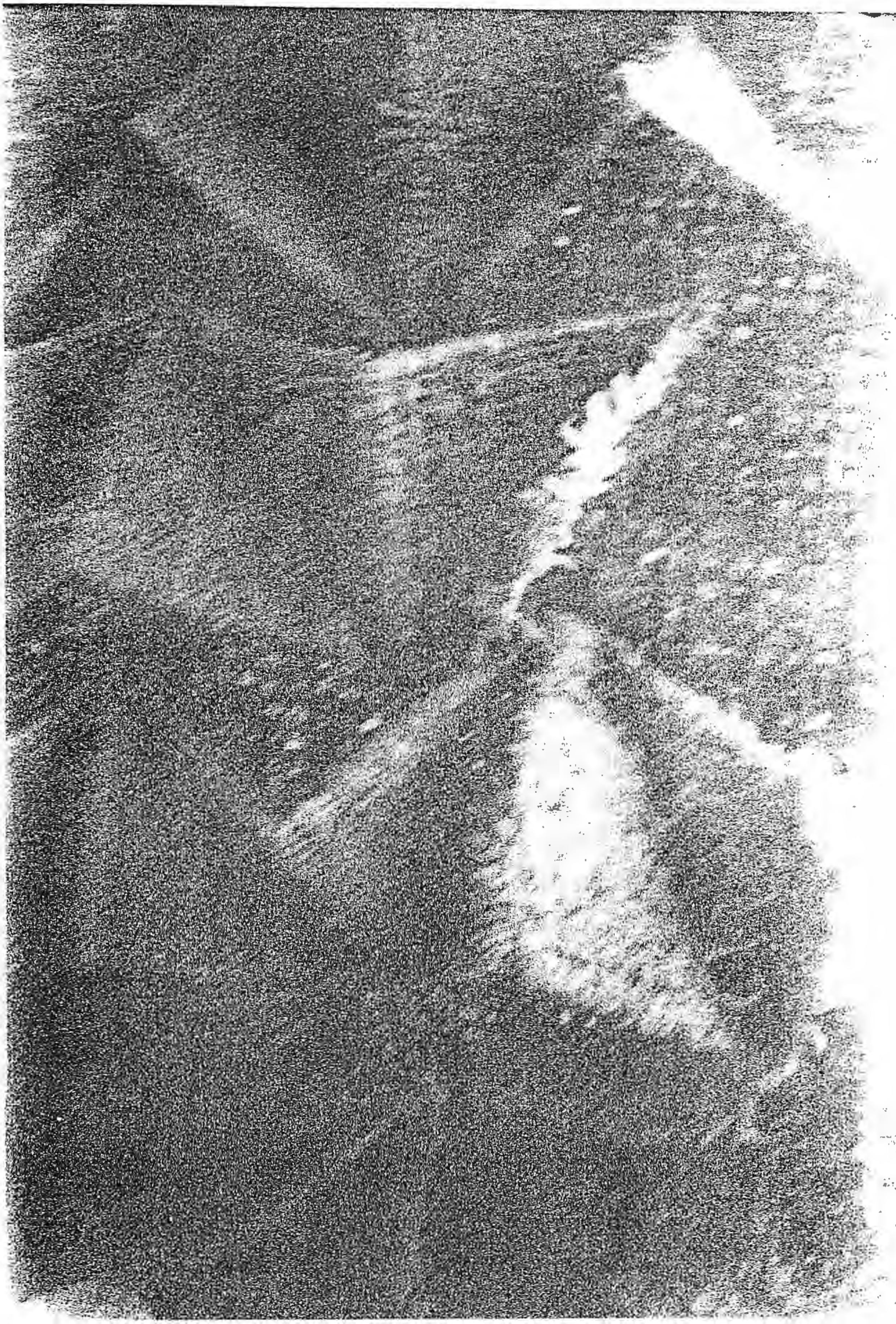


FIGURE 16 REEF 1



Photo

Photo



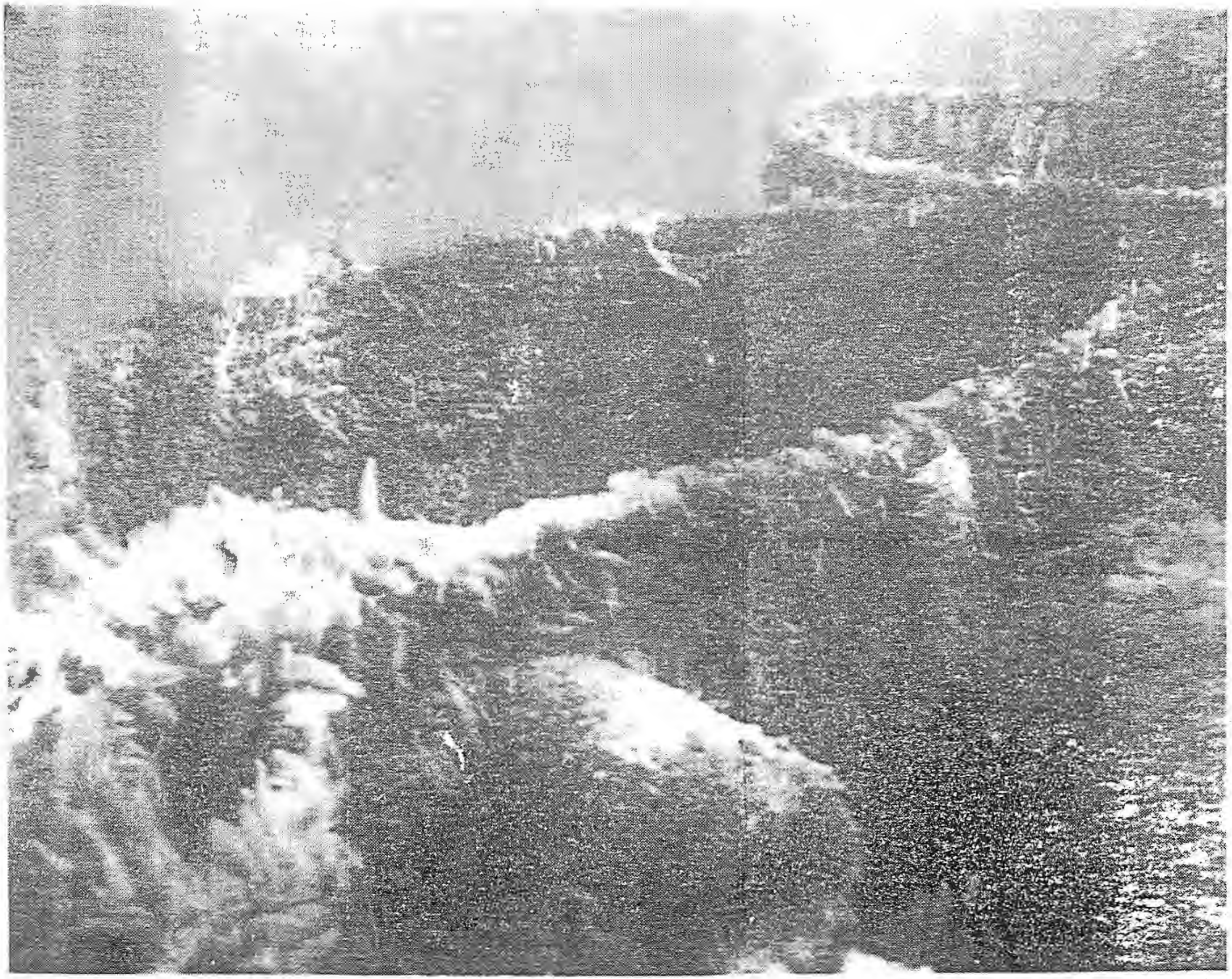


Photo 6

Photo

3.2.1. Reef 2. This construction consists of identically folded galvanized wire mesh formations of two different gauges with a total area of 144 sq. ft. (Figure 17). Direct current electricity was provided by an unregulated power supply. The anode and cathode wire consist of 6AWG type THW insulated copper wire with a length of 250'-0" ea. All wire connections are insulated with clear silicon. The structure is submerged 215'-0" north of the W.I.L. pier laboratory in 8'-0" of water on sandy bottom (Figure 15, Position 1). Ambient water temperature ranged between 82°F and 88°F. Electrical readings were taken with a Micronta double range 22-204A meter.

3.2.2. Fifteen hours after submersion wite accreted material was visible on all surfaces of the structure. Power supplied to the structure was irregular due to circuit overlaods (Figure 18). Seventy two hours after submersion the same growth as on Reef 1 was observed covering the entire structure (Photos 9, 10 and 11) reaching a length of 8 cm, 190 hours after submersion. Schools of samll fish were observed grazing off the growth and inhabiting the structure (Photo 7). Three hundred and eighty four hours after submersion a 12" barracuda was first seen inhabiting the formation. The first material sample was taken 413 hours after submersion (Table 6, Sample 32). Mineral deposition thickness on the 1" x 2" wire mesh measured 6.2 mm (diameter of metal wire = 1.75mm) after 485.5 hours of electrodeposition.

Table 6: X-ray Diffraction Analysis

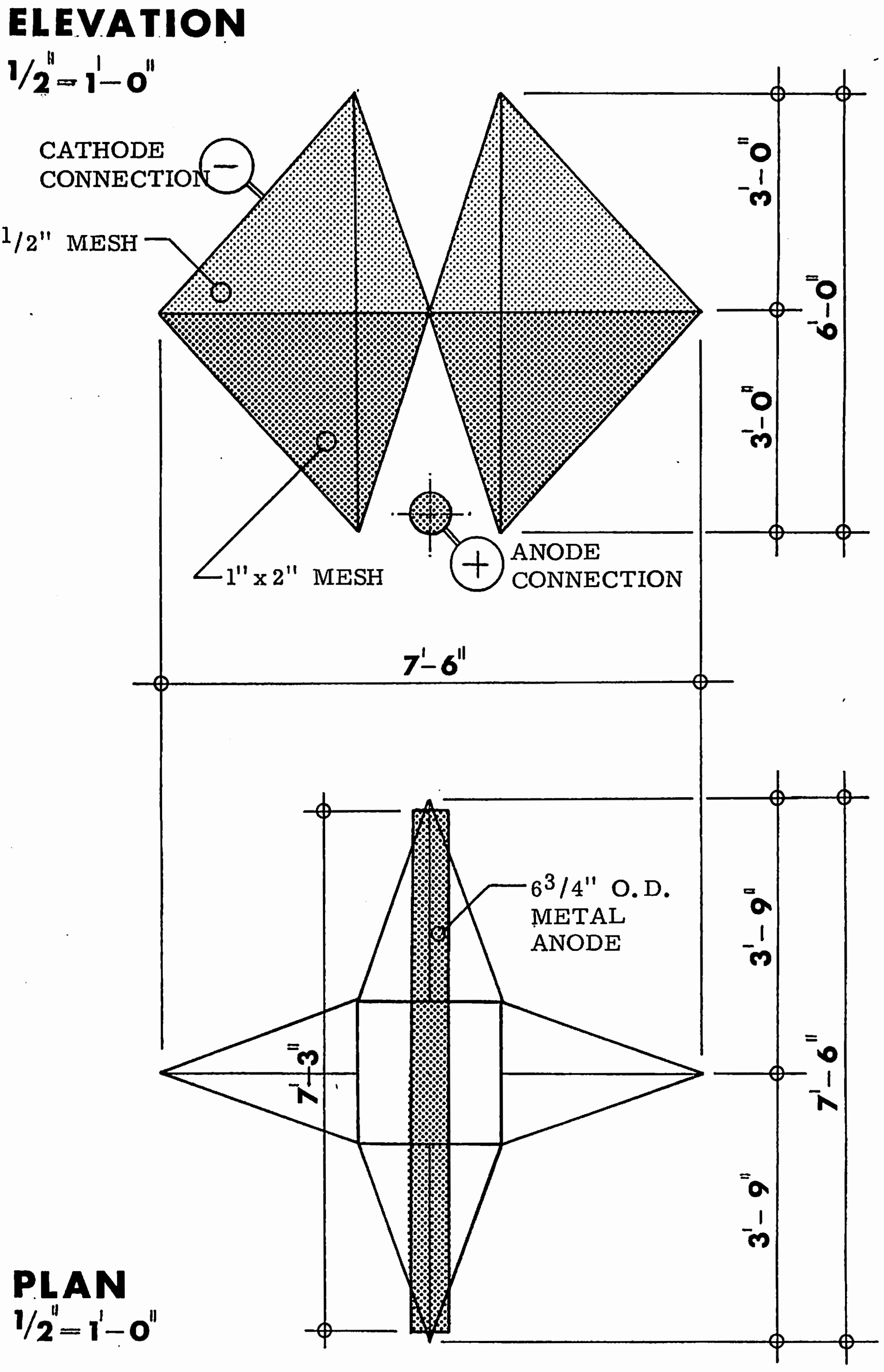
		Chemical Composition					
Sample #	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
32	-	40%	3%	1%	2%	trace	54%
96	-	51%	13%	1%	3%	trace	32%

3.2.3 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 avialability of protected spaces, attracted various fish populations. The electrical field between anode and cathode did not affect algae growth, as was clearly established by the observation of an electrodeposited control sample without electric field under identical conditions. Inhabiting fish populations were visibly not affected by the electric field; individual animals moved freely in and around the structure. Detailed data on observed diatomatious and blue-green algae growth as well as observed fish population numbers, species, and behavior will be given in the forthcoming addendum to this report.

4. Architectural Components.

Several large architectural components were built and submerged to determine the parameters for the electrodeposition of minerals and subsequent phasing.

4.1.1 Drum 1, (W.I.L., St. Croix). This construction consists of 3 layers of galvanized wire mesh with various gauges (Figure 19). The anode was positioned in the center of the cylinder. Surface area of the cathode



ARTIFICIAL REEF 2

Fig. 17

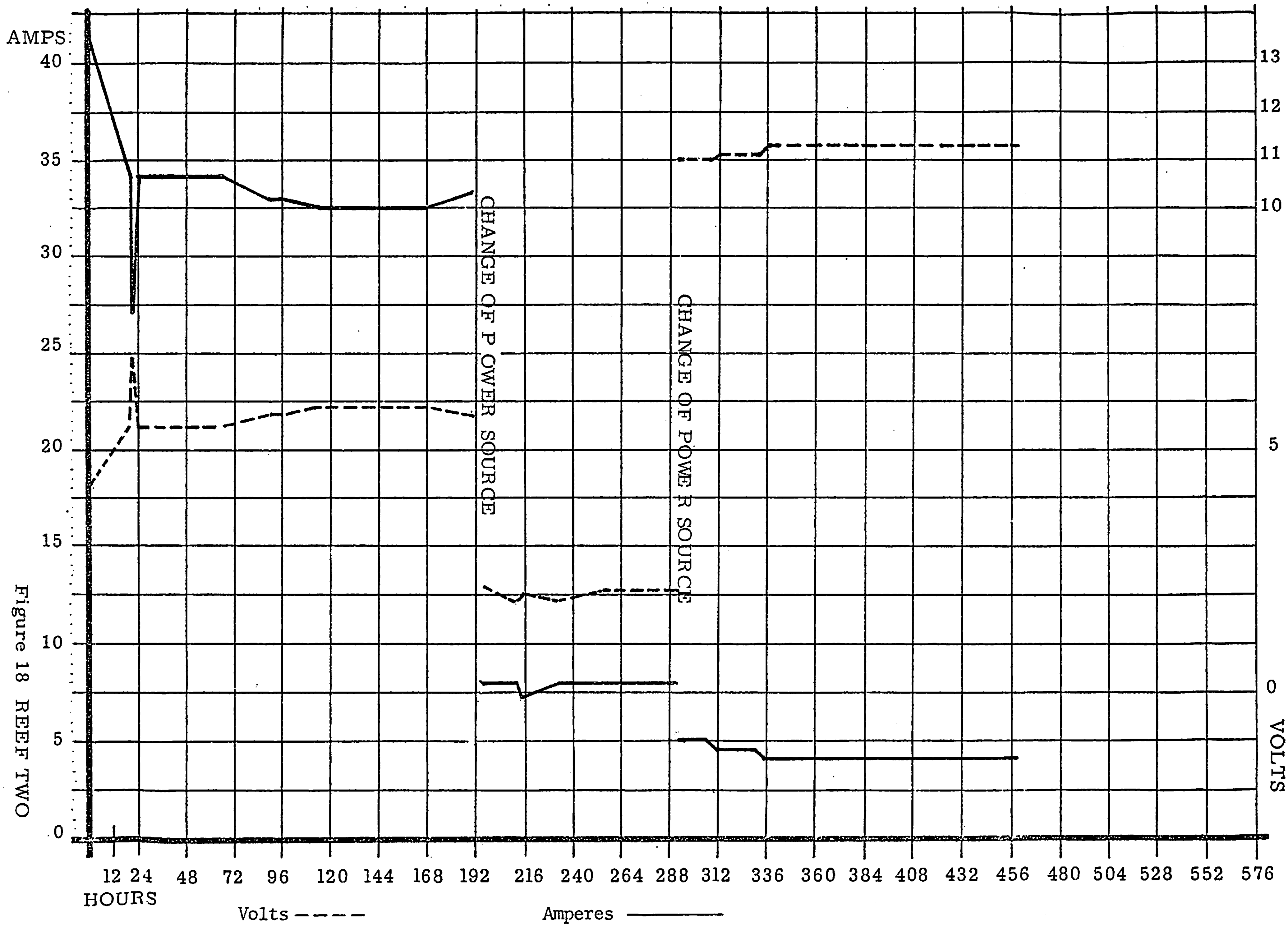
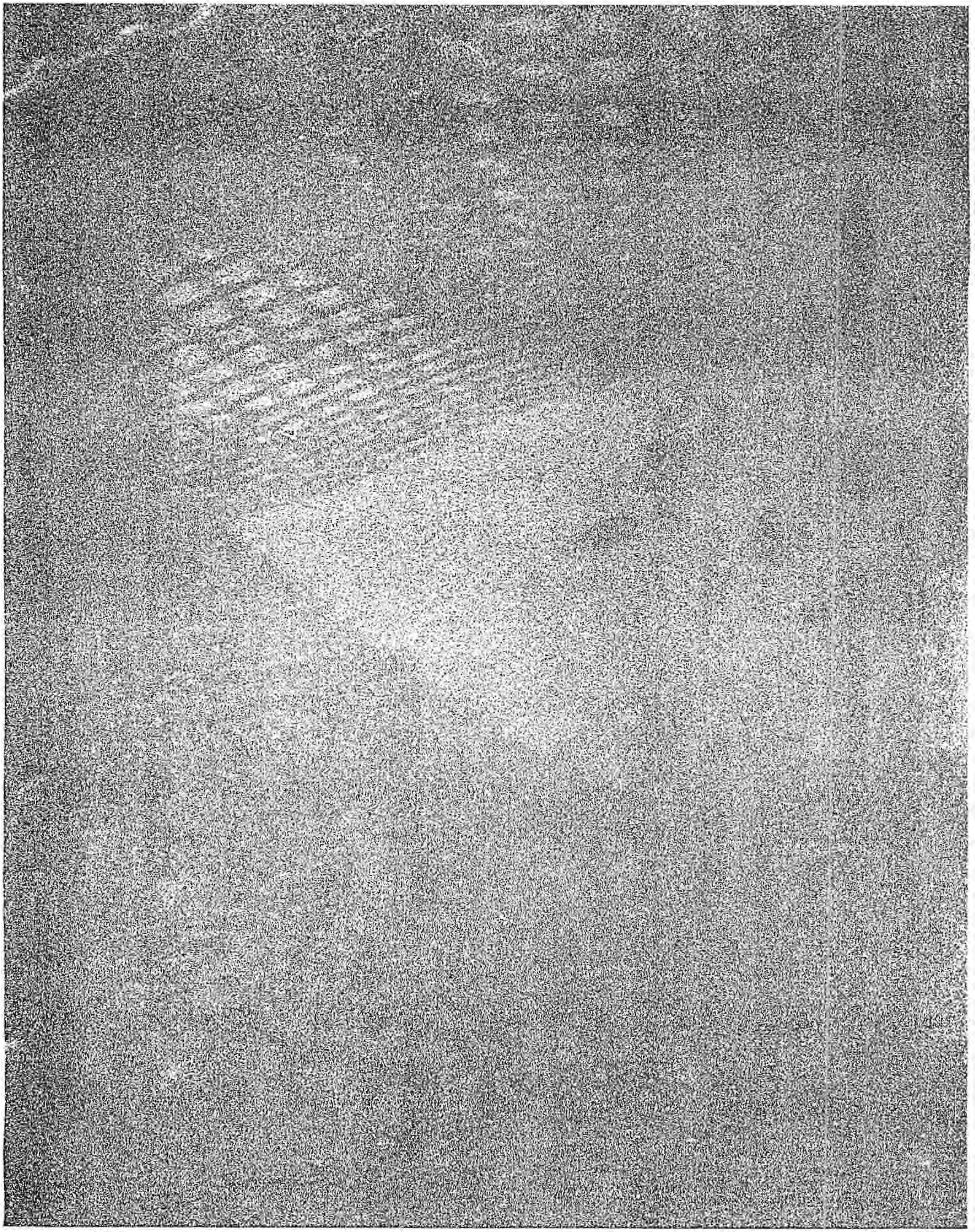


Figure 18 REEF TWO



Photo

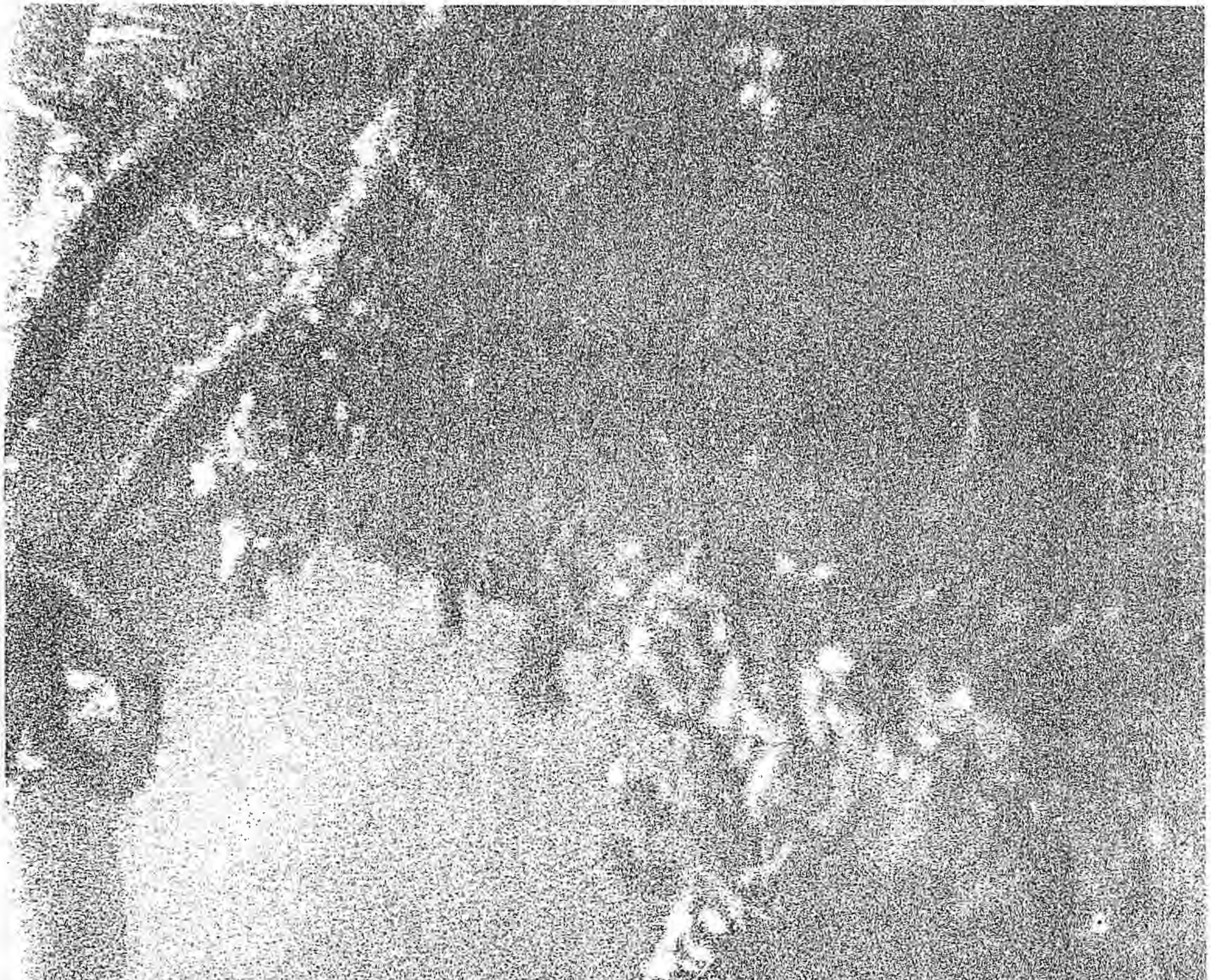


Photo 1

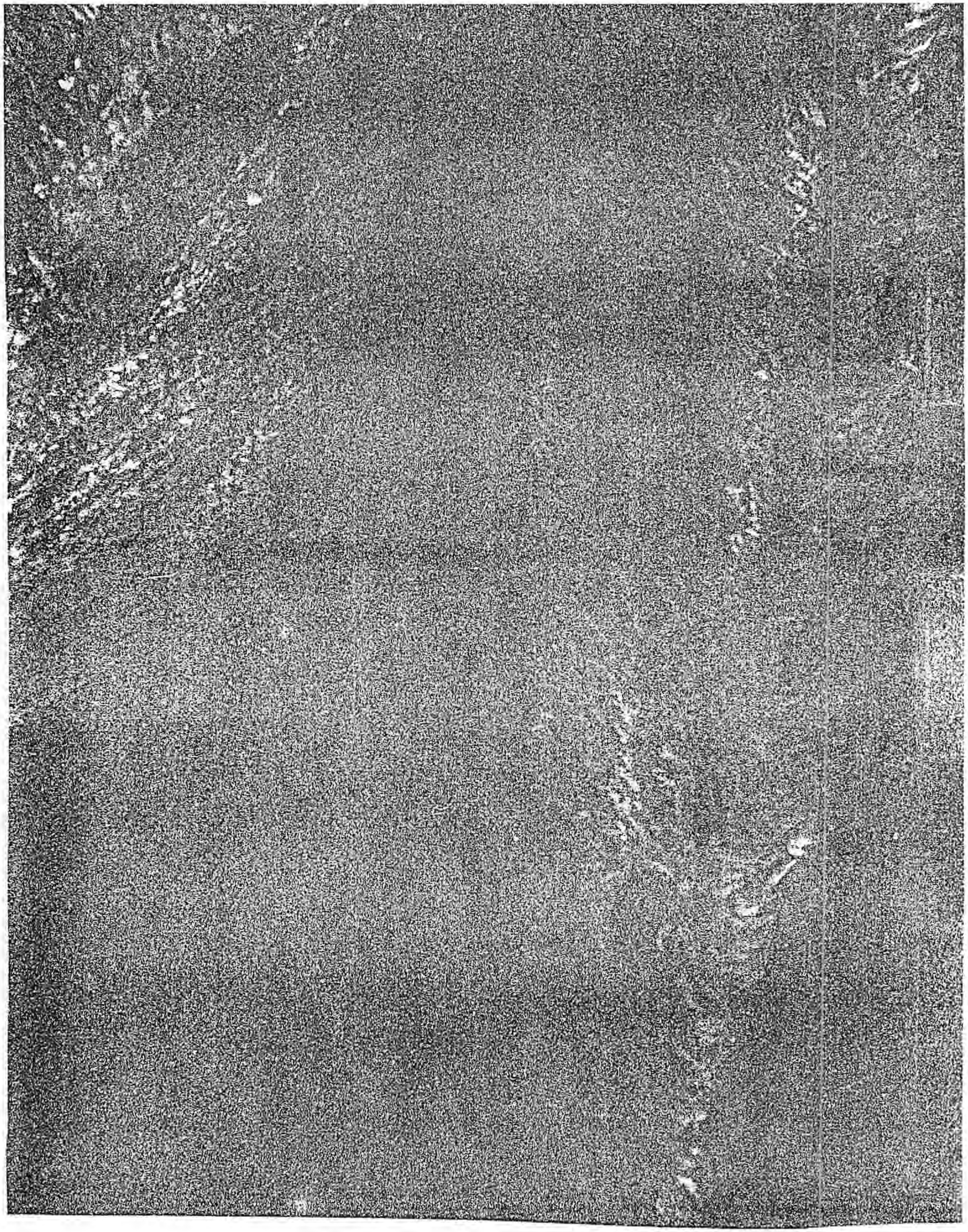


Photo 1

Photo

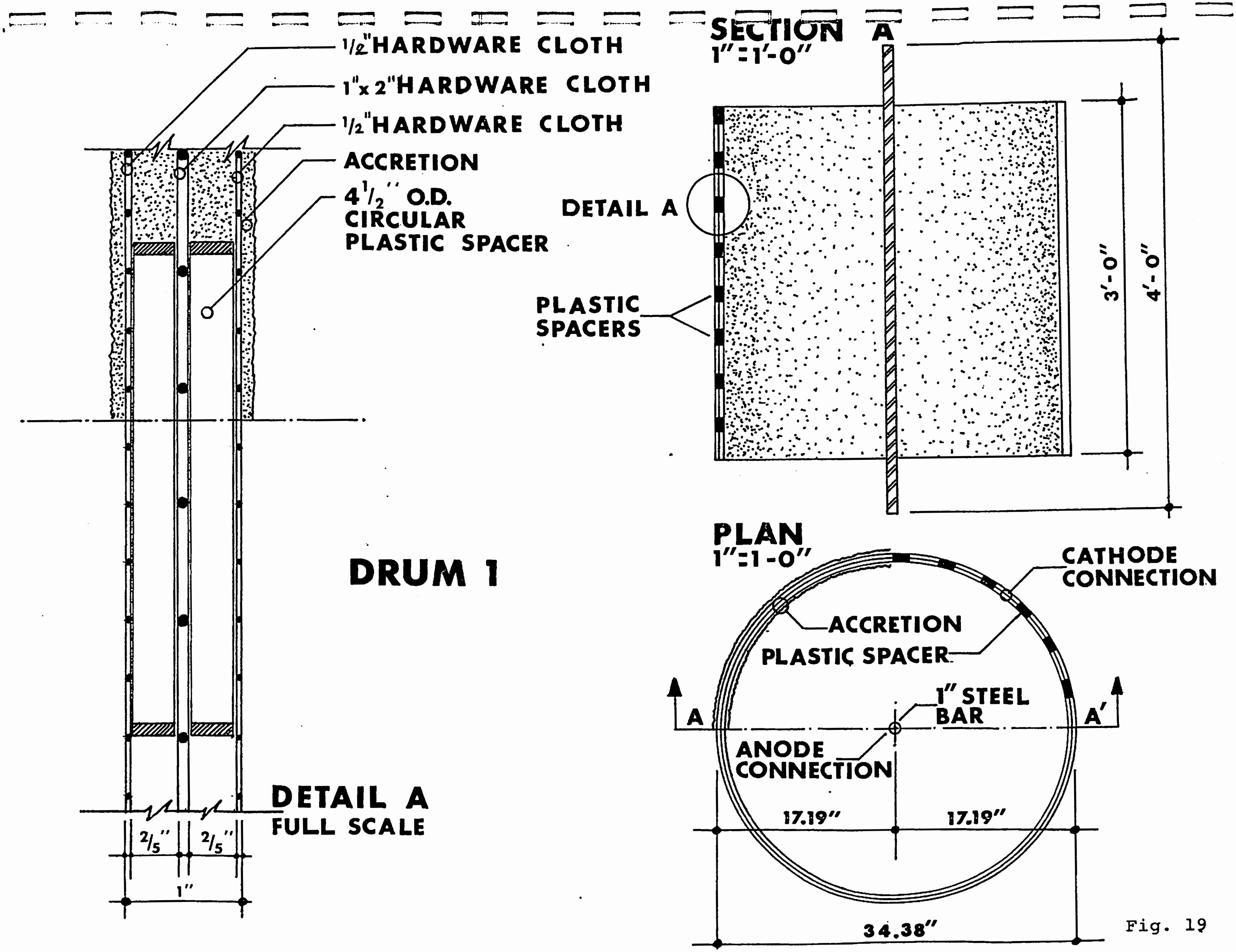

1/2" HARDWARE CLOTH
1"x 2" HARDWARE CLOTH
1/2" HARDWARE CLOTH
ACCRETION
4 1/2" O.D. CIRCULAR PLASTIC SPACER
DETAIL A FULL SCALE
2/5"
2/5"
1"
DRUM 1
SECTION A 1"=1'-0"
DETAIL A
PLASTIC SPACERS
3'-0"
4'-0"
PLAN 1"=1-0"
CATHODE CONNECTION
ACCRETION
PLASTIC SPACER
1" STEEL BAR
A
A'
ANODE CONNECTION
17.19"
17.19"
34.38"

Fig. 19

measures 81 sq. ft. The anode was a 1" steel rod with a length of 4'-0". Anode and cathode wires consisted of 4AWG flexible neoprene welding cable with a length of 30'-0" each. Direct current electricity was provided by three unregulated power supplies operating in sequence. All wire connections were insulated with clear silicon. Drum 1 was submerged for electrodeposition in 5'-0" of water next to the W.I.L. pier laboratory (Figure 15, Position 1). Ambient water temperature ranged between 82°F and 88°F. Electrical readings were taken with a Micronta double range 22-204A meter.

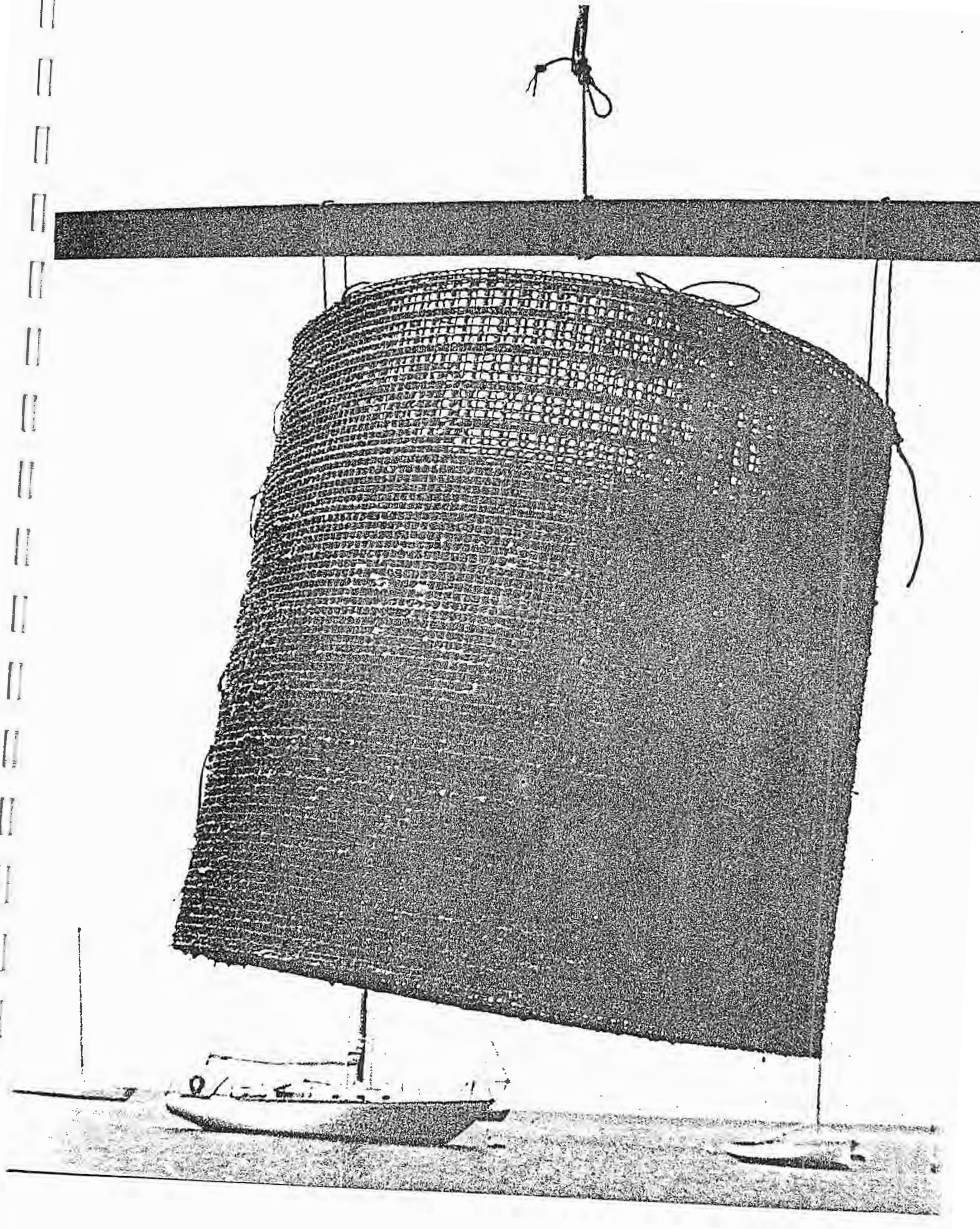
4.1.2. An electrodeposited layer of minerals was produced which nearly filled the entire section of the 3-layer construction (Photos 12, 13, 14). The plastic spacers did not interfere with the accretion process. The structure was under power for 714 hours. Electrical power consumption is given in Figure 20. After 714 hours of electrodeposition, two material samples were taken (Table 7, Samples 35, 36). Mineral layers on the inner 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 1/2" mesh measured 8.5mm (Photo 14), 10.5mm on the 1"x2" mesh (Photo 15), and 6mm on the outside 1/2" mesh. Heavy marine growth was observed on the structure (Photos 16 and 17). After 714 hours of electrodeposition, Drum 1 was positioned in 37'-0" of water north of Buck Island (Figure 15, Position 4) in order to provide a substrate for marine growth and to begin phasing.

Table 7: X-ray Diffraction Analysis

Sample #	Description	Chemical Composition 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%

4.1.3. Analysing 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 7, Samples 35, 36), the outer mesh provided a material superior to that found on the inner mesh, but at a slower growth rate. Data on the effects of phasing now underway to change material properties will be reported in the forthcoming addendum to this report.

4.2.1. The circle segment, (UT M.S.I., Port Aransas). This structure consisted of a double-layered 1/2" galvanized wire mesh construction seperated by 3/4" plastic spacers (Photo 19). It was suspended from a floating rig (Photo 18), total mesh area measured 112 sq. ft. (Figure 21). The structure was submerged for 480 hours in the boat basin of the UT M.S.I. at Port Aransas; direct current electricity was supplied by an unregulated power supply. The inner layer of the



Photo

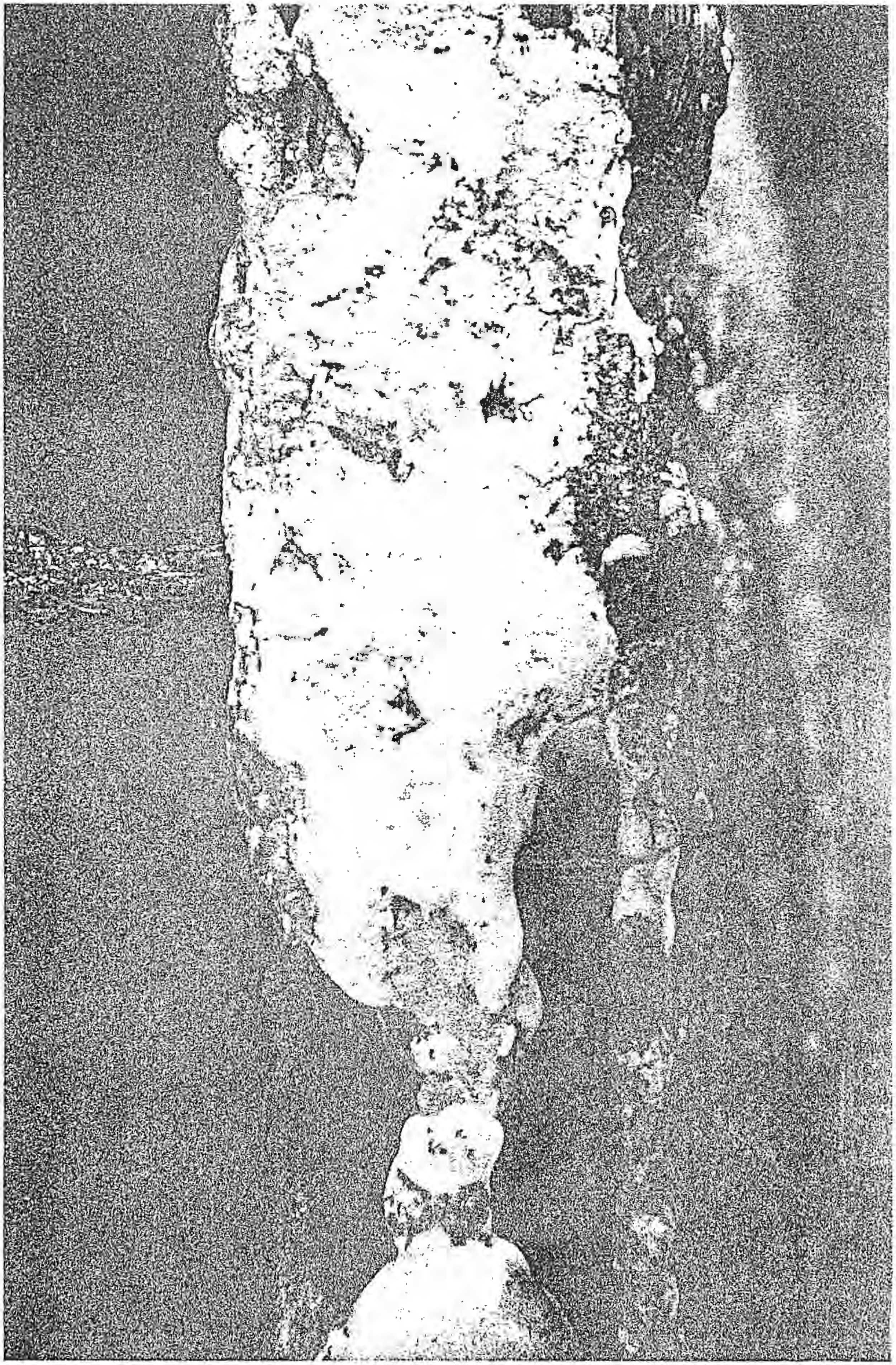


Photo 1

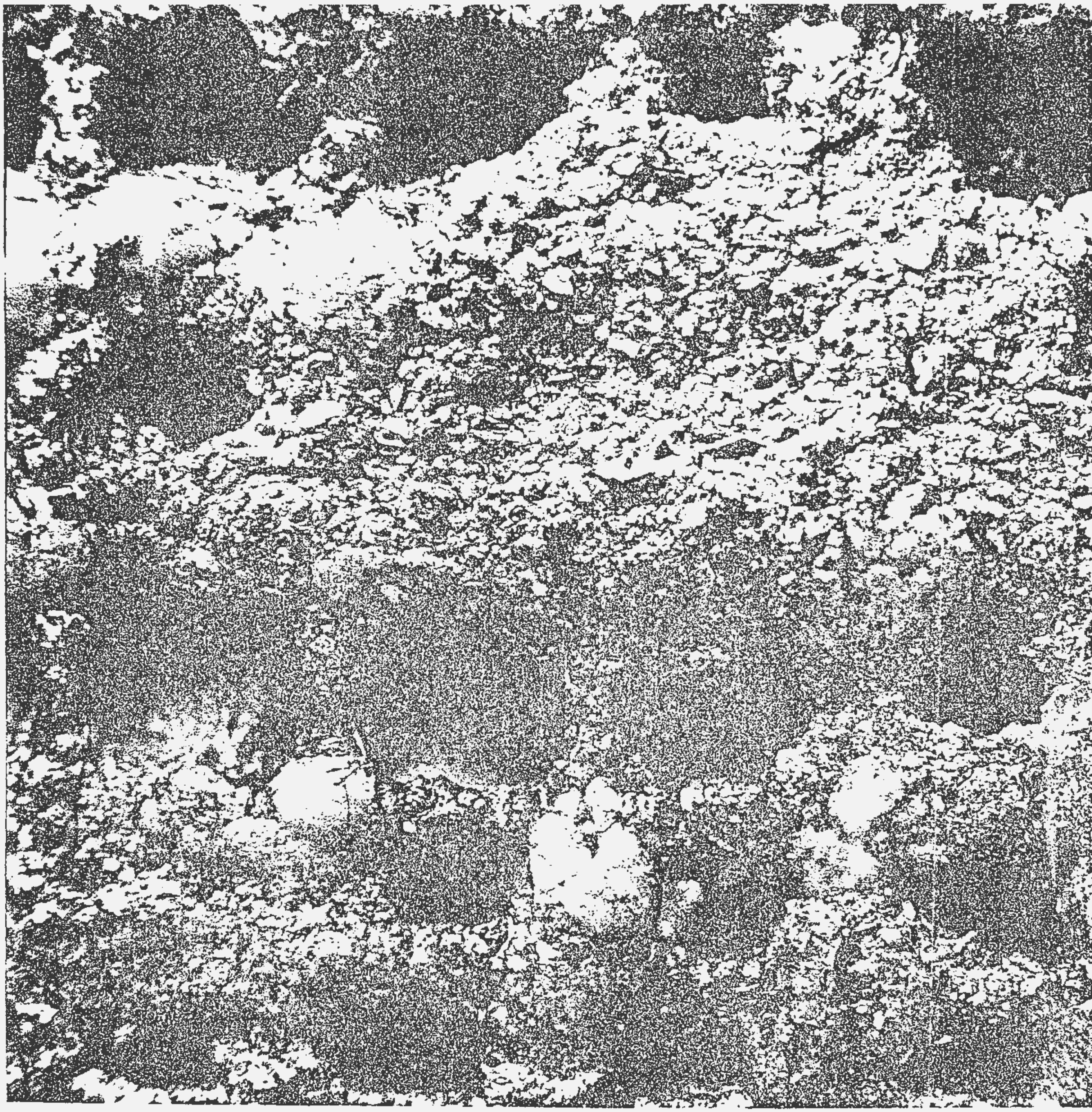


Photo 1

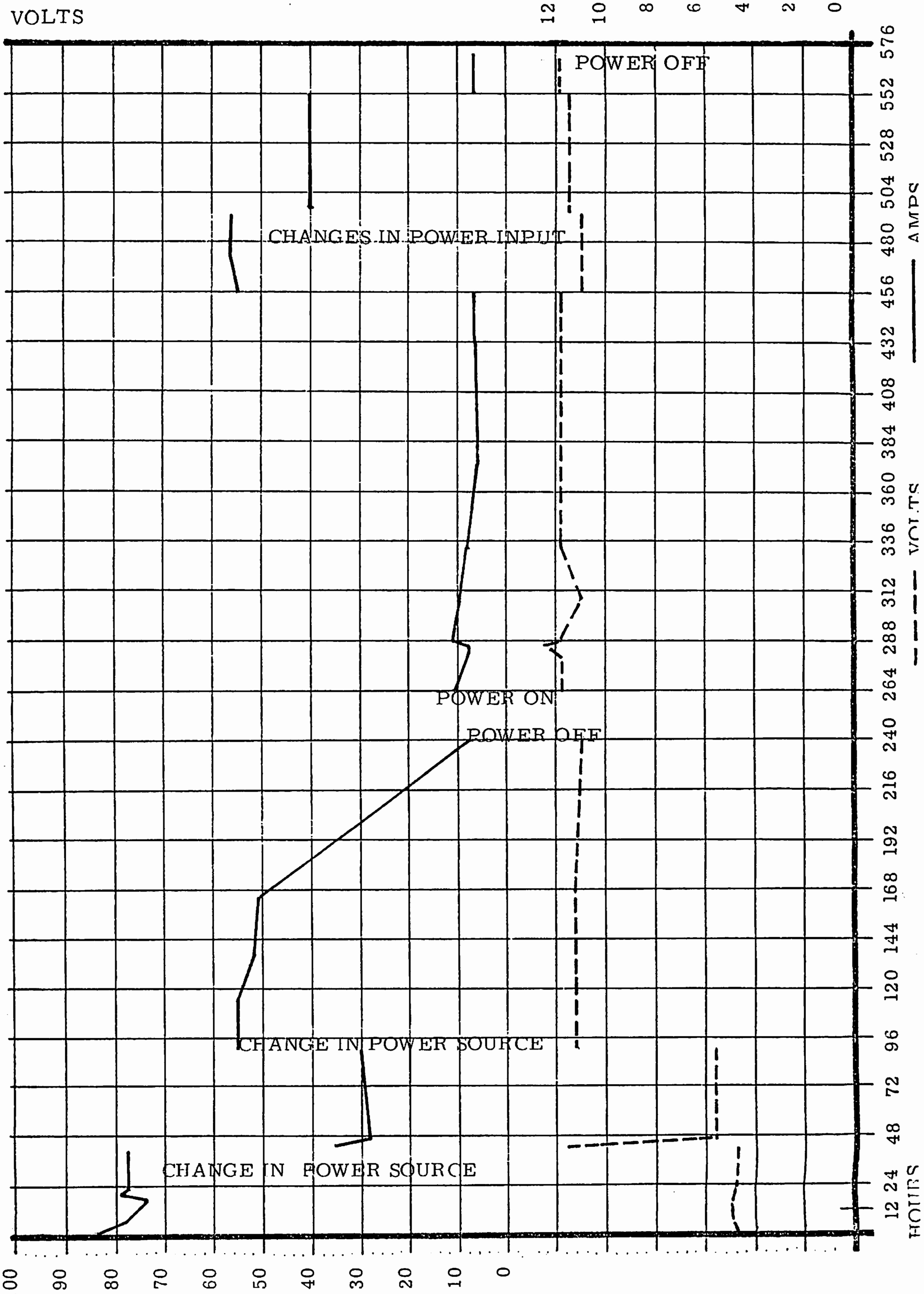


FIGURE 20 DRUM 1

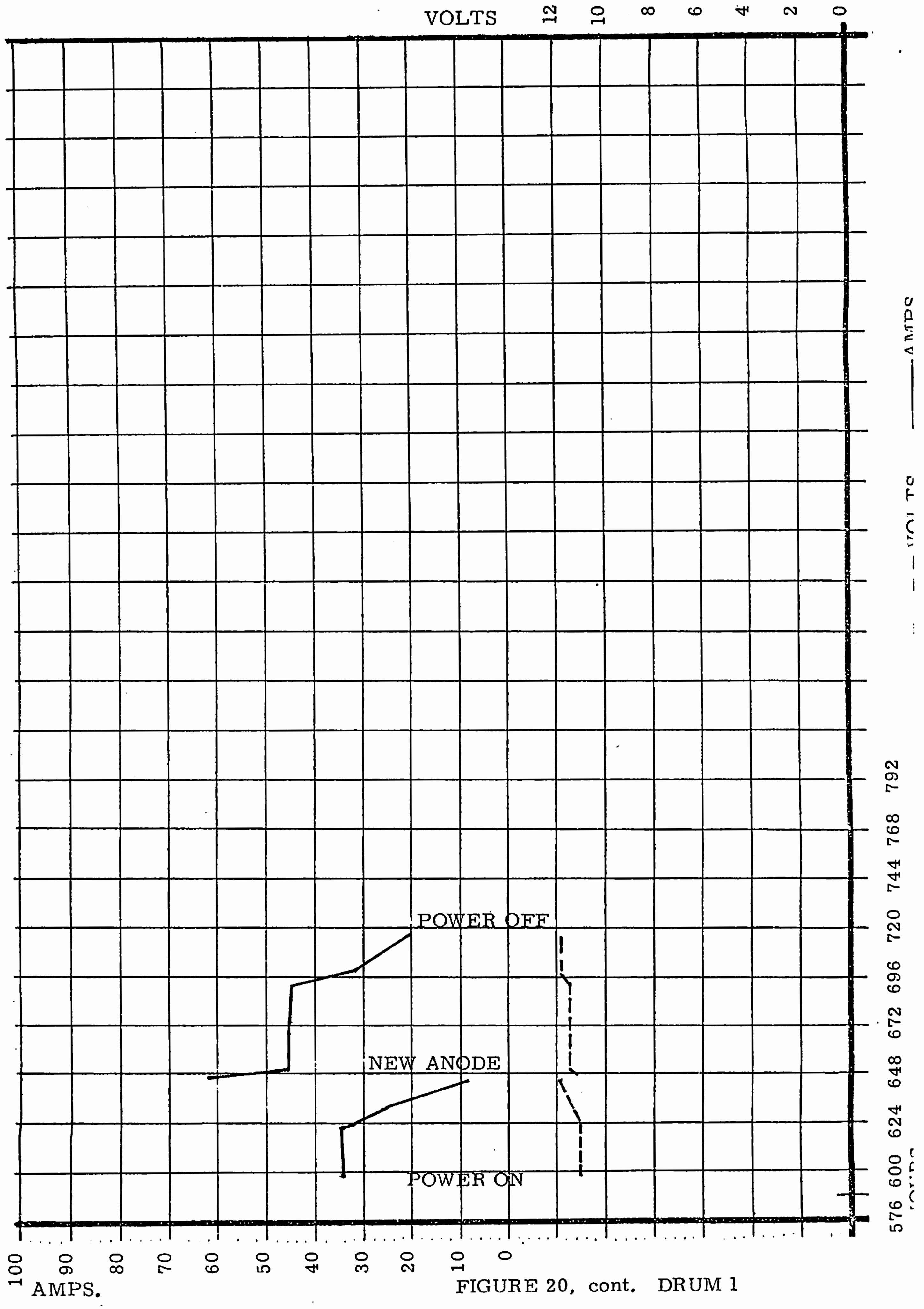
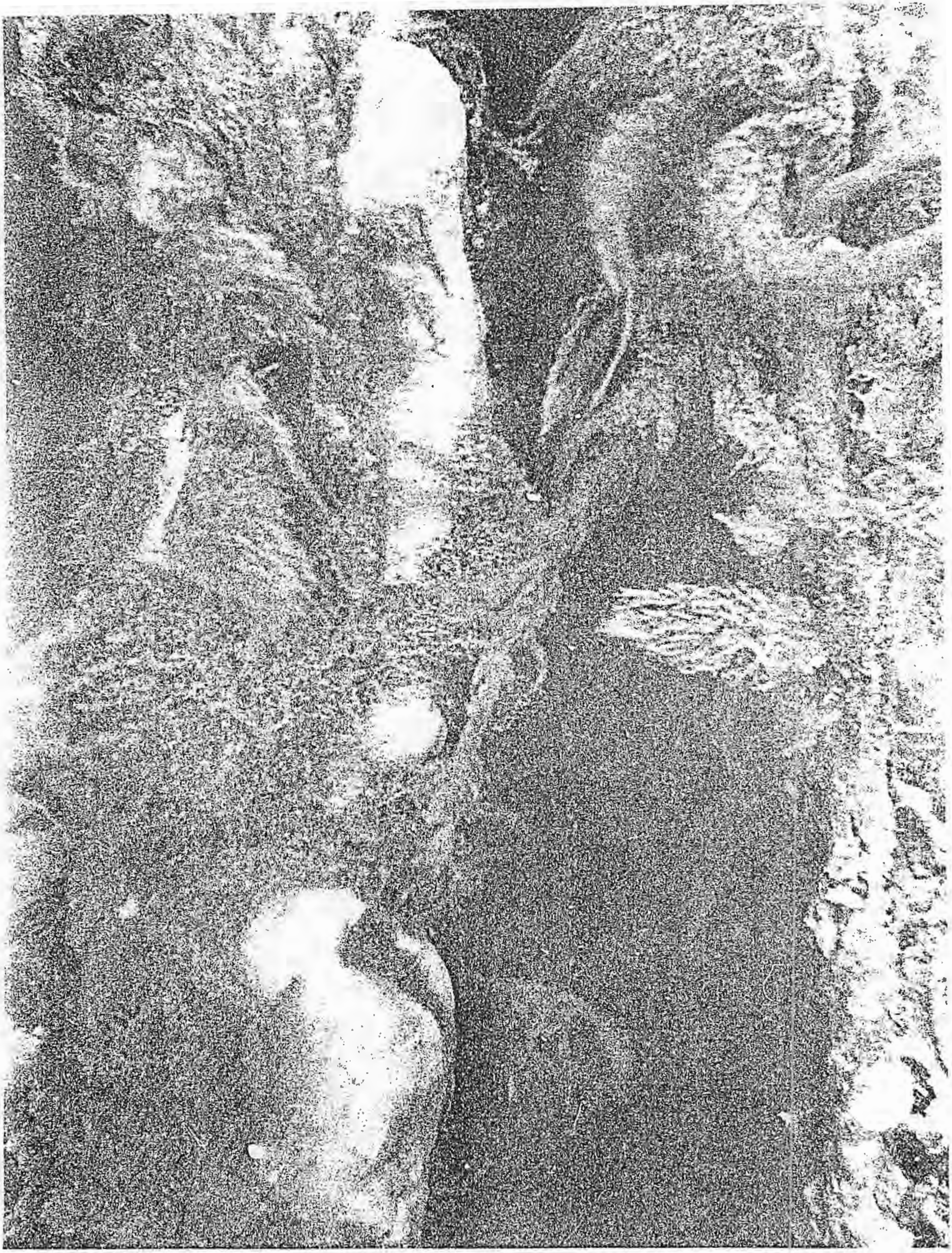


FIGURE 20, cont. DRUM 1

Photo 1



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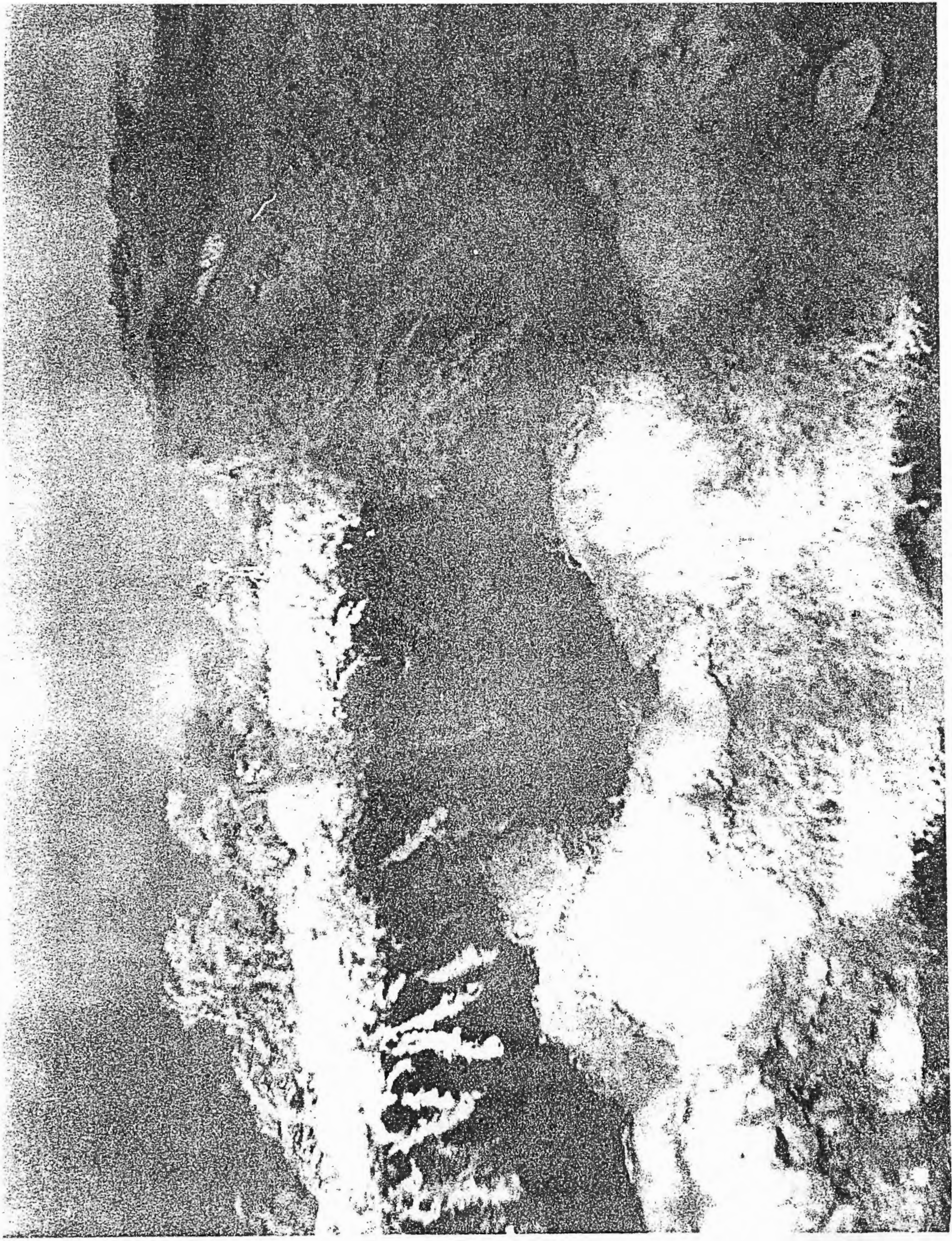


Photo 17

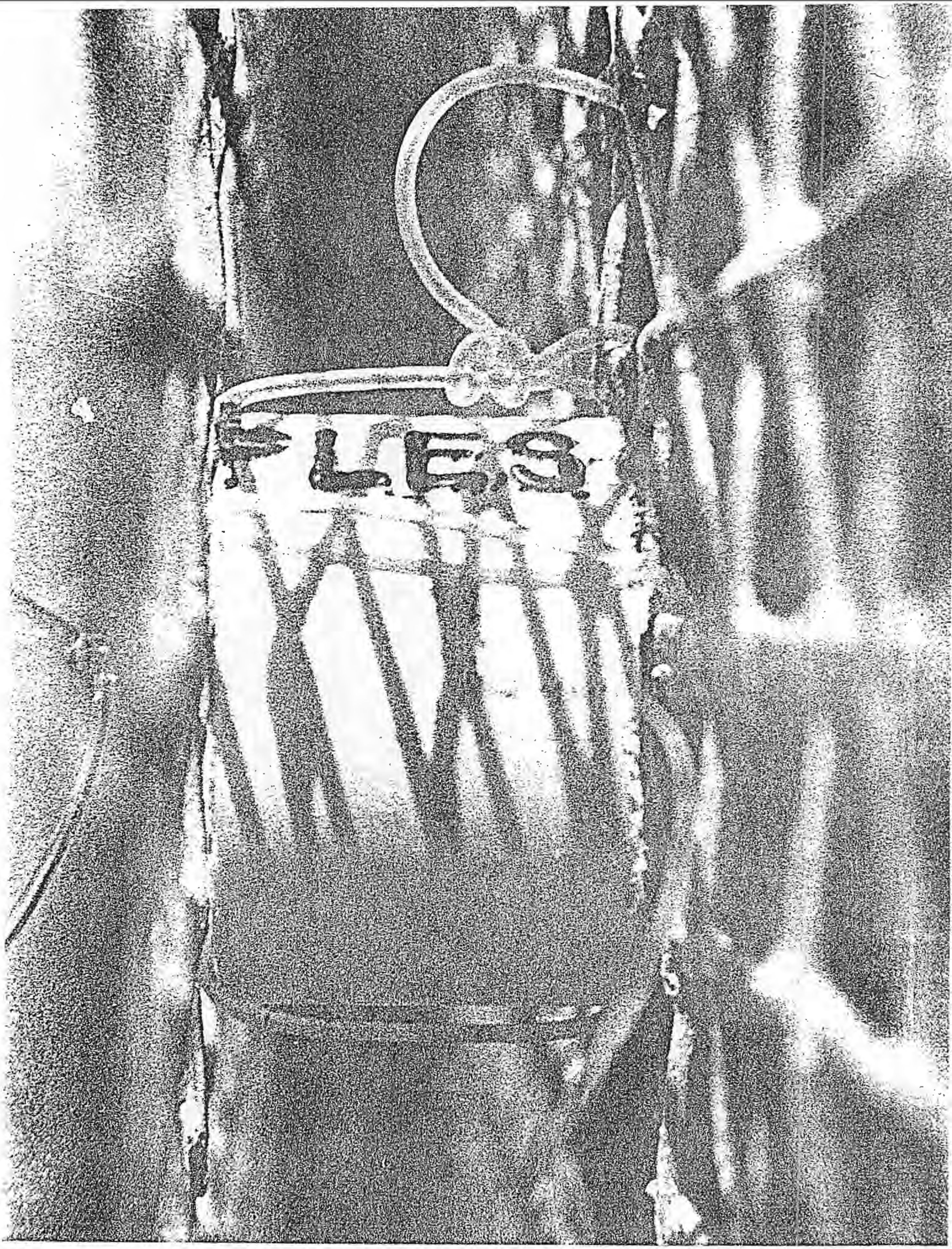
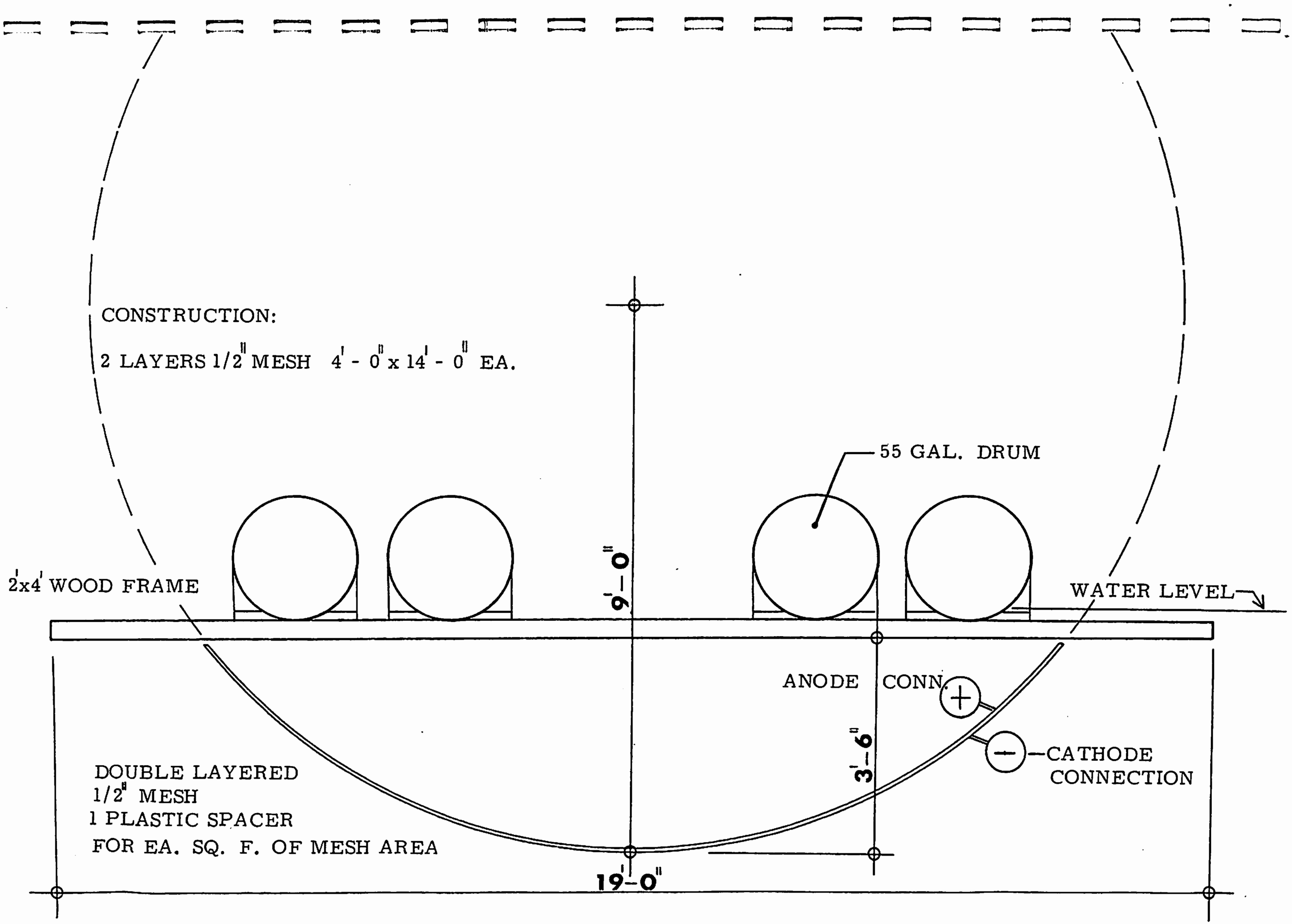


Photo 1


CONSTRUCTION:

2 LAYERS 1/2" MESH 4' - 0" x 14' - 0" EA.

DOUBLE LAYERED
1/2" MESH
1 PLASTIC SPACER
FOR EA. SQ. F. OF MESH AREA

CIRCLE SEGMENT

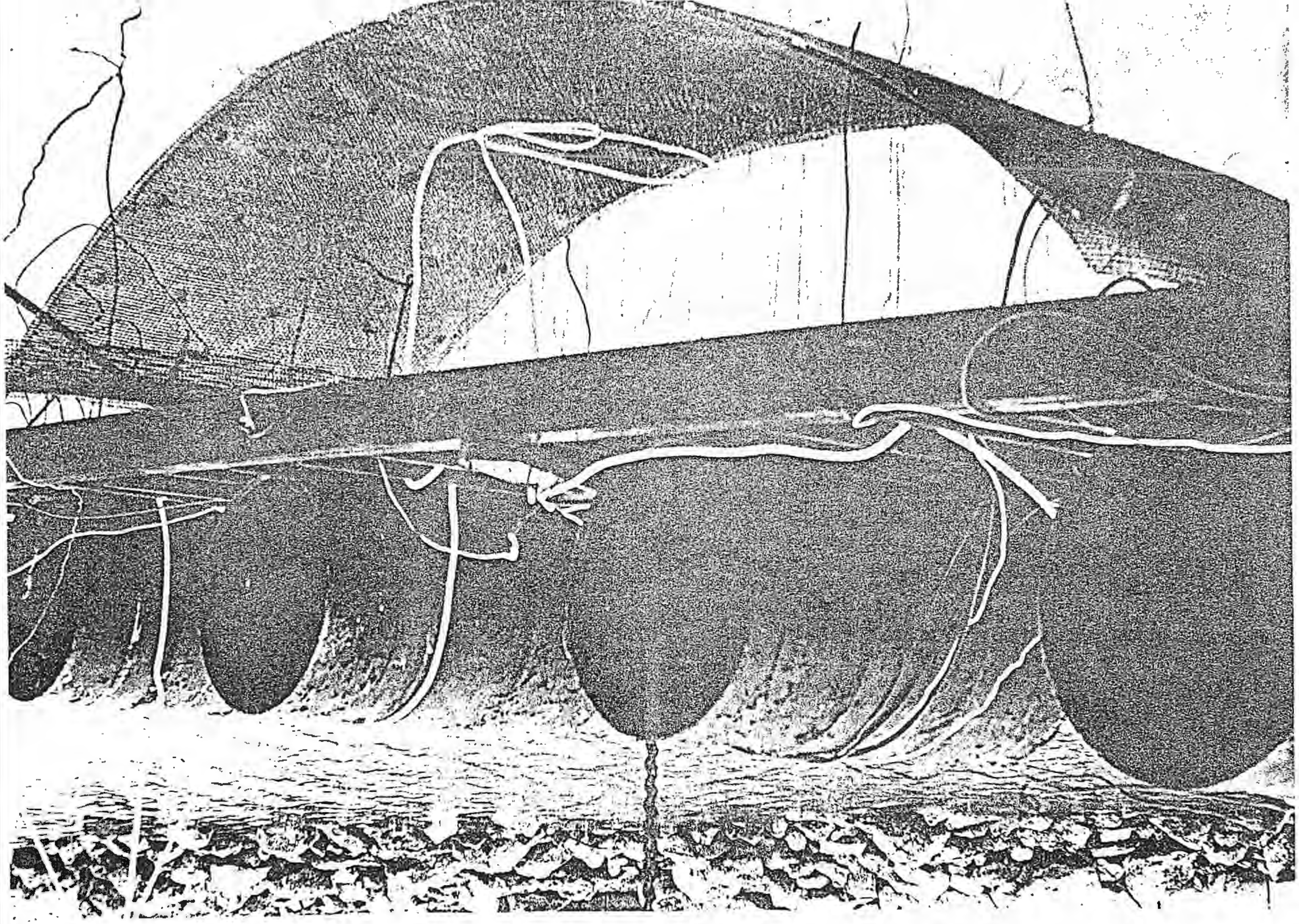


Photo 1

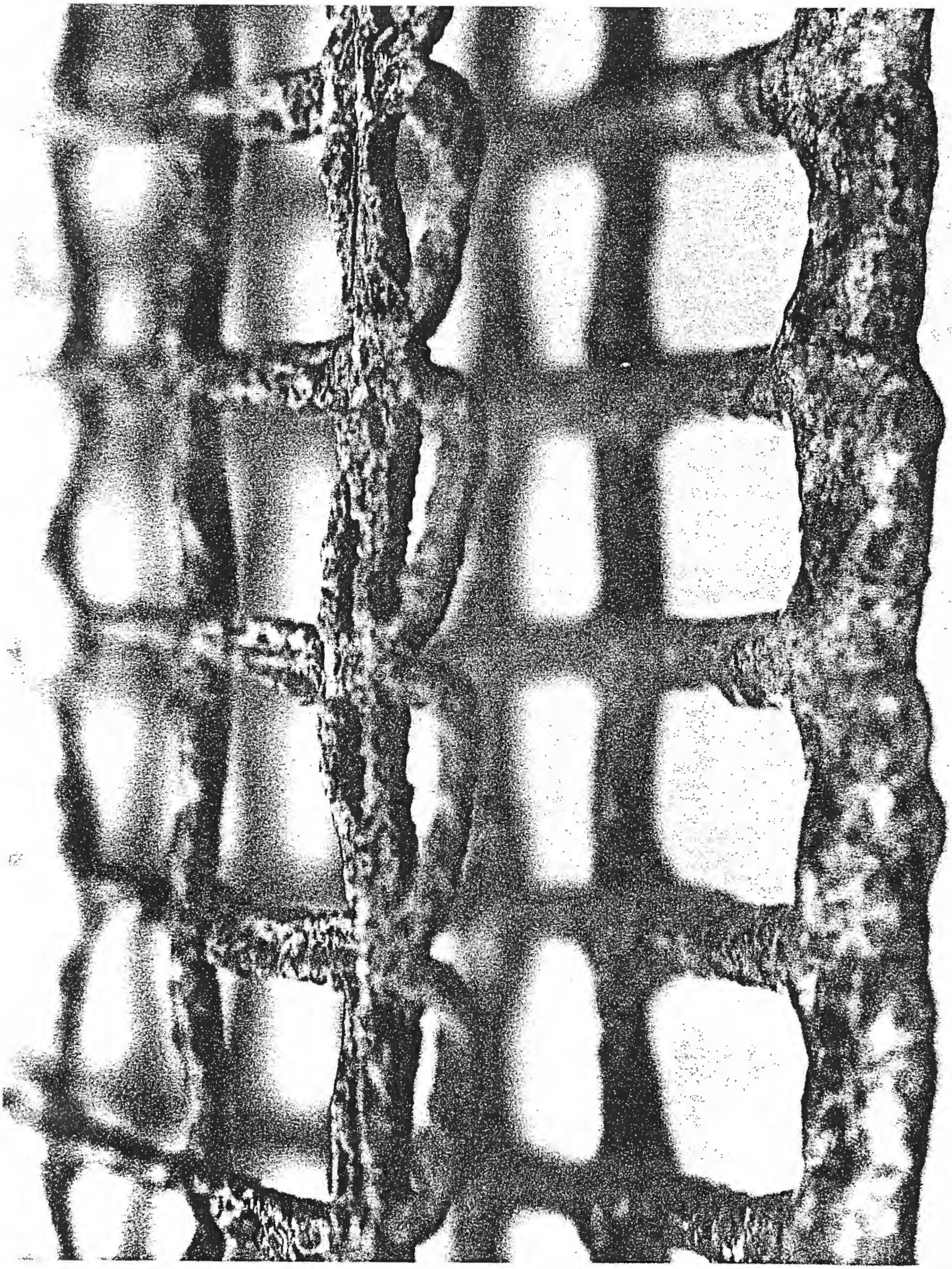


Photo 2

mesh construction performed as anode for 240 hours, while the inner layer performed as cathode. Both anode and cathode cables were 6 AWG multistrand insulated copper cable with a length of 30' - 0" each. All connections were insulated with clear silicon. Electrical measurements were taken with a Micronta double range 22-204A meter.

4.2.2. Electrical power consumption of the structure is shown in Figure 22. After 240 hours, 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 sq. ft. After polarity was switched for 240 hours, an electrodeposited layer of 3mm had formed on the cathode (inner mesh). 3.2 sq. ft. of the anode (outer mesh) had fallen off. Sporadic marine growth was observed on both layers (Photo 21.).

4.2.3. 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 mineral layer with the capability to keep the integrity of the structure has formed. Then, polarity switching of the solidly embedded electrodes can be undertaken. Iron or steel is a rapidly oxidizing anode material. Once embedded in a mineral the iron oxide will be integrated into the mineral and maintain its conductive property. 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 during the mineral electrodeposition process of larger components and the phased construction of walls or shells with very thick sections.

4.3.1. Catenary 1, 2 (University of Texas Marine Science Institute, Port Aransas). Both catenary structures are identical in materials and dimensions. They consist of 1/4" galvanized wire mesh suspended from a floating rig, each with a surface area of 32 aq. ft. (Figure 23).

Both catenaries have been submerged in the boat basin of the University of Texas Marine Science Institute, Port Aransas for 2664 hours, the first 1896 hours under direct current electrical power delivered by an unregulated power supply (Figure 24). 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 measurements were taken with a Micronta double range 22-204A meter.

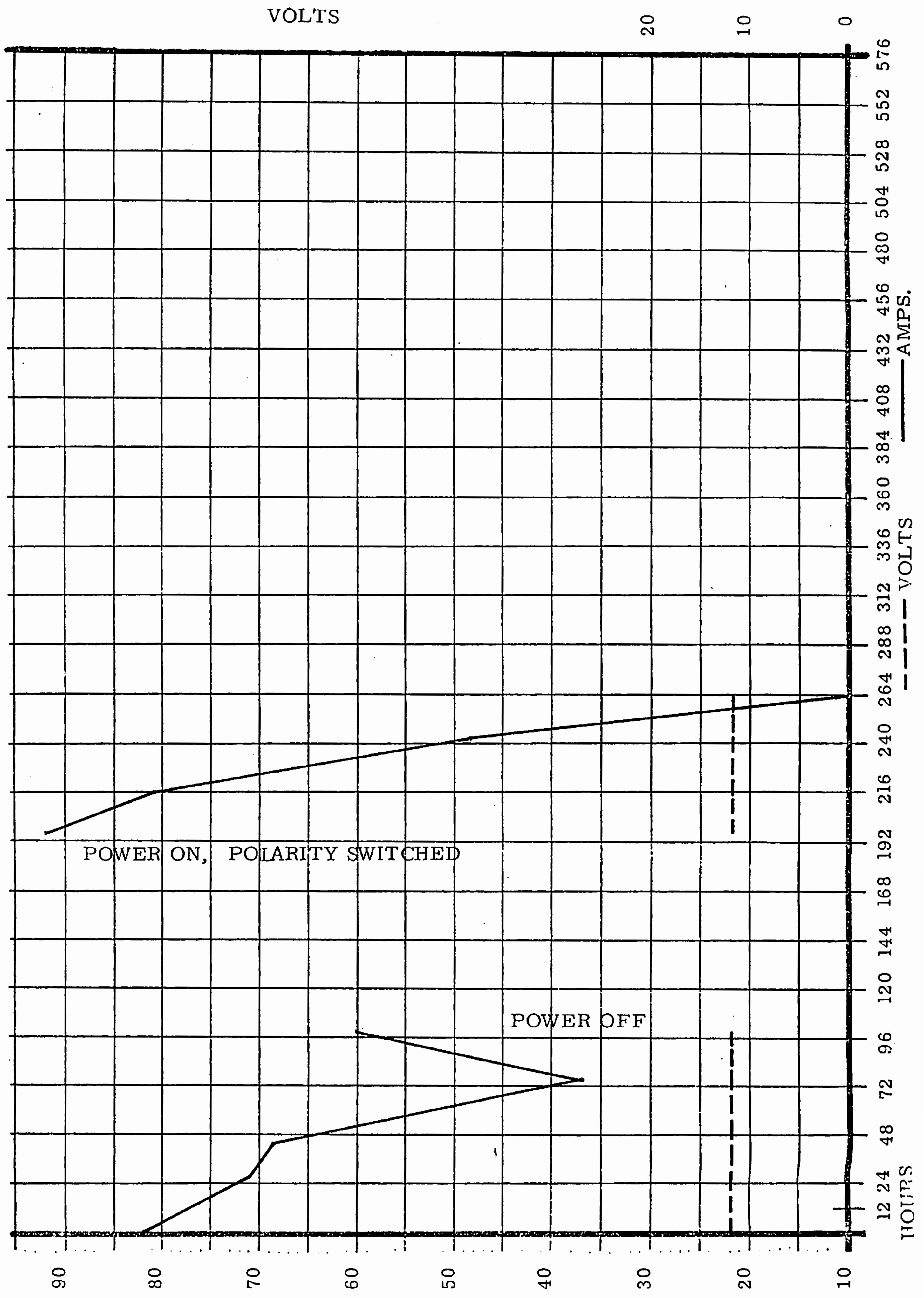
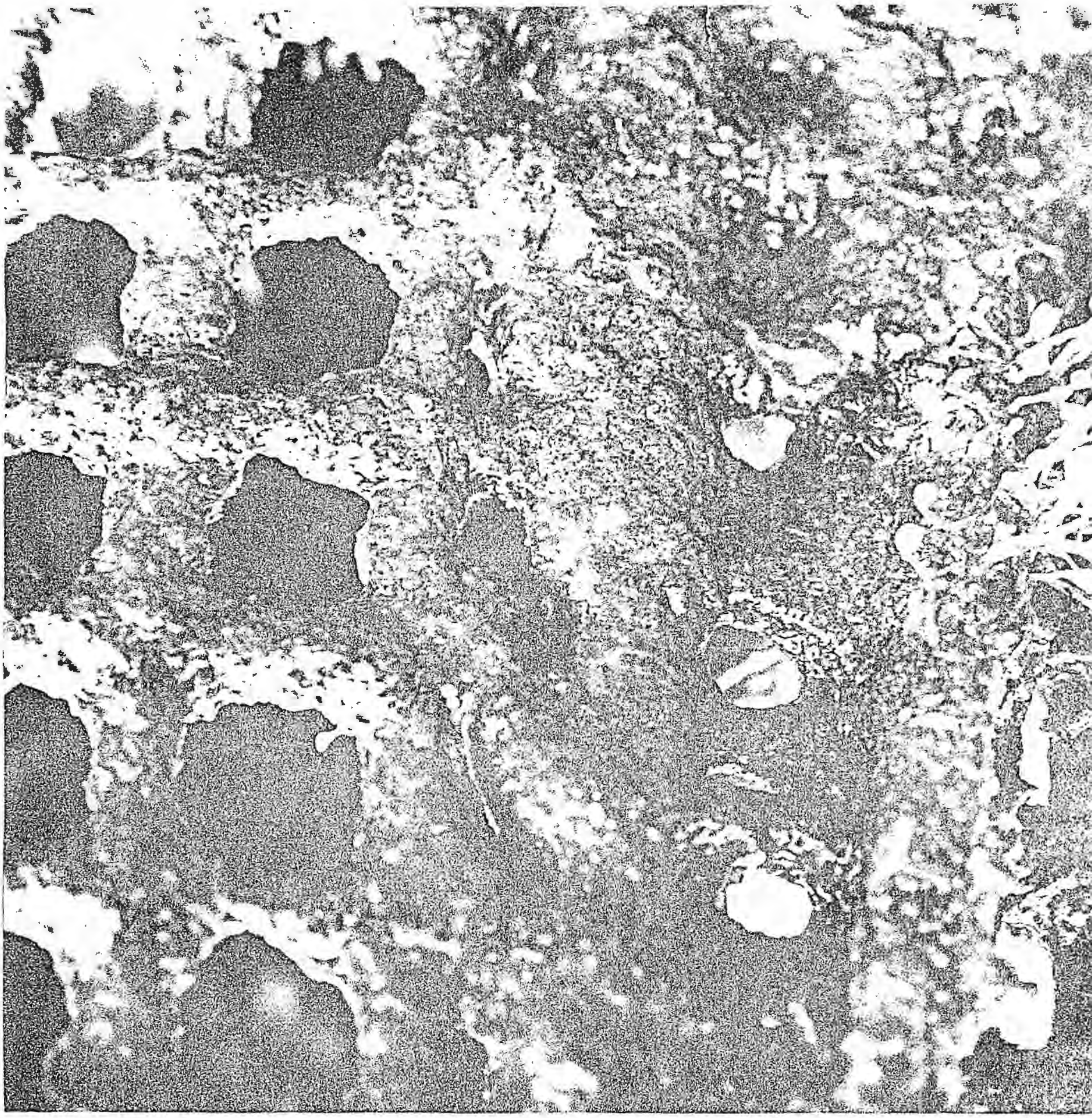


FIGURE 22 CIRCLE SEGMENT



Photo

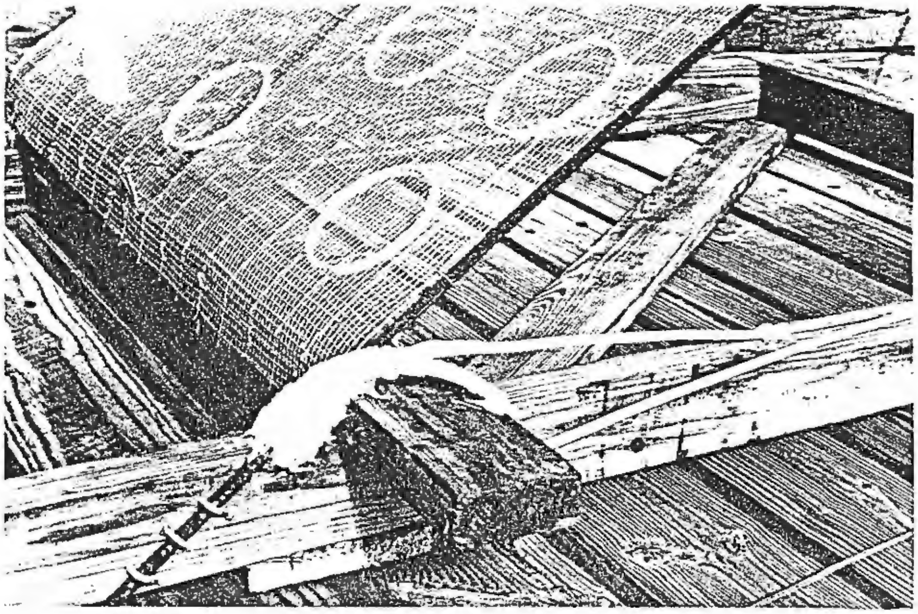


Photo 22

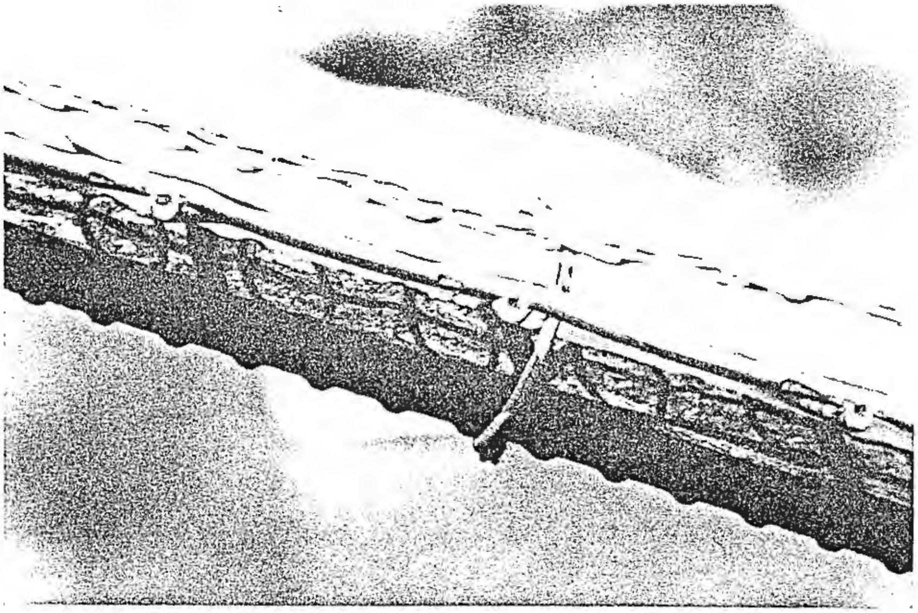


Photo 23

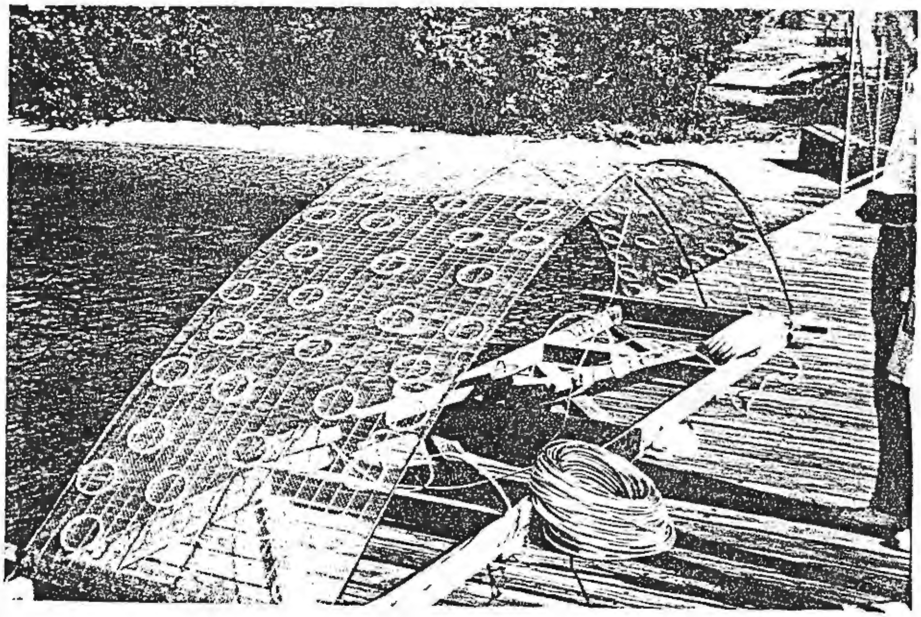
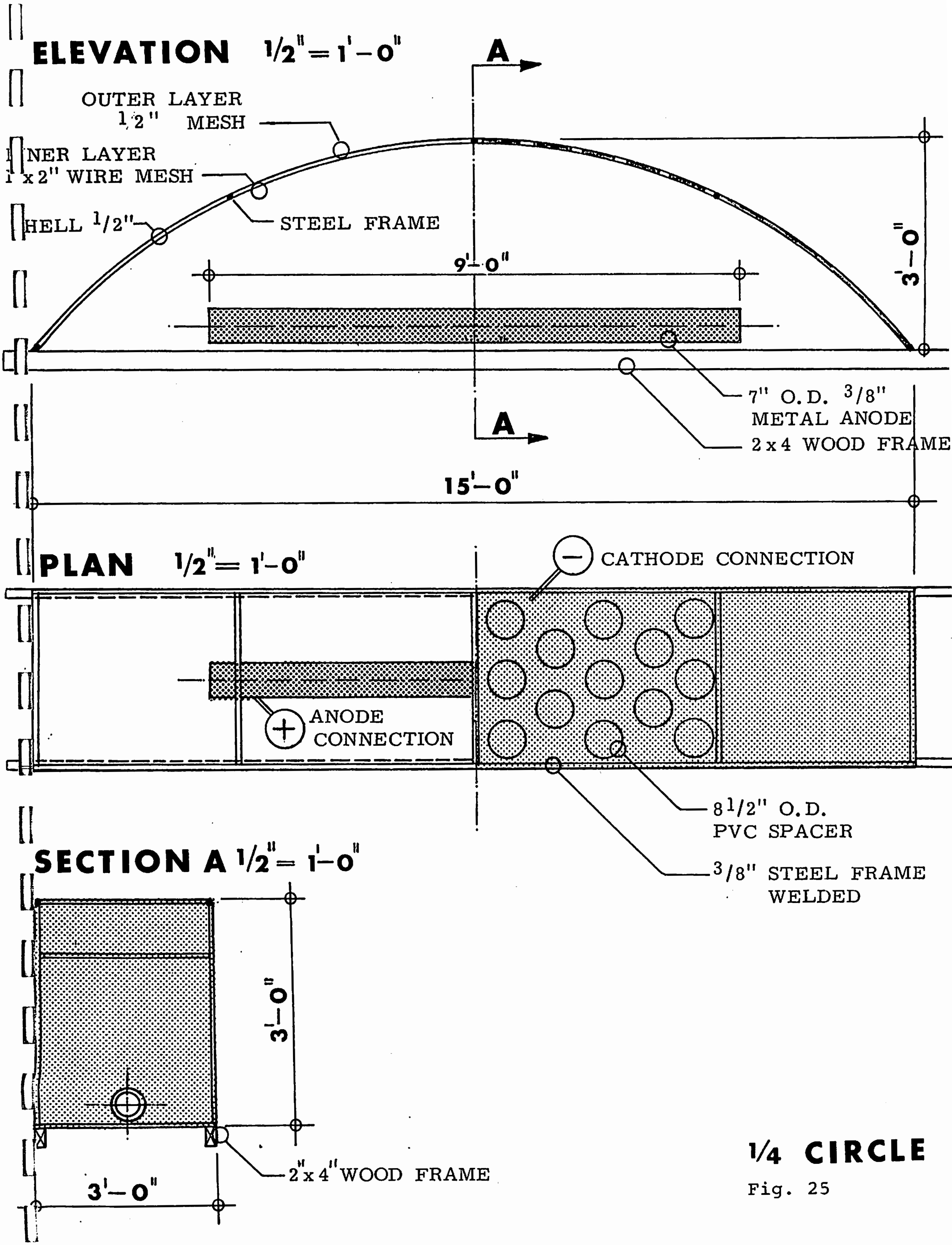


Photo 24



1/4 CIRCLE

Fig. 25

4.3.2. After 1896 hours an electrodeposited mineral layer of 7.5 mm had formed on both catenaries. The first material sample was taken after 1896 hours of operation Table 8, Sample 88. The second sample was taken 768 hours after phasing Table 8, Sample 92. The electrodeposited material then was densely populated by various algae and acorn barnacles. A comparative analysis of results of Sample 89 and Sample 92 shows the following percentages:

Table 8: X-ray Diffraction Analysis

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

4.3.3. This experiment was devised to secure data from low electric field conditions between electrodes on large architectural components to provide a more economical and simpler system for building the architectural component with a more uniform composition of deposited material.

It was found that accreted material on the catenary cathode 'hardened' during the no-power phase, and quantitative analysis reveals little change comparatively between samples, therefore a change must have occured physically between crystals. There is 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 contains 10,770 ppm where as Texas coastal water contains only 2,130. Sodium and Chloride ion concentration (ppm) in Texas coastal water is one-sixth of that found in natural sea water.[6] It seems that from these figures, and the comparative X-ray diffraction data, reactions that take place in sea water from Port Aransas will occur at a much slower rate than in waters in which there are greater concentrations of the various ions.

4.4.1. The 1/4 Circle (West Indies Laboratory, St. Croix). This construction consists of double-layered galvanized wire mesh with plastic ring spacers standing on a 2" x 4" wood frame (Figure 25, Photos 22, 23, and 24). The total surface area measures 133 1/4 sq. ft. A 3/8" welded steel frame was integrated into the structure to provide support. The 1/4 circle was submerged 215' - 0' north of the West Indies Laboratory pier laboratory in 5' - 6" of water on sandy ground (Figure 15, Position 1).

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 silicon. Electrical measurements were taken with a Micronta double range 22-204A meter. The ambient

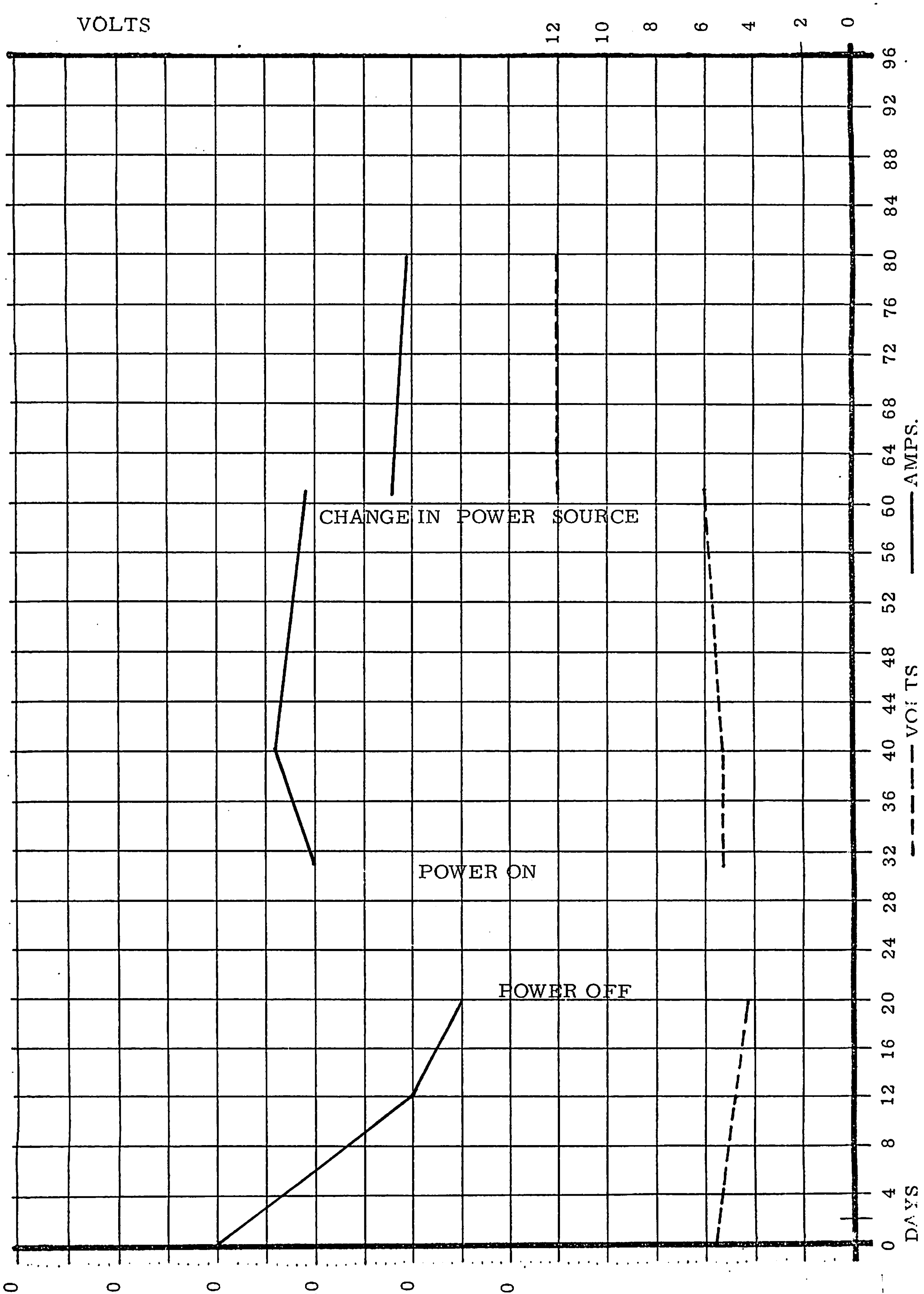
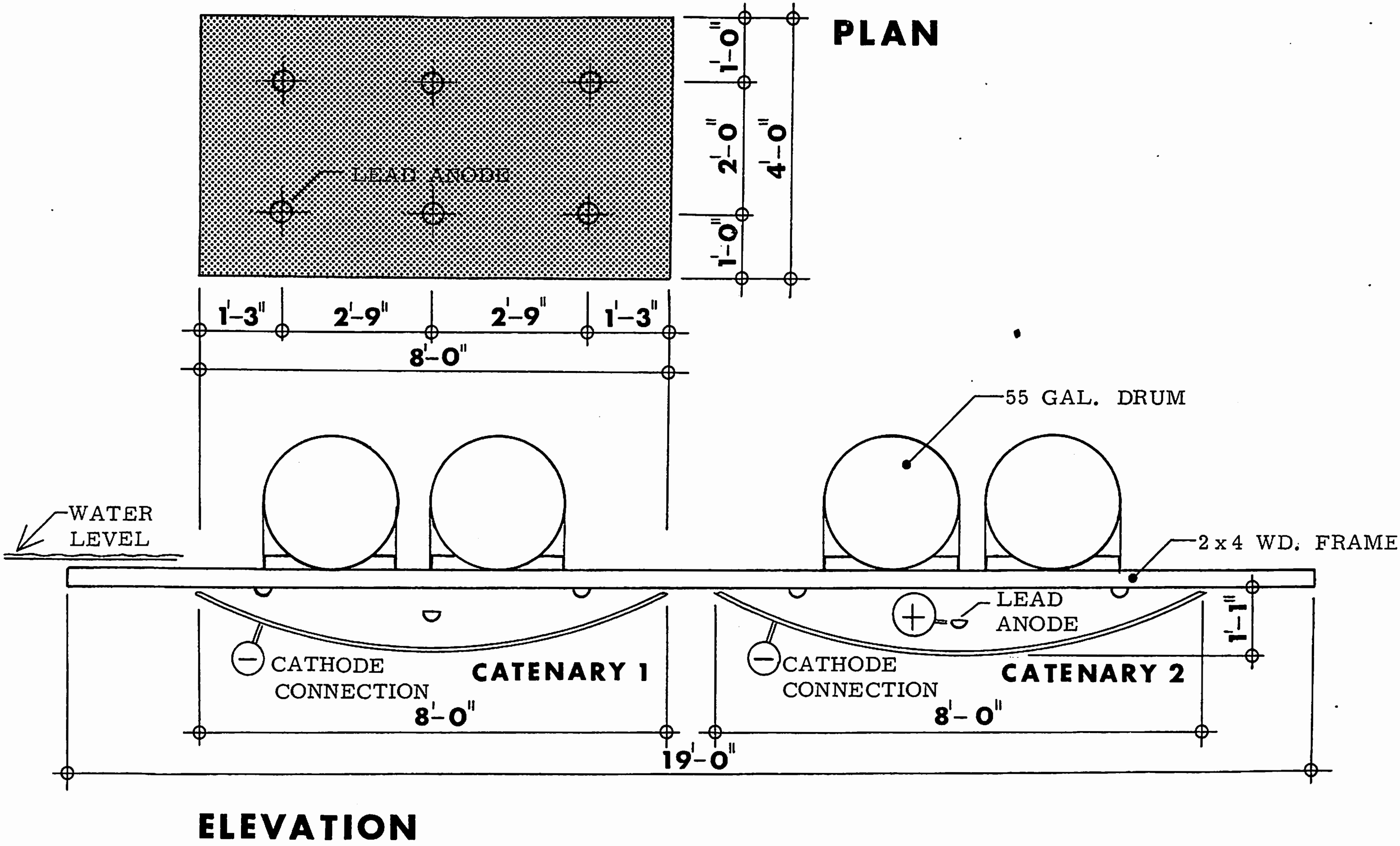


FIGURE 24 CATENARY 1, 2


PLAN
1'-0"
2'-0"
4'-0"
1'-0"
LEAD ANODE
1'-3"
2'-9"
2'-9"
1'-3"
8'-0"
55 GAL. DRUM
WATER
LEVEL
2 x 4 WD. FRAME
LEAD
ANODE
1'-1"
CATHODE
CONNECTION
CATENARY 1
CATHODE
CONNECTION
CATENARY 2
8'-0"
8'-0"
19'-0"
ELEVATION

CATENARY 1,2

water temperature ranged between 82^{o}F and 88^{o}F.

4.4.2 The structure was supplied with electricity for 576 hours after submersion (Figure 26). A material sample was taken 546 hours after the start of electrodeposition (Table 9, Sample 34).

Table 9: X-Ray Diffraction Analysis

		Chemical Composition					
Sample	Description	Brucite	Acagonite	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%

4.4.3. When conductive materials with different sections are used as cathode materials, the electric field between the electrodes concentrated on the material with the larger section. Therefore, a mineral layer with a thickness directly proportional to the resistance between the cathode meterial with the smallest section and the anode has to be formed before electrodeposition on the material with the smallest section can begin. This observation bears directly on the future design of architectural 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 but did not interfere with the electrodeposition process. After 576 hours of continuous operation, mineral accretion thickness on the 1" x 2" wire mesh measured 5.5 mm. Mineral layers on the 3/8" steel frame measured up to 3.8 cm after 576 hours (Photo 25). Marine growth was observed on all wire mesh portions (Photo 25).

4.5.1. The 1/2 Circle (West Indies Laboratory, St. Croix). This architectural component was a double-layered construction of 1/2" galvanized wire mesh supported by a welded frame of 3/8" steel profiles (Figure 27, Photos 26, 27, and 28). Spacing was provided by 1/2" x 8" O.D. plastic sections. The double shell was being held in tension by two marine ropes. The total surface area measured 158 1/3 sq. ft. The component was submerged under the West Indies Laboratory pier laboratory in 4' - 0" of water on sandy ground. (Figure 15, Position 1). Both anode and cathode wires consist of 6 AWG insulated multistranded copper wire. Direct electrical current was supplied by an unregulated power supply. All electrical connections were insulated with clear silicon. Electrical readings were taken with a Micronta double range 22 - 204A meter.

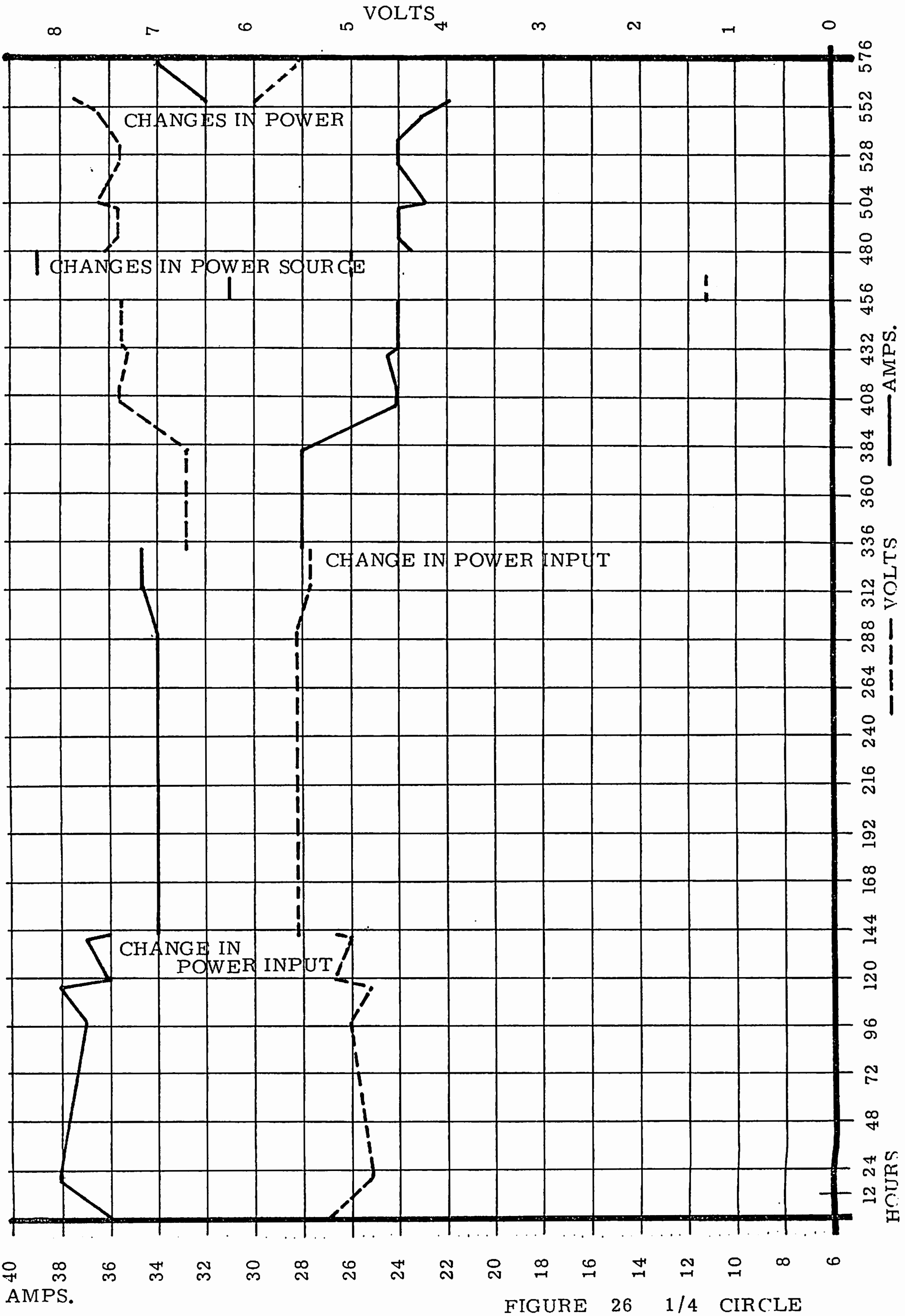


FIGURE 26 1/4 CIRCLE

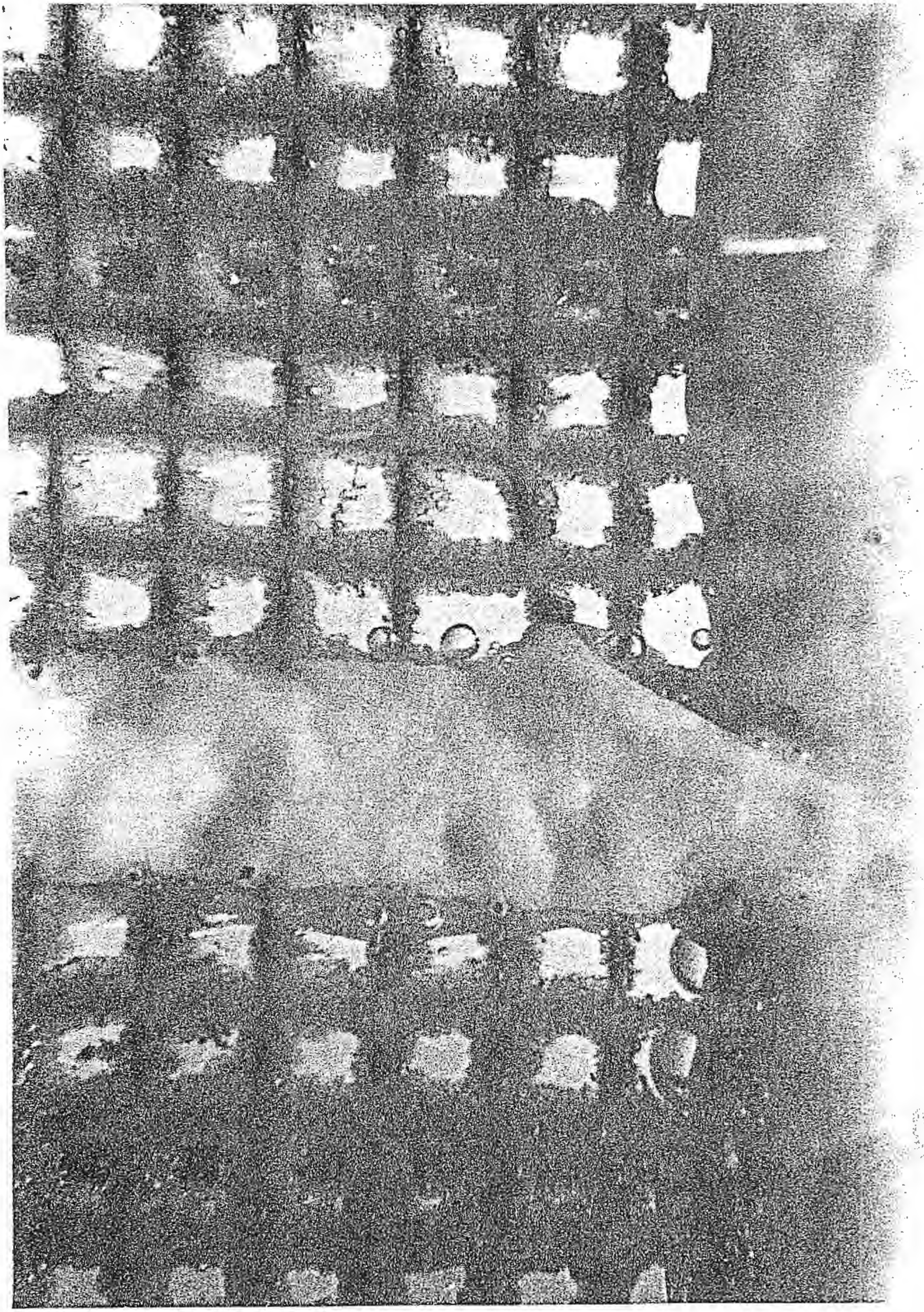
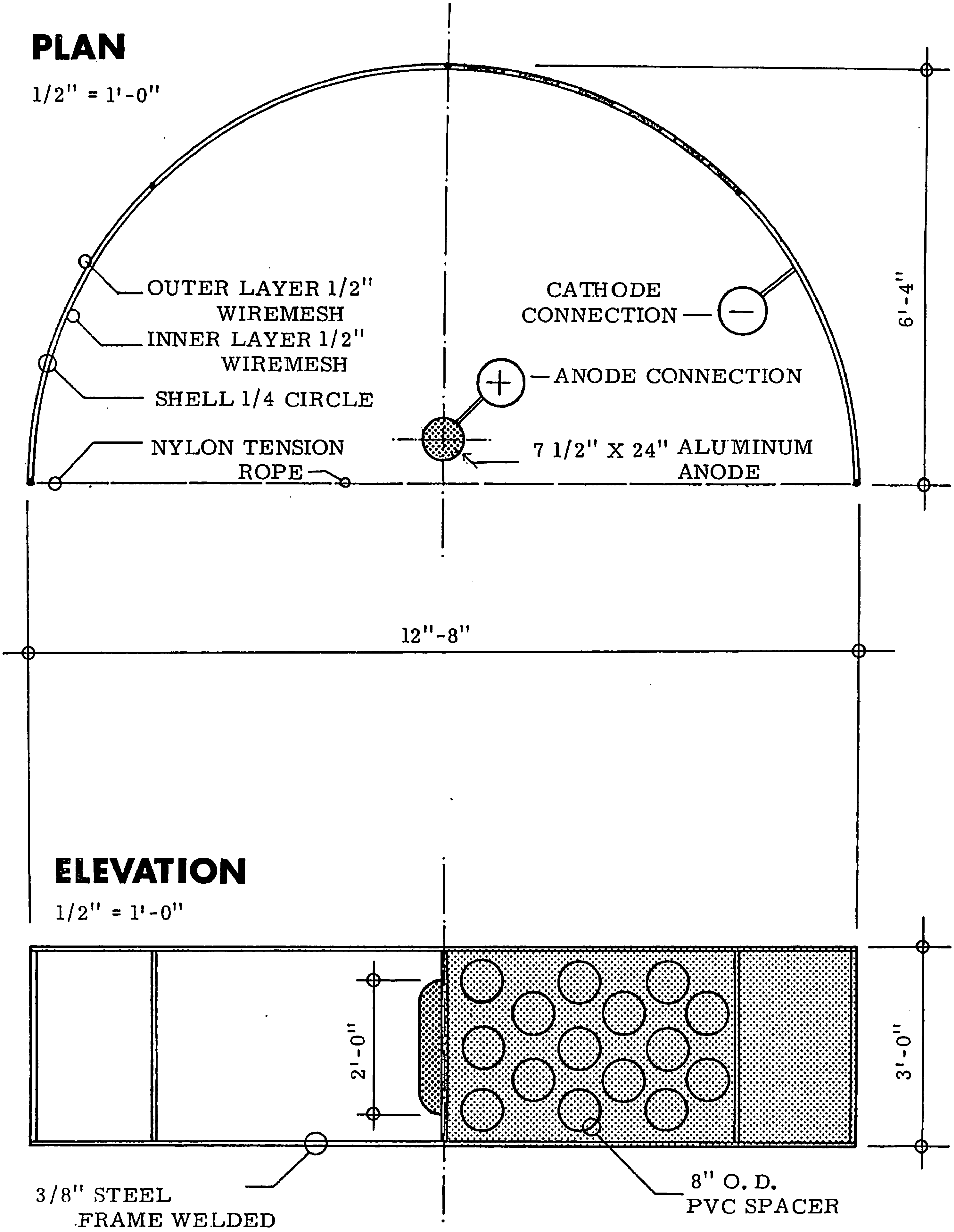


Photo 2



1/2 CIRCLE

Fig. 27

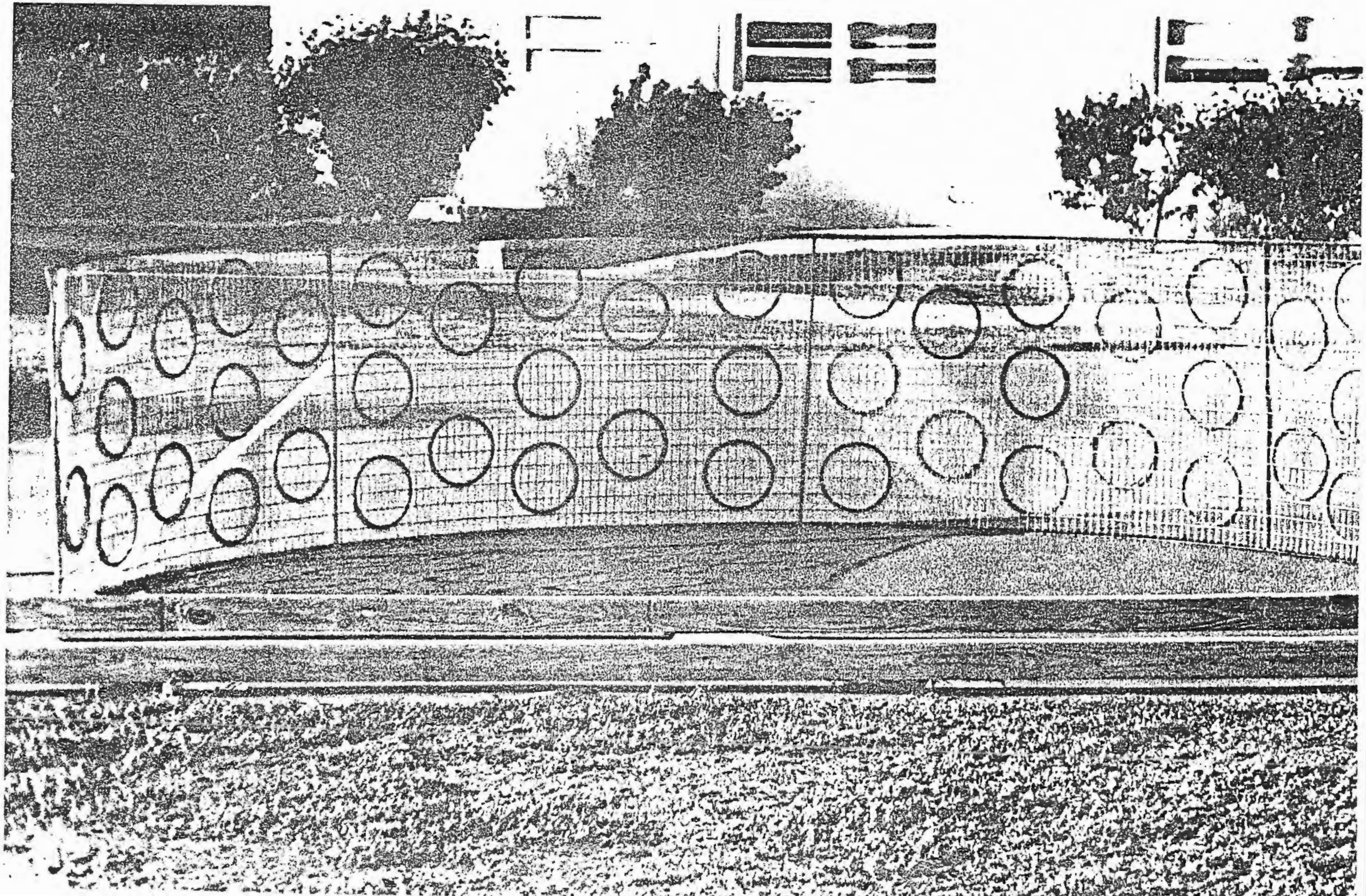
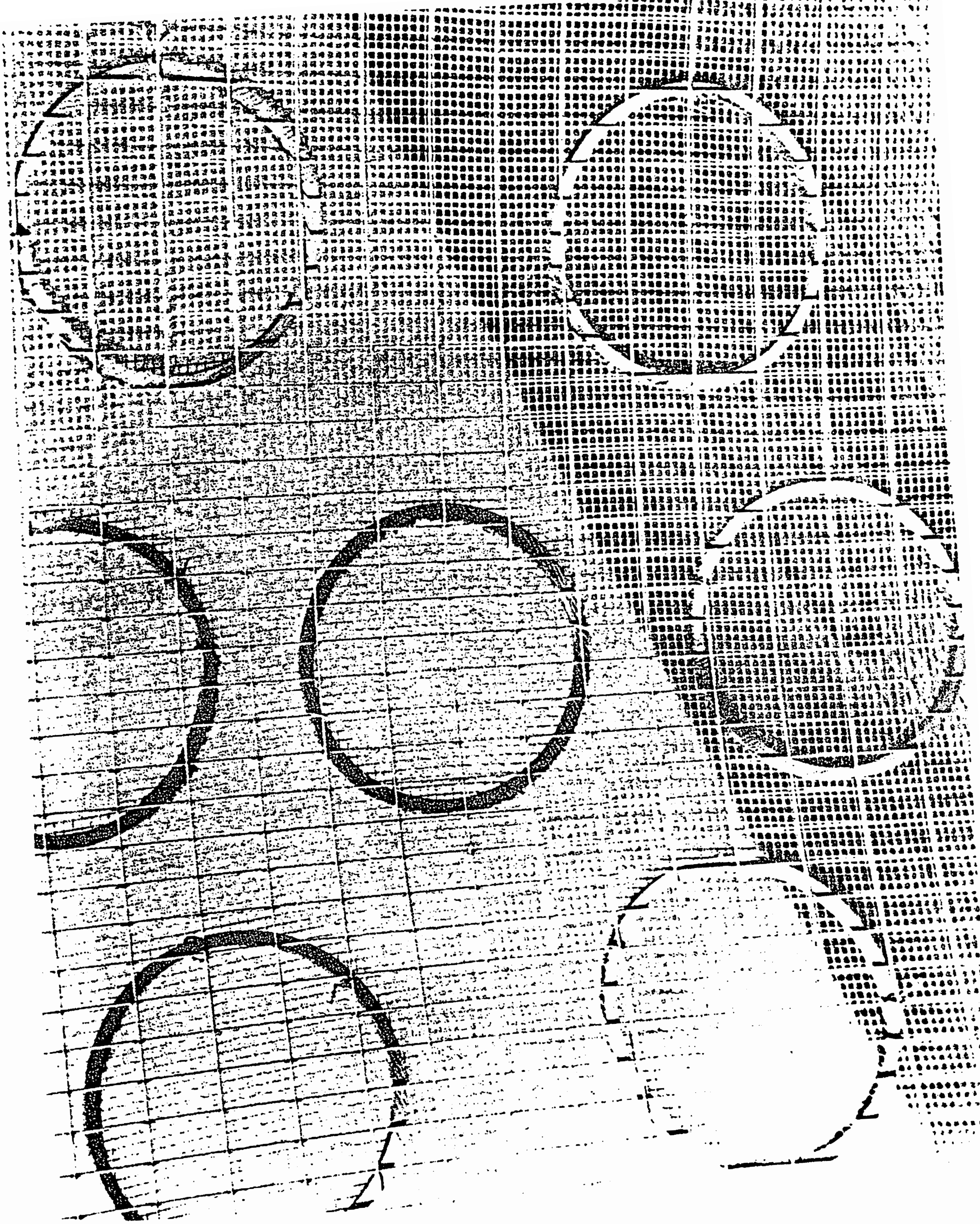


Photo 2



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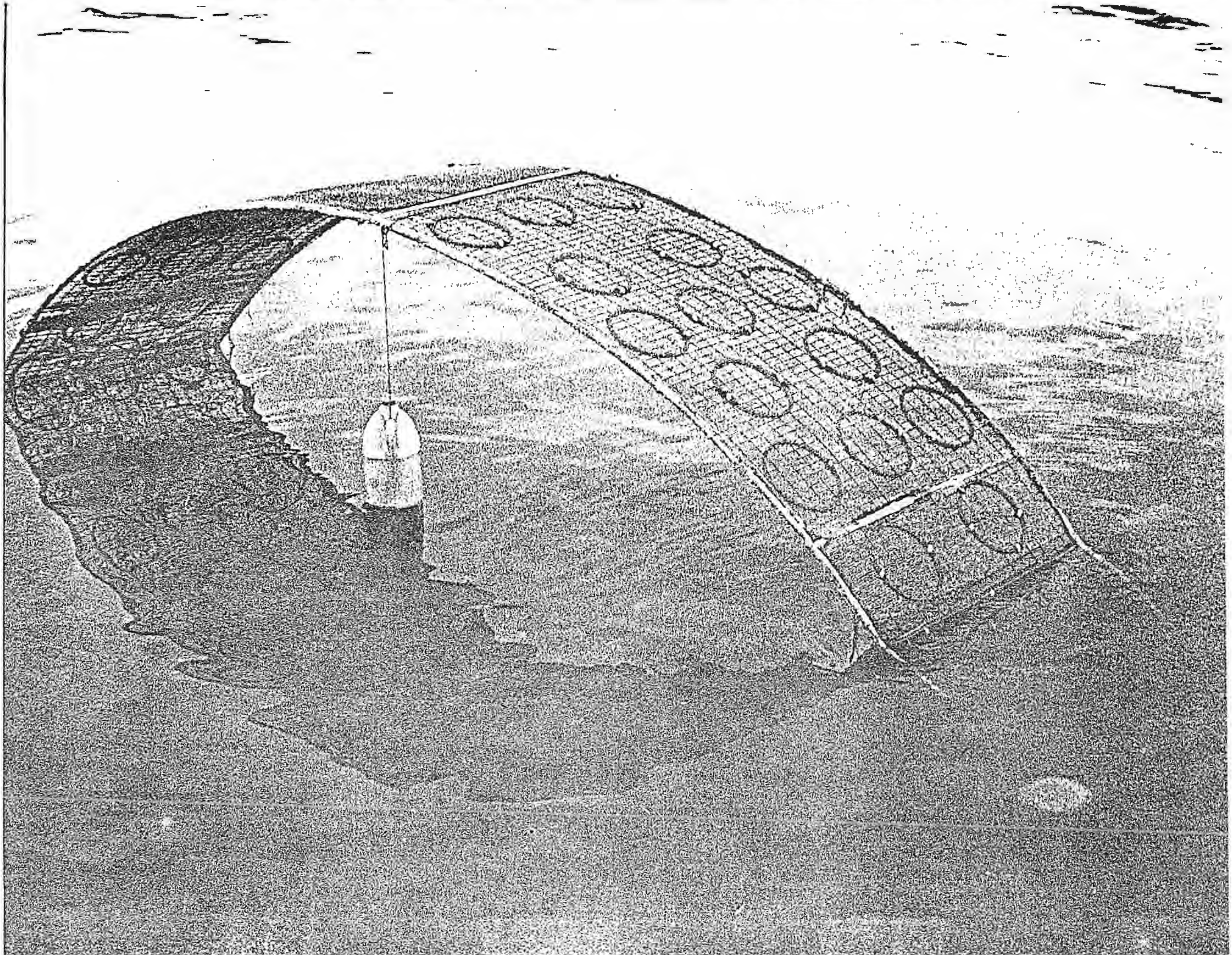


Photo

4.5.2. The structure was supplied with electricity for 170 hours (Figure 28). At the end of this period, a sample was taken (Table 10, Sample 31). After 170 hours, accretion thickness measured 2.7 cm on the 3/8" steel frame, and 2.3 mm on the 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 parts of the structure (Photo 30).

4.5.3. An explanation concerning electrodeposition of minerals on metal cathodes composed of different sections can be found in section 4.4.3. A comparative analysis of material sample 31 (Table 10), and a sample to be taken in January 1977 will be given in the forthcoming addendum to this report to further investigate possible effects of phasing.

Table 10: X-Ray Diffraction Analysis

		Chemical Composition					
Sample	Description	Brucite	Aragonite	Calcite	Halite	Quartz	Other
31	taken at disconnect	61%	5%	1%	20%	trace	13%
94	taken 96 days after	58%	9%	2%	8%	1%	22%

4.5.3. Very slight changes occurred in the accretion matrix of samples taken from the 1/2 circle. 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 non-crystalline matter and/or less well-ordered crystals during the non-powered phase.

4.6.1. The Truss Circle (University of Texas Marine Science Institute, Port Aransas). This structure is a multi-layered construction consisting of 1/2" galvanized wire mesh (Figure 29, Photo 31). The total surface area measures 791 1/3 sq. ft. Flexible vinyl plastic hose with a diameter of 3/4" formed the spacer for the outer double shell construction. The truss circle was sunk in 6' - 0" of water in the boat basin of the University of Texas Marine Science Institute at Port Aransas, (Photo 32). Both cathode and anode wires were 8 AWG single strand insulated copper wire with a length of 20' - 0" each. Direct electrical current was provided by an unregulated power supply. Electrical readings were taken with a Micronta double range 22 - 204A meter.

4.6.2. Electricity consumption of the structure is shown in Figure 30. Material samples have not yet been taken. No other data are available at this time.

4.6.3. No discussion is possible at this time.

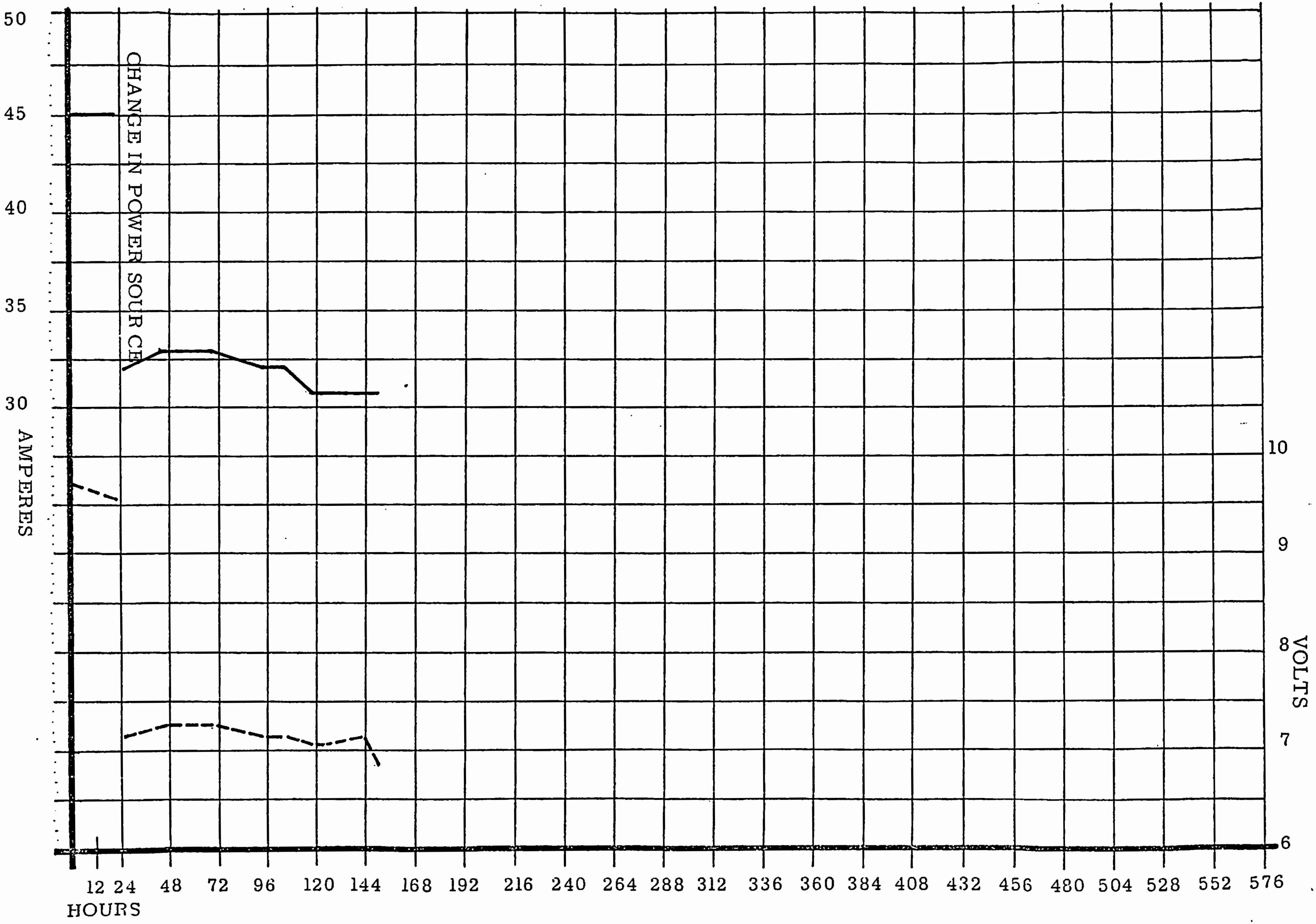
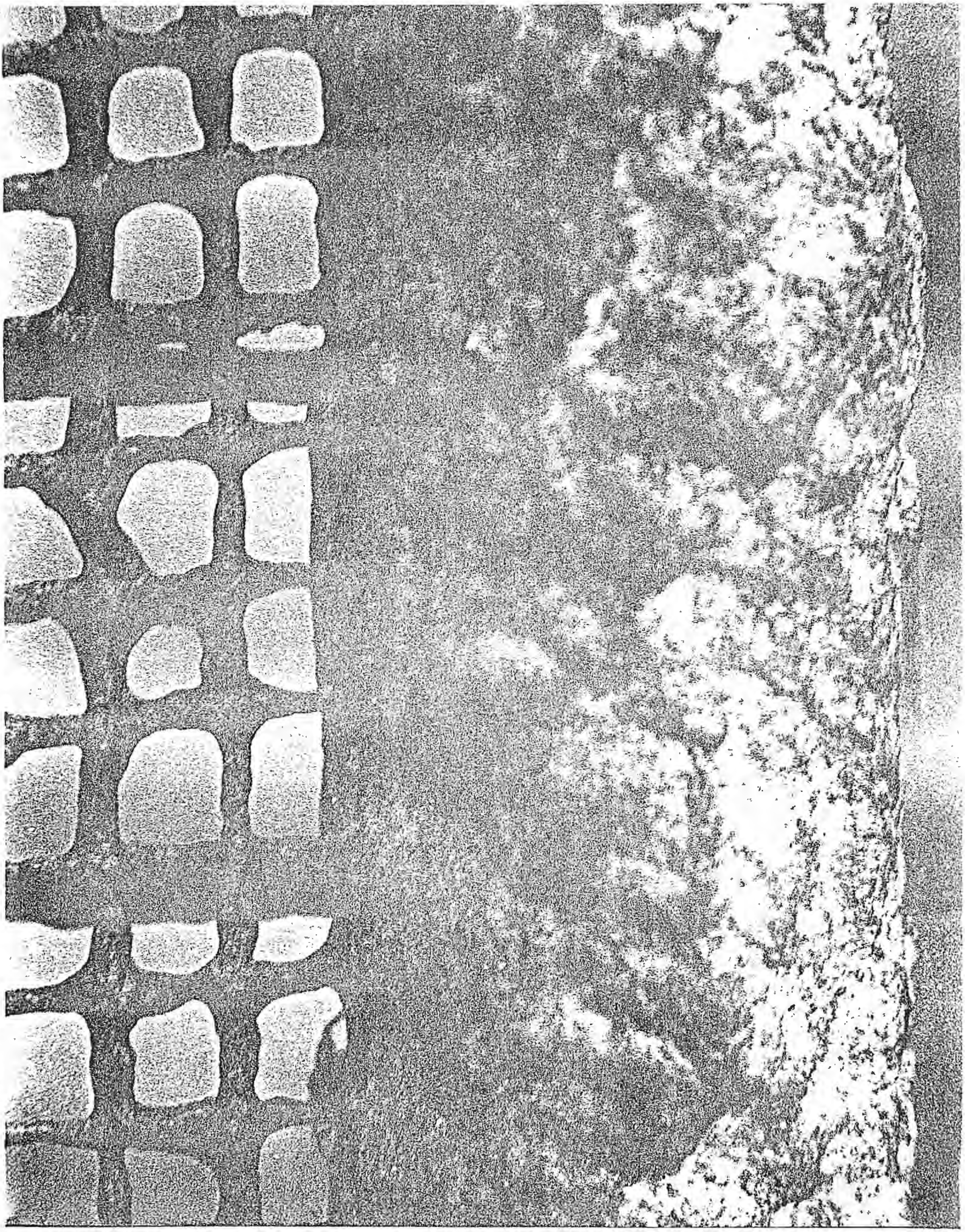


FIGURE 28 1/2 CIRCLE



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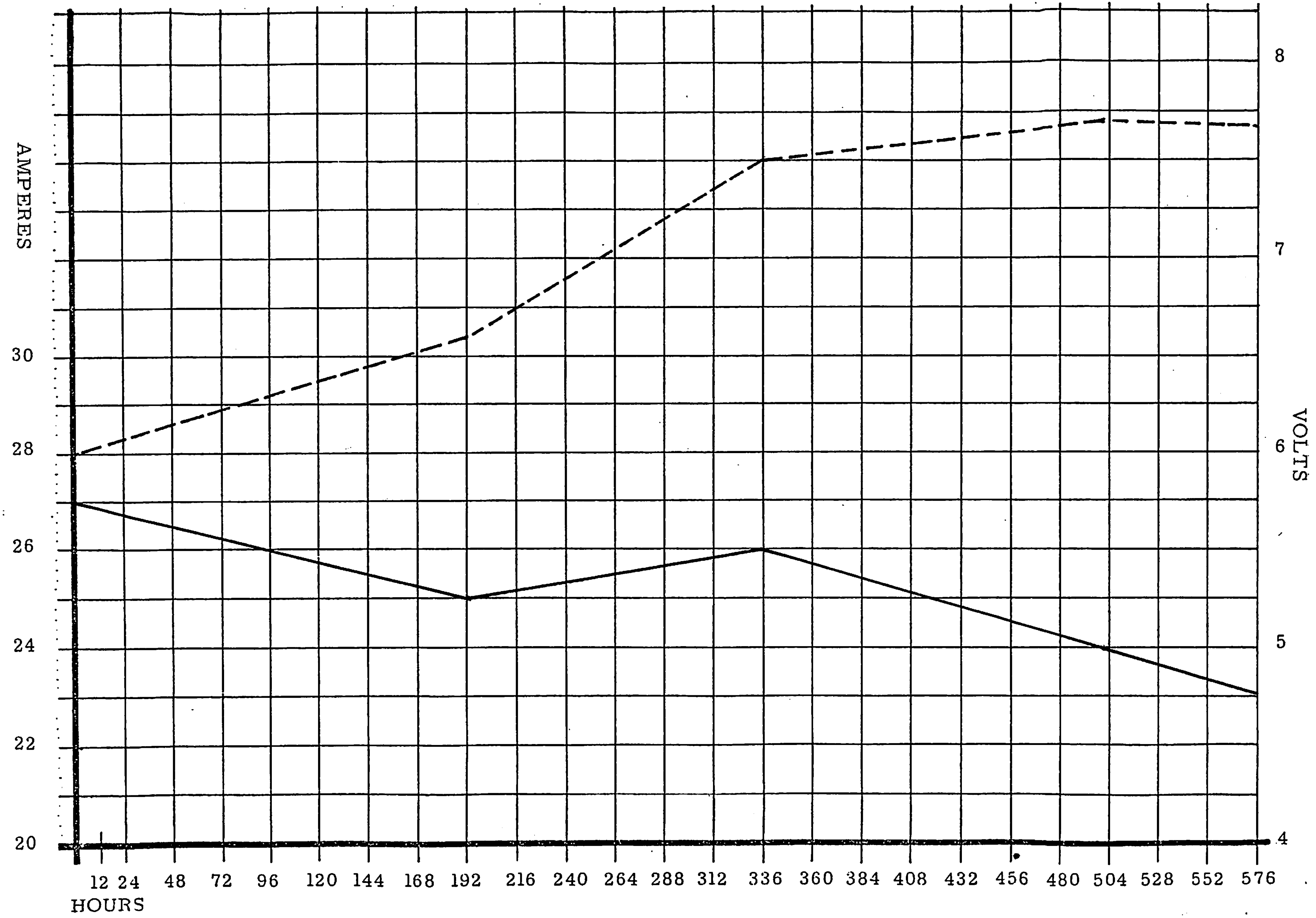


FIGURE 30 TRUSS CIRCLE

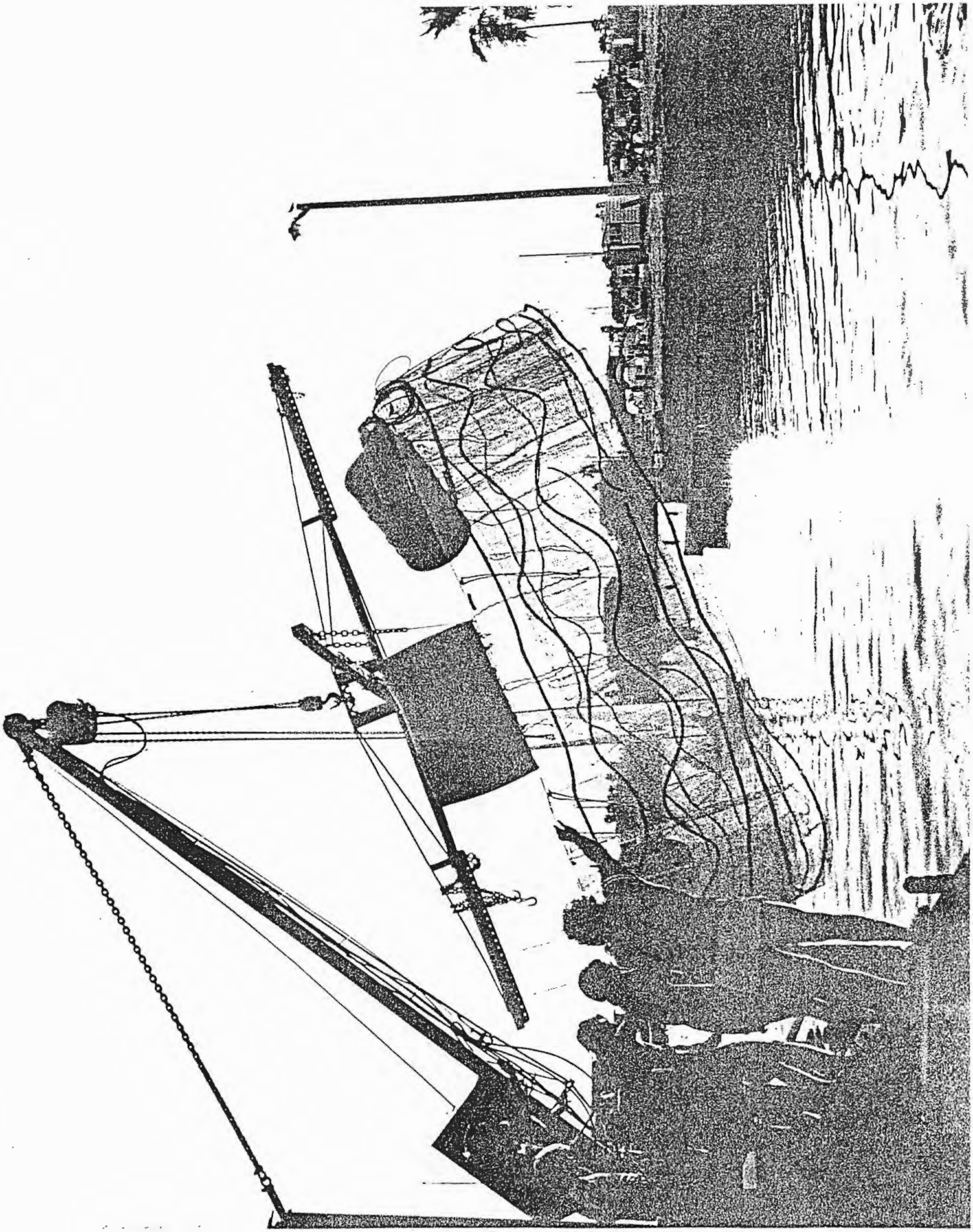
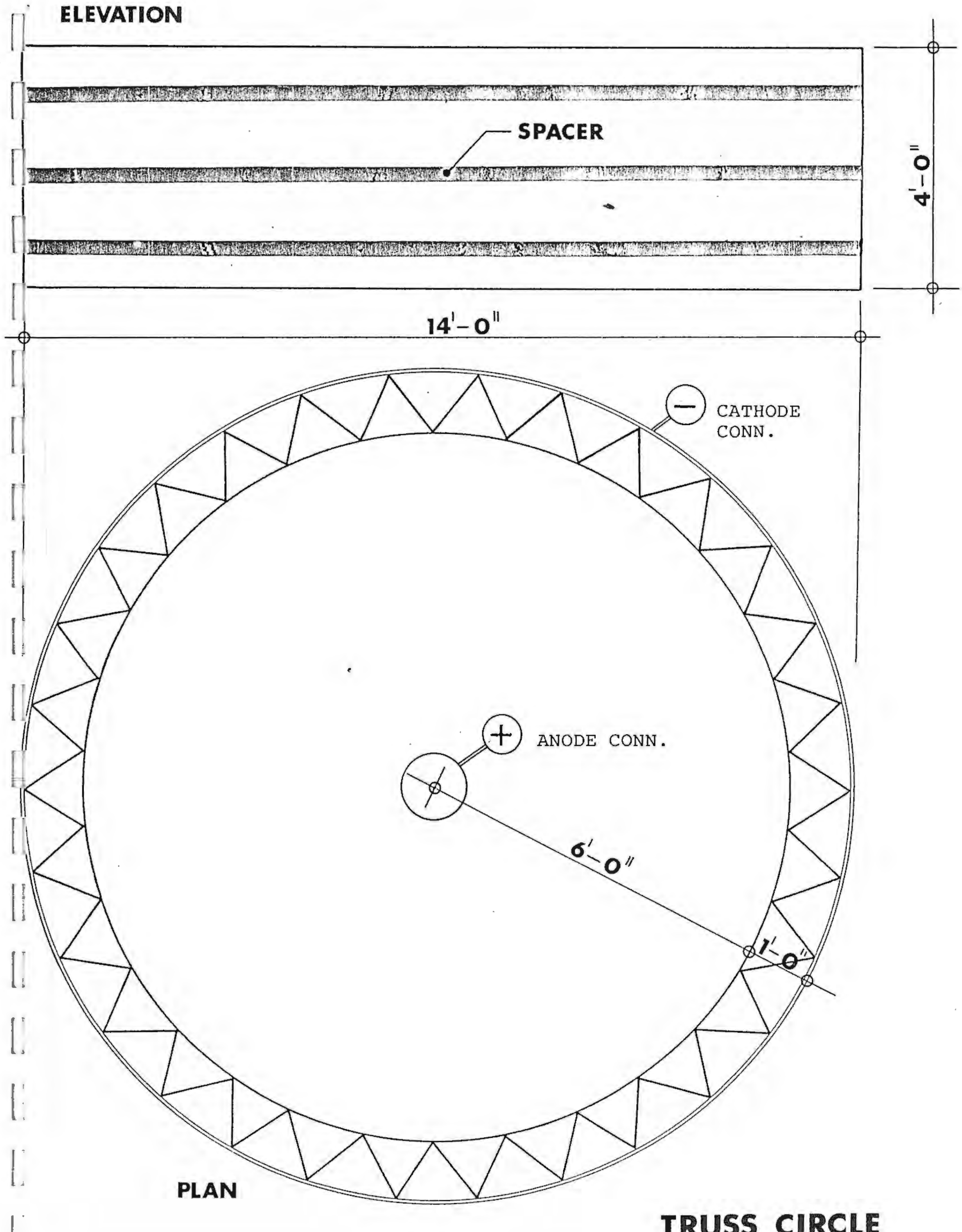


Photo 3:

Photo 3



TRUSS CIRCLE
Fig. 29

Photo 3

5. Phasing of test samples to investigate changes in material properties.

Observations made of previous test components showed that phasing appeared to alter the properties of the electrodeposited material. Therefore, a controlled series of phasing tests was performed at the West Indies Laboratory in order to verify these observations.

5.1. The first phase of the test was conducted in 15 gallon aquaria supplied with water at a rate of 4.5 gallons per minute. Cylindrical cathodes of 1/4" hardware cloth were used, with a circumference of 18", a height of 8", and a total surface area of 144 sq. in. (Photos 33 and 34). A 5" x 3/4" diameter 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 Amps/3.5-8.0 Volts. All cages were under power for 8 - 11 days at which time a white, fairly structural material approximately 0.5 cm in thickness had been deposited. Material samples (Table 11) were taken at this time for x-ray diffraction analysis.

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

- Two cages on the barrier reef at Tague Bay, at a depth of 15 ft. and 18 ft. (Position 2, Figure 15).
- Four cages on a reef patch north of Buck Island at depths varying from 20 - 30 ft. (Position 4, Figure 15).
- Two cages on the inner reef north of Buck Island, at depths of 12 ft. and 14 ft. (Position 3, Figure 15).
- One cage on the deep water upwelling pipeline at a depth of 135 ft. (Position 5, Figure 15).

In addition to these test cages, Drum 1, described in Section 4.1.1-4.1.3, was placed at Position 4, at a depth of 37 ft. on a sandy bottom surface. Test strip 2, described in Section 2.-2., was also placed at Position 4, at a depth of 35 ft. on the reef patch.

Water temperature for Positions 2, 3, and 4 varied between 82^{o} - 86^{o}F, and 27^{o}C at Position 5.[7]

Material samples were again taken from all test cages (except the cage at Position 5) at Position 2 after 19 days, Position 3 after 10 days, and Position 4 after 7 days.

5.2. Small amounts of organic growth; including blue-green algae, diatoms, immature anemones, and coralline algae, were observed several days after the test cages were placed at Positions 2, 3, and 4. (Figure 15). A comparison of the X-Ray diffraction analyses of the material samples, (Table 11), taken before and after the initial phasing shows the following:

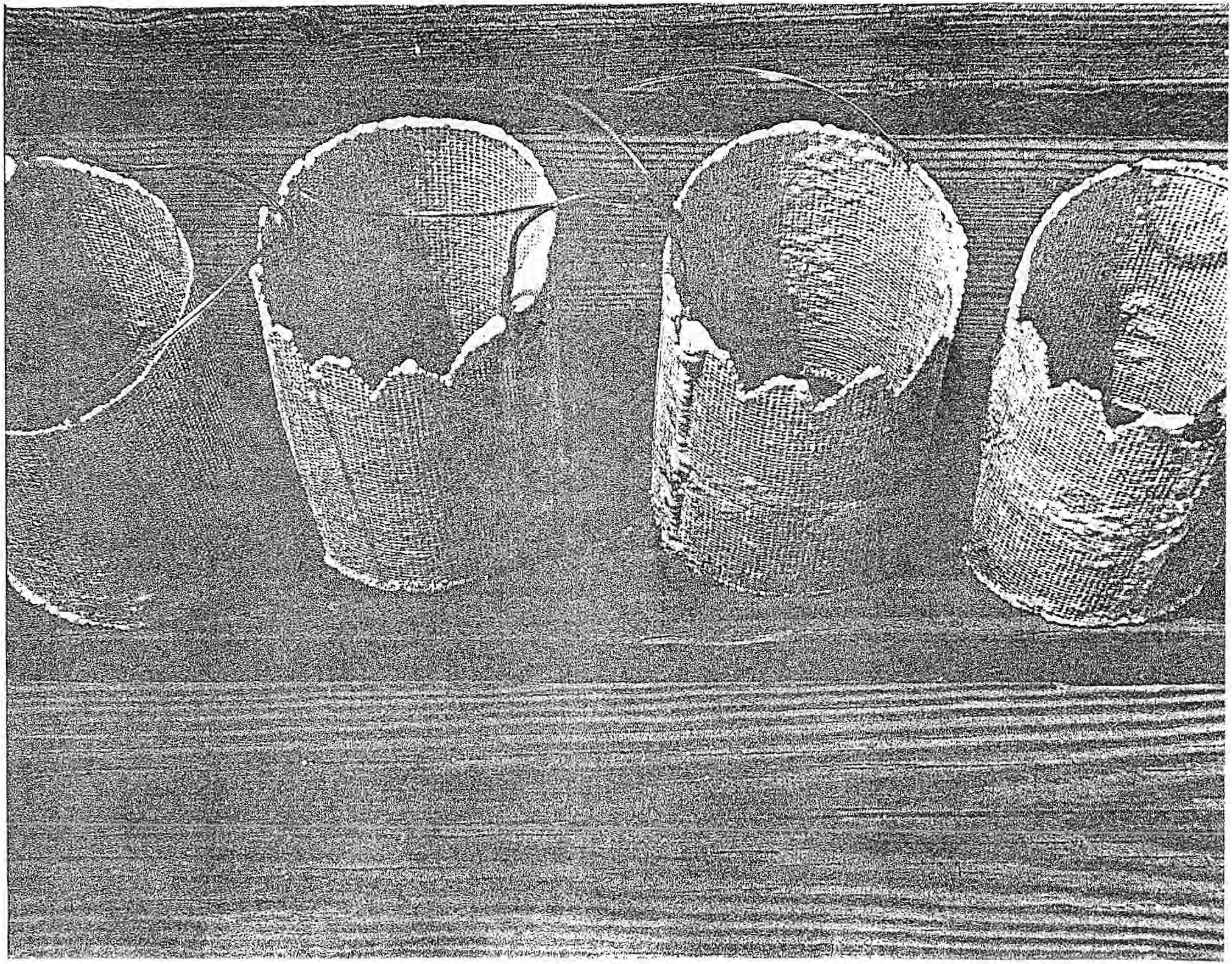


Photo 3

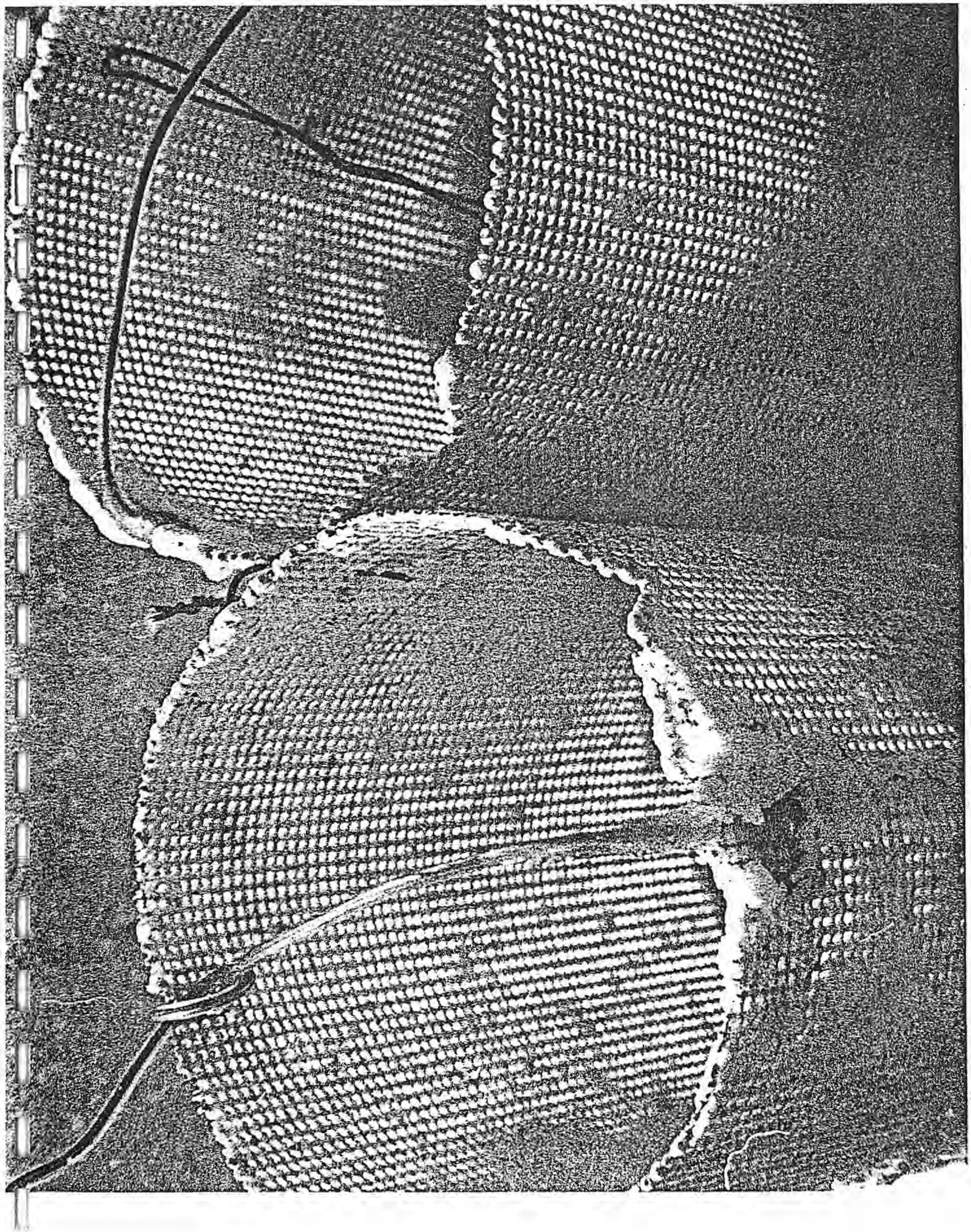


Photo 3

Table 11: X-Ray Diffraction Analysis

Sample No.	Description	Chemical Composition Brucite	Aragonite	Calcite	Halite	Other
17	Typical test Cage	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%

5.3. From the percentages of compounds outlined above, 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 can be either poorly crystalized compounds or non-crystalline material. Considering these percentage shifts, two conclusions are possible: 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 seawater. A possible mechanism for this dissolution of brucite (discussed generally in Section 2.4.3), is the drop in pH at the cathode surface, occuring when electrical current is discontinued. These two situations may be occuring simultaneously, or one may be entirely responsible. Further data must be collected to be conclusive. More material samples, to be taken during January 1977, will help provide further data on phasing.

6. Controlled environments.

6.1.1.Closed Systems. In order to determine the quality and rate of chemical changes due to the electrodeposition process and the effects on seawater composition, it was necessary to establish a closed system in which specific parameters could be measured over time. It was also vital to the understanding of the process to determine whether different initial water chemistries influenced the quantity and/or quality of the deposited material. Precipitation of calcium carbonate greatly depends on the availability of bicarbonates and the total carbonate level in the water, and this level, in turn, is influenced by the pH of the water. Therefore, total alkalinity and pH were of particular concern in measuring changes in water chemistry.

6.1.2.All closed system tests were performed at the University of Texas St. Croix Marine Station, Rust-op Twist, in a semi-protected shelter constructed in close proximity to the water sources. Test tanks consisted of 55 gallon drums cut in half longitudinally, lined with two layers of reinforced PVC plastic sheets, and placed in approximately 6" of gravel. Each tank held 25 gallons of seawater, and all tanks were protected from direct sun, wind, and rainfall. (Photo 35).

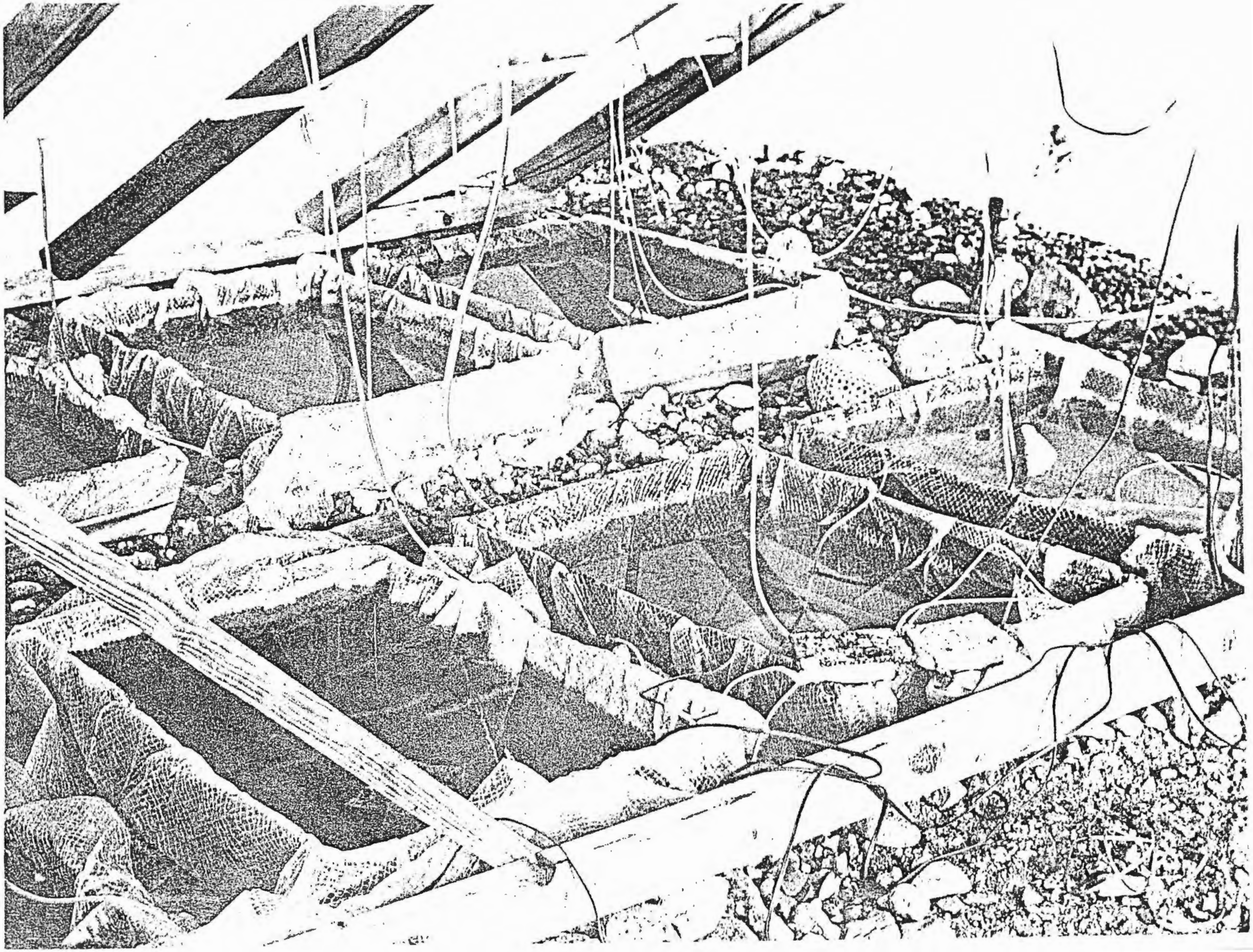


Photo 3

Test samples consisted of a 3" x 5" x 1/6" lead plate as the anode, and a cathode of 1/4" hardware cloth, cut 4" x 6" with a 1" spacer between them of 4" O.D. PVC tubing (Figure 31, Photo 36 and 37). Surface areas of the cathode and anode were 24 sq. in. and 15 sq. in. respectively. All samples were powered by a 0-100 V/0-10A capacity transformer combined with a Variac rheostat. Four sources of seawater with varying compositions were on location:

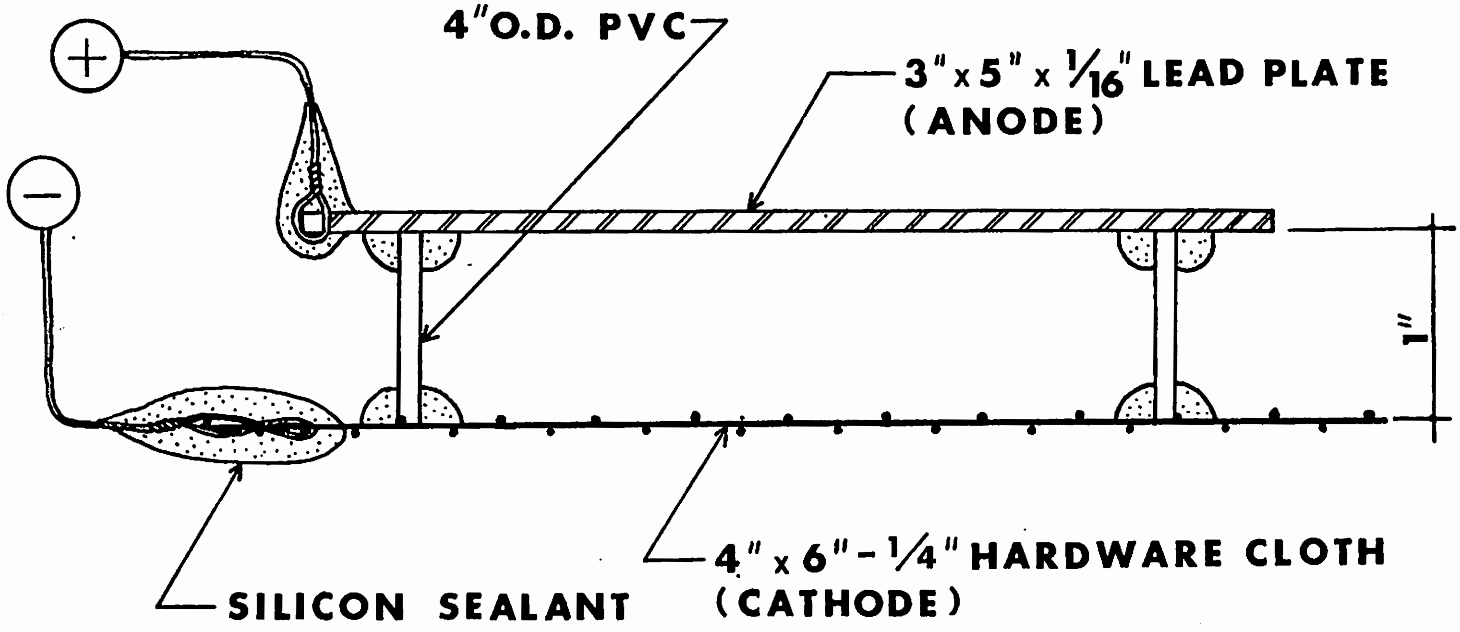
- Seawater pumped directly from a depth of 870m, (direct deep water).
- Deep seawater containing a dense population, 10^4-10^6 cells per ml, of unialgal cultures of planktonic diatoms (phyto-plankton rich water).
- Effluent water from troughs containing shellfish nourished by algal cultures in the deep water. Ninety percent (90%) of the culture is removed by the mollusks (effluent mollusk water).
- Surface water direct from the coast (surface water).

One test sample was submerged in each of the different types of seawater, and was under current for 6-9 hours. Water samples were taken every hour and tested to determine pH, total alkalinity, chlorinity, and temperature. Voltage and amperage were also recorded hourly, and resistance calculated.

pH was measured with a Beckman pH meter. Total alkalinity was determined by the potentiometric method, using a sulphuric acid titrant,.01N, and setting 4.5 pH as the equivalence point. Chlorinity was determined using an iodometric method. Voltage and amperage readings were measured with a Micronta double range 22-204A meter. Material samples were taken after the running time of each test, and prepared for quantitative and qualitative analysis by a Philips X-Ray Diffractometer, Chemical Engineering Lab, The University of Texas at Austin.

6.1.3.As Figures 32, 33, 34, and 35 show, total alkalinity and pH dropped considerably in a short period of time in the closed systems tested. Overall, several observations can be made from the data collected:

- Alkalinity and pH decreased in proportion to power input; that is, at higher current inputs to the test samples, alkalinity and pH decreased faster. This is apparent if results from Test Two and Test Four are compared. The average amperage and voltage, in Test Two were .43A and 3.8 V, respectively, with a drop in pH from 8.5 to 7.0, and a total decrease in alkalinity of 40 mg/l (from 135 mg/l-95 mg/l). While in Test Four, (and, in particular, in the direct deep water, with an average amperage and voltage of 1.7A and 6.3V, the pH dropped from 8.2 to 4.7, and total alkalinity decreased 115mg/l (from 125 to 10).
- Resistance appears to drop over time in all four tests, in spite of material deposition occuring on the cathode (Figures 36, 37, 38, and 39). This must be due to an increase in the conductivity of the electrolyte.
- As neither voltage nor amperage were kept constant by the power supply, both fluctuated in relation to an increase in electrolyte conductivity (or conversely, a decrease in resistance), (Fig. 36, 37, 38, and 39).



TYPICAL TEST SAMPLE

Fig. 31

Photo 3

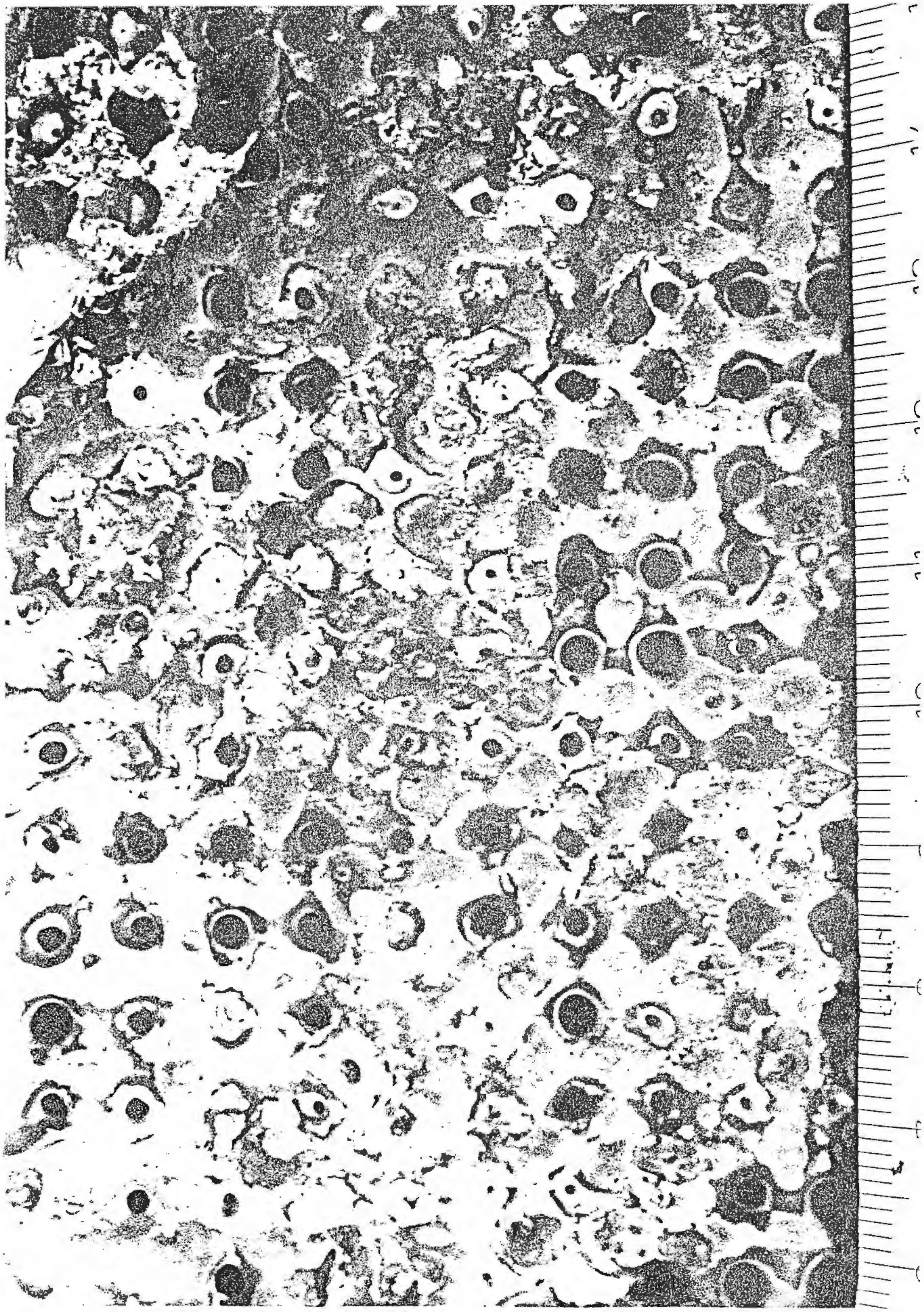


Photo 3

TEST ONE

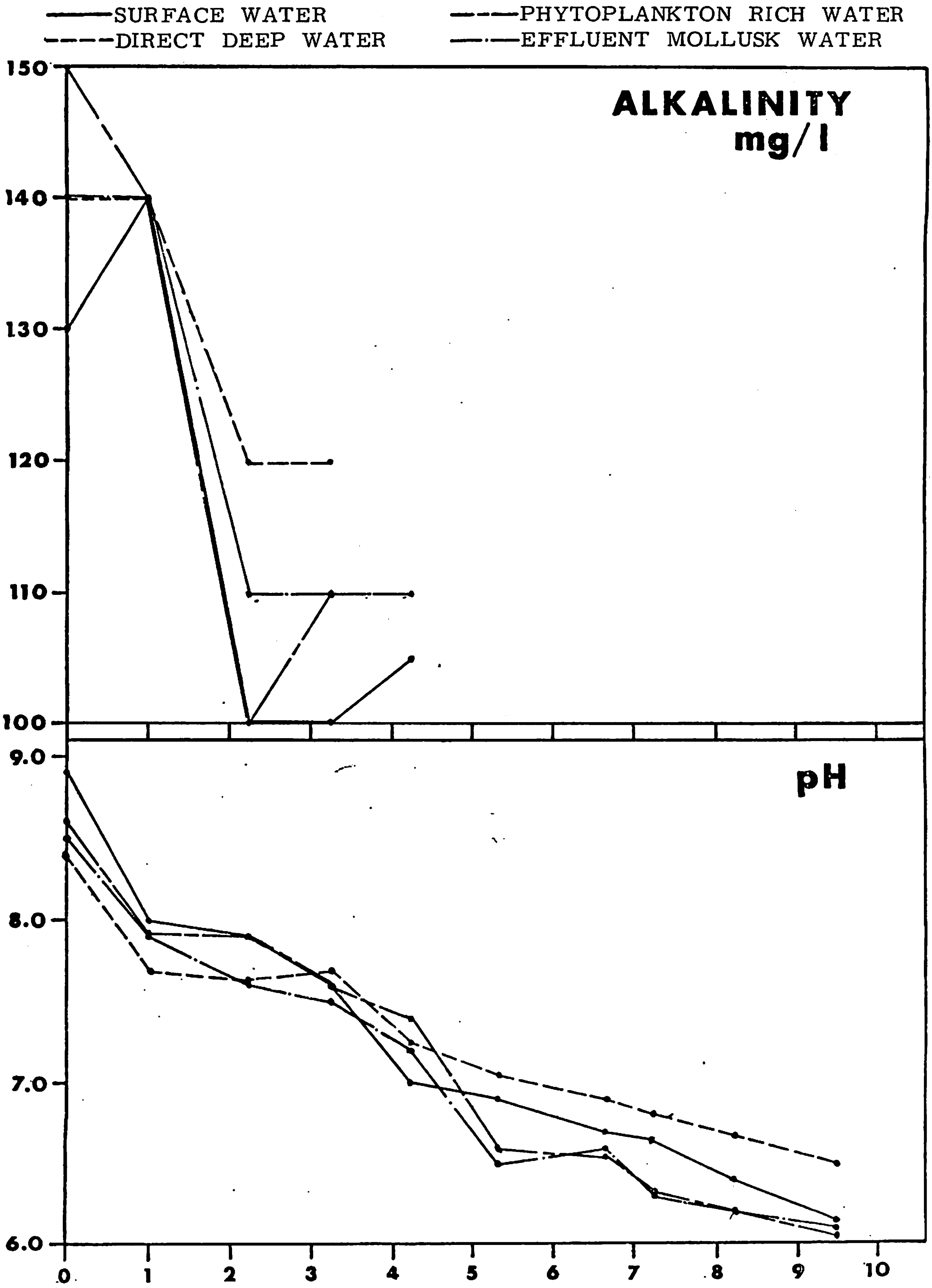


Fig. 32

TEST TWO

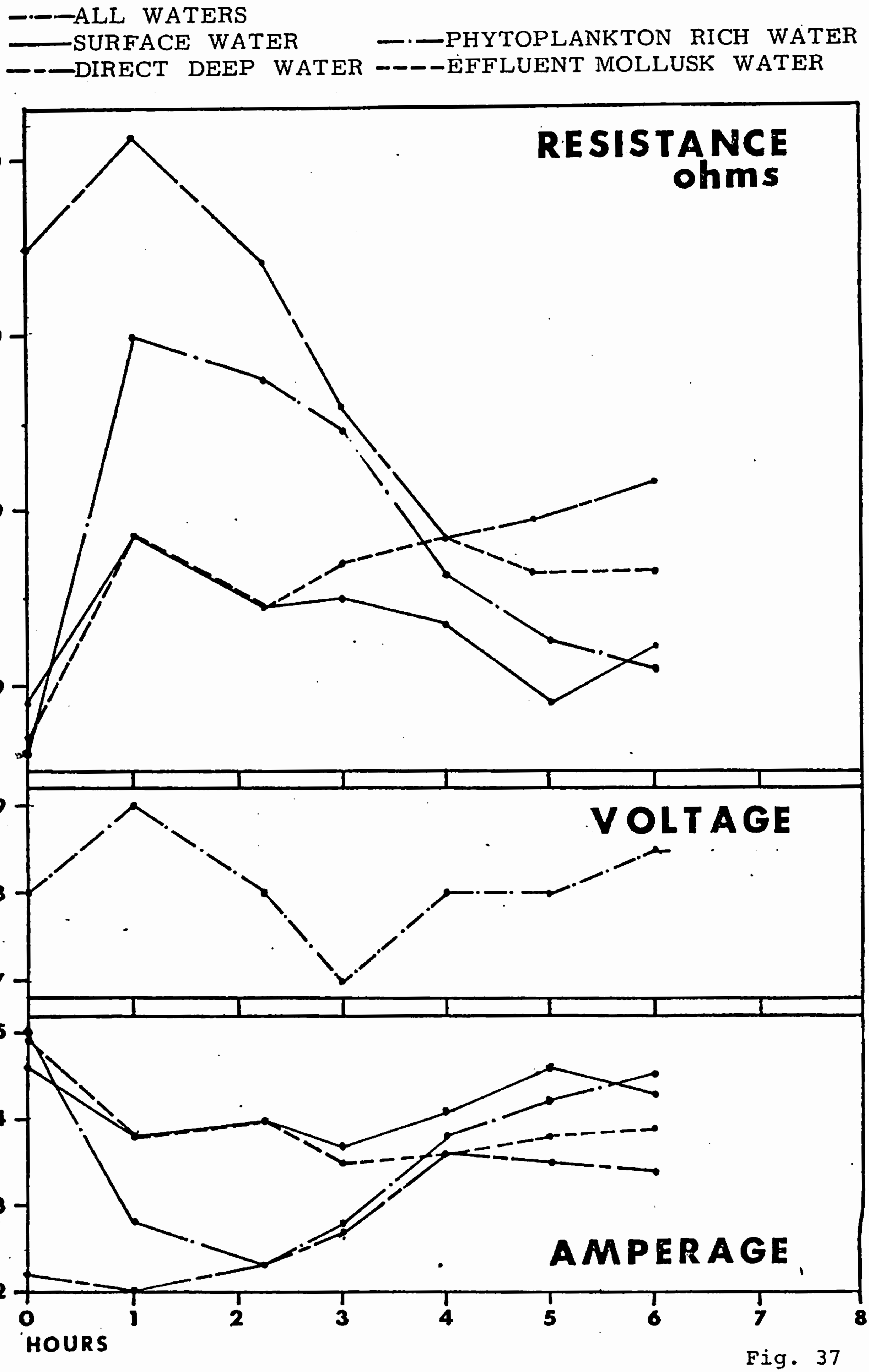
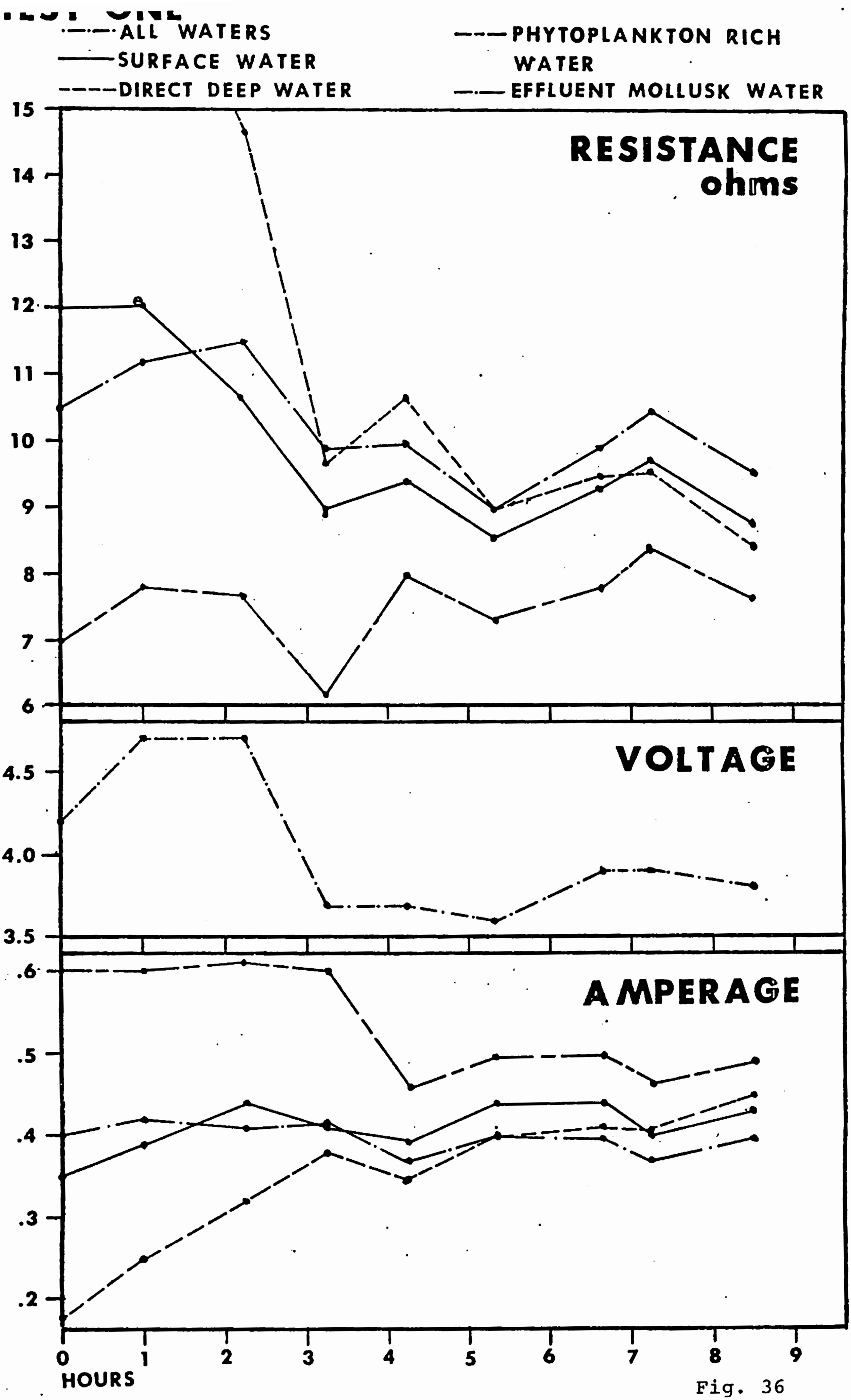


Fig. 37



ALL WATERS
SURFACE WATER
DIRECT DEEP WATER
PHYTOPLANKTON RICH WATER
EFFLUENT MOLLUSK WATER
RESISTANCE ohms
15
14
13
12
11
10
9
8
7
6
VOLTAGE
4.5
4.0
3.5
AMPERAGE
.6
.5
.4
.3
.2
0
1
2
3
4
5
6
7
8
9
HOURS

Fig. 36

TEST FOUR

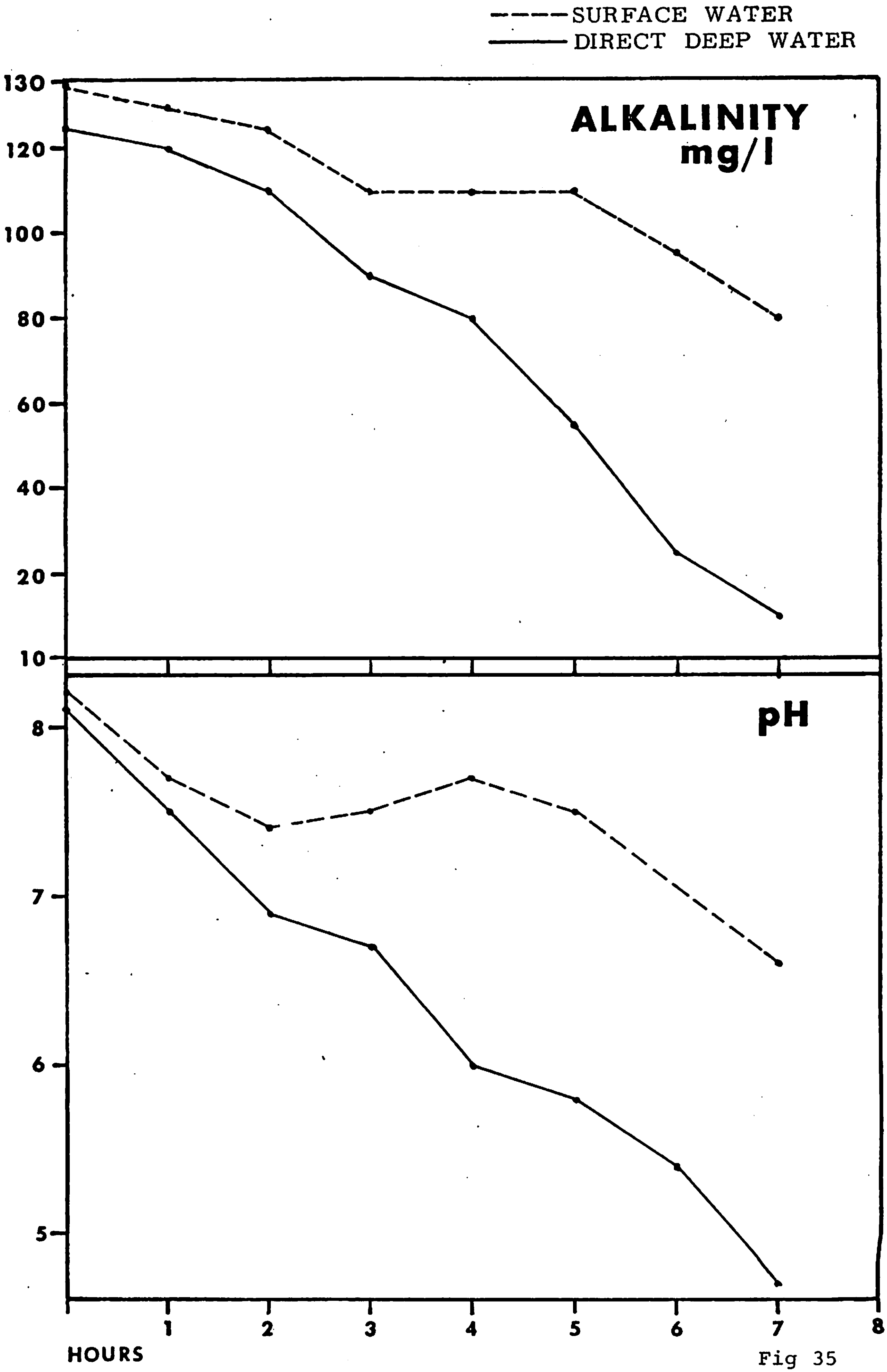


Fig 35

TEST THREE

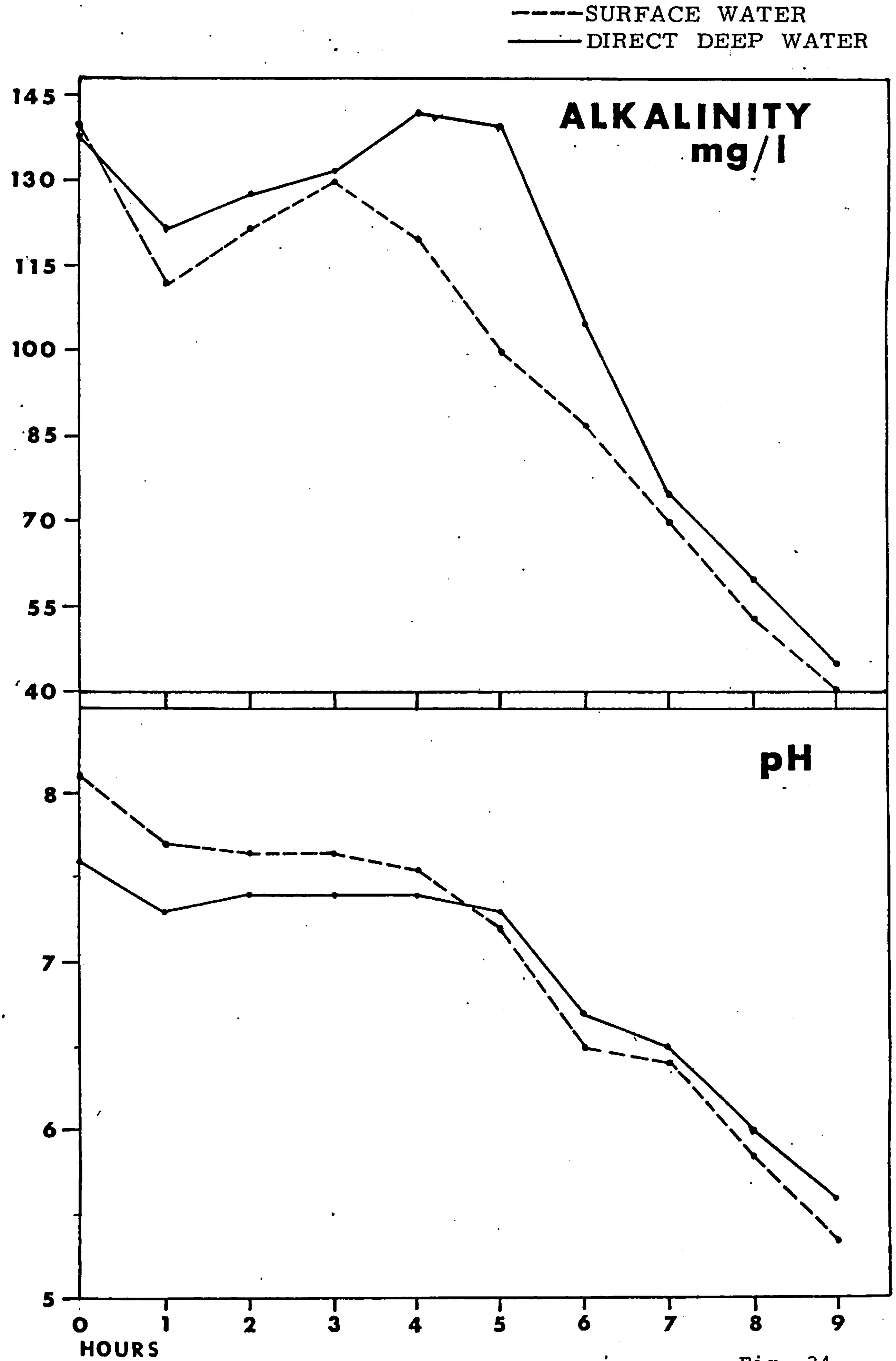


Fig. 34

TEST TWO

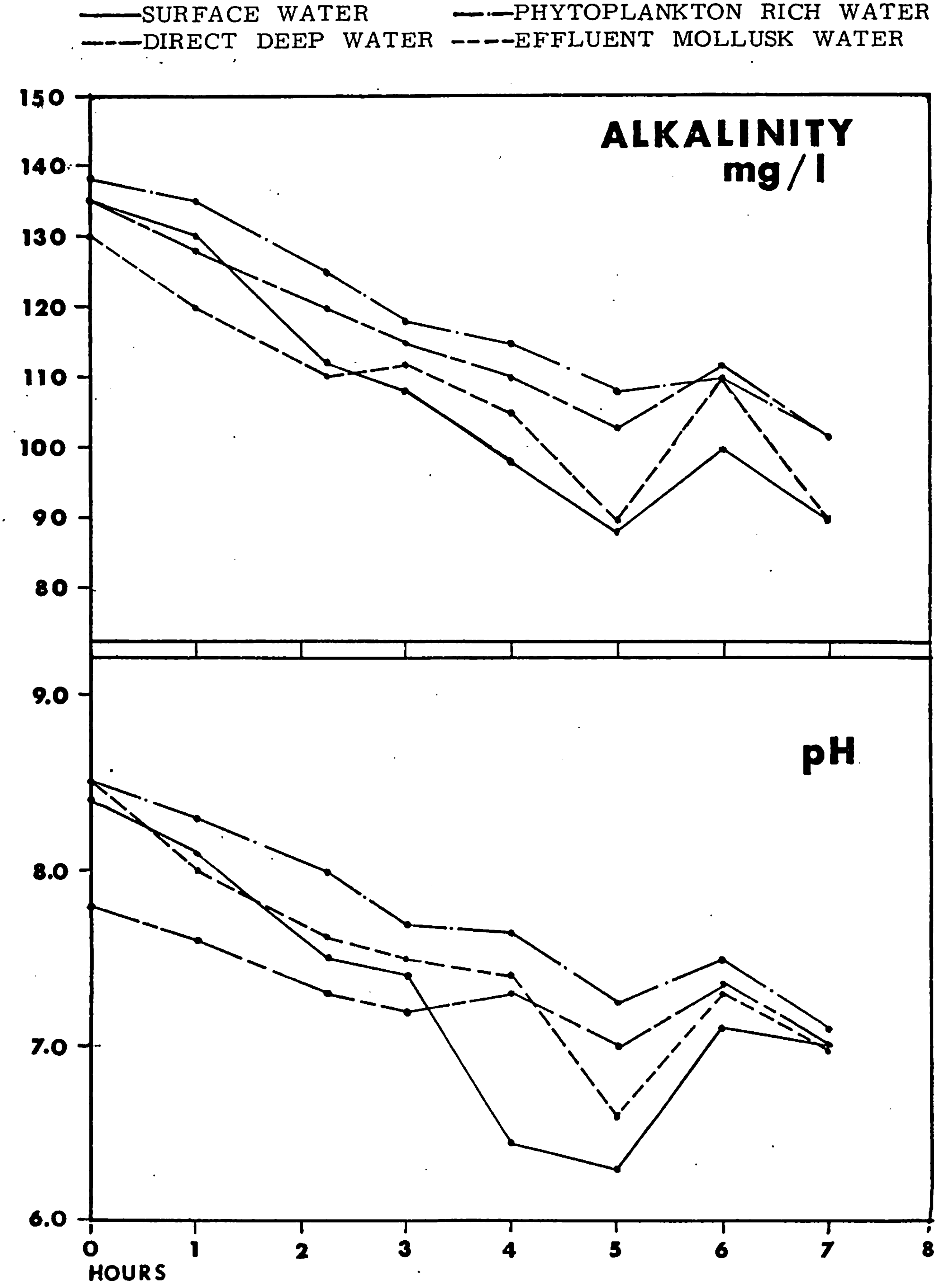


Fig. 33

TEST THREE

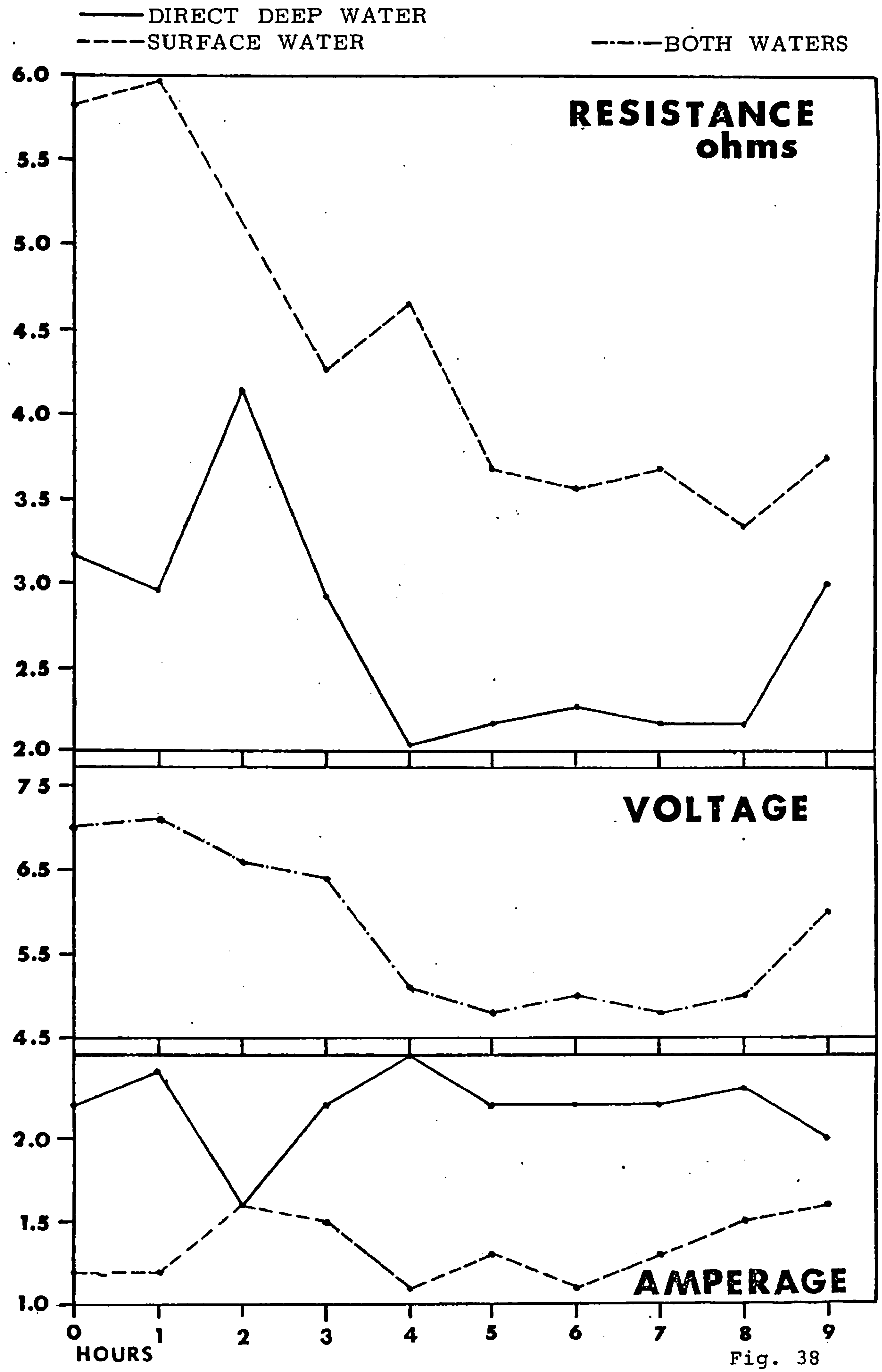


Fig. 38

TEST FOUR

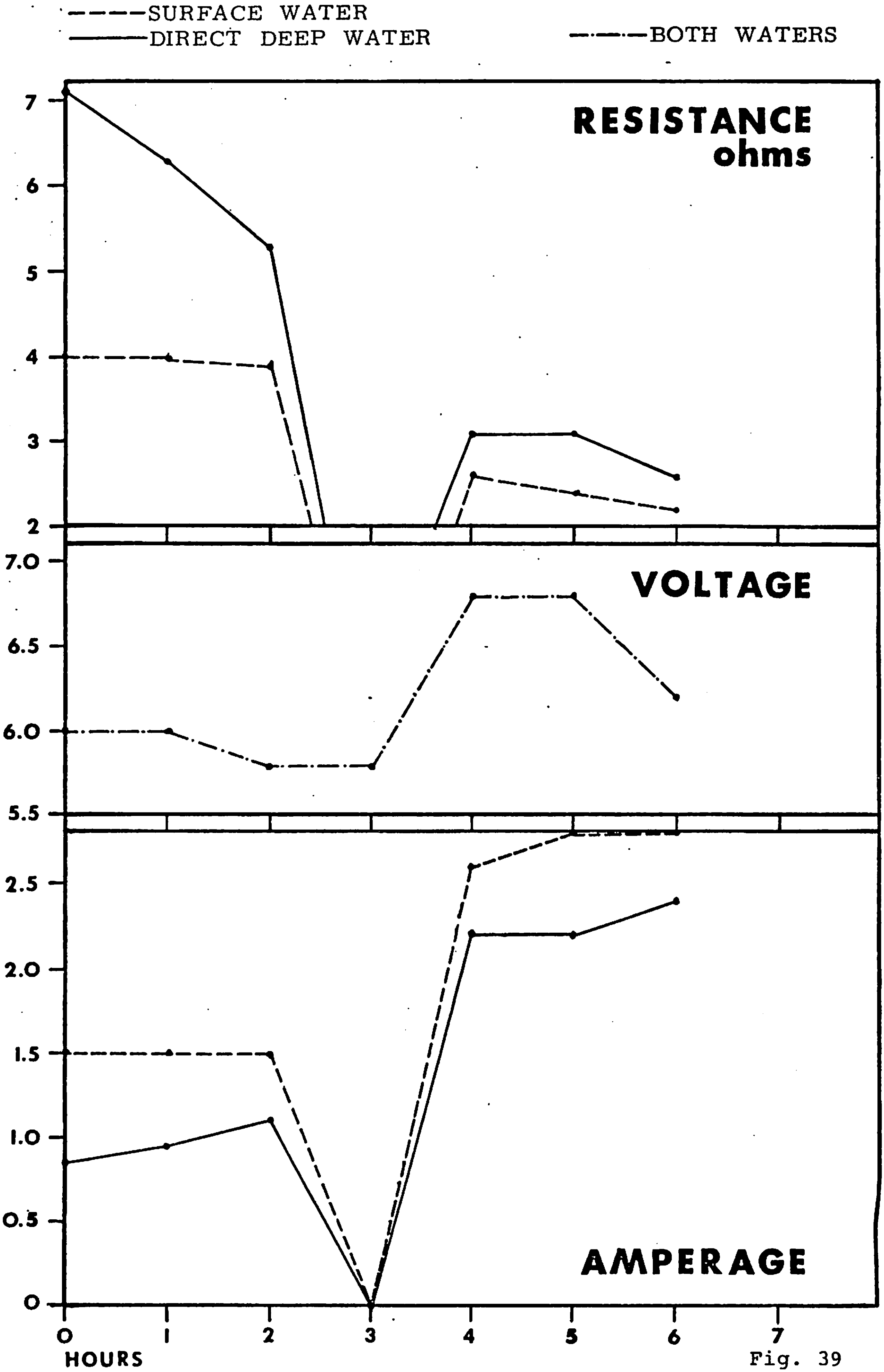


Fig. 39

- All tests run during each series were connected concurrently to the same power supply. Therefore, changes in amperage/voltage of one test sample caused changes in amperage/voltage of another test sample in a different electrolyte. The amperage readings shown in Test Three with only two test samples under power show this effect clearly (Figure 38).
- Consistent measurements of chlorine content for all four tests were impaired due to improper test methods for Test One, and the difficulty in performing the iodometric titration method in a field situation. Chlorinity measurements were consistent for Test Two over a five (5) hour period and showed a significant increase in chlorine content:

Table 12: Chlorinity (mg/ml), Test Two

Hour Sampled	Surface	Mollusk Effluent	Direct Deep	Phytoplanktion Rich Deep
0	-	-	-	-
1*	8.5	12.8	7.1	9.2
2	2.8	4.3	4.3	4.3
3	7.1	6.7	5.0	5.7
4	14.9	9.9	7.1	5.7
5	15.7	13.5	9.9	9.2
6	20.6	18.4	15.6	14.2

*These data after the first hour, may be incorrect due to possible faulty testing. Since this testing method appears inadequate, we have been using conductivity and temperature measurements to determine chlorinity This method has been determined by R.A. Horne to be more efficient and accurate.[6]

- Material analysis from each test sample (taken after 6 hours from Test Two) showed the following results:

Table 13: X-Ray Diffraction Analysis

Sample	Electrolyte	Chemical Composition % Brucite (Mg(OH)2)	% Aragonite ($CaCo_3$)	% Calcite ($CaCo_3$)
21	surface	75	8	5
24	phytoplankton	80	5	6
23	direct deep	95	5	-
22	effl. mollusk	95	4	-

Two points must be considered in evaluating these percentages. The method used in this analysis allows for a (+ or -) 10% error factor on all figures. Also, a better crystalized material will be detected as a greater percentage by X-ray diffraction than a lesser crystalized form of that material. Therefore, these percentages represent particularly the well crystalized portions of the materials tested and may not include total percentages of the compounds listed.

In addition, analysis of deposited material taken after longer periods under power in identical conditions provided different percentages:

Table 14: X-Ray Diffraction Analysis

Sample	Electrolyte	Chemical Composition Hours Under Power	% Brucite	% Aragonite	% Calcite
21	Surface	6	75%	8%	5%
26	Surface	24	90%	10%	-
28	Surface	30	73%	8%	1%
23	Direct deep	6	95%	5%	-
27	Direct deep	24	70%	12%	2%

- All material deposited on each test sample was very unstructural, being of a chalky nature when dried. Section 2.4.3. discusses the nature of this material more thoroughly.

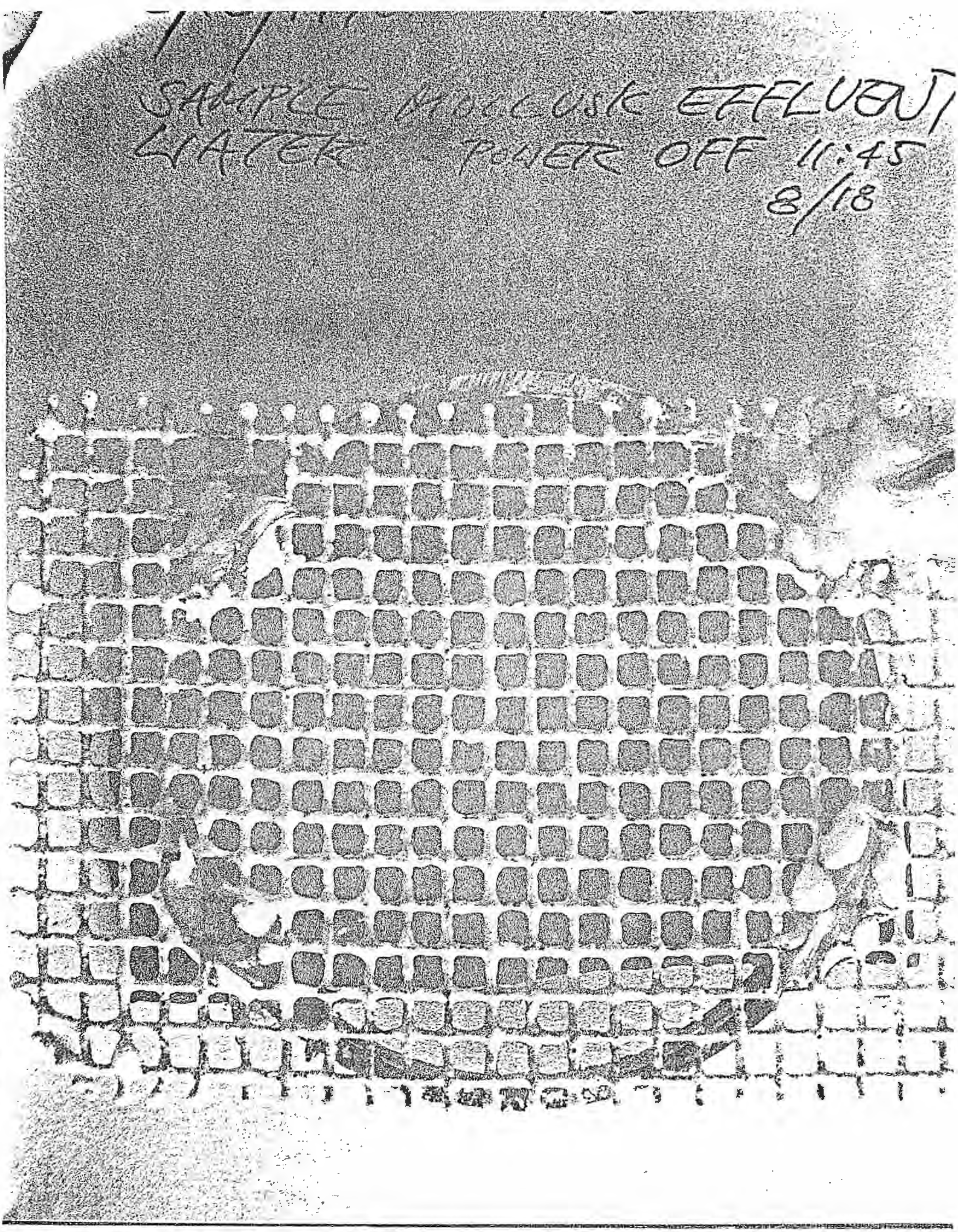
6.2.1. Open Systems. The sources of water available at the St. Croix Marine Station, St. Croix, United States Virgin Islands, had distinct compositions which allowed an initial study into the effects of different electrolytes on the electrodeposited material. This information will be of interest in determining whether different regions of the ocean would be advantageous over other locations with respect to this process.

An open system was established such that the compositional changes of the electrolyte, found in the closed system experiments, would not occur. The necessary rate of water circulation was established to insure that initial conditions of the water (pH, total alkalinity, temperature) and power input (voltage and amperage) remained as constant as possible.

In addition, the availability of phytoplankton-rich deep water made it possible to perform initial observations on the viability of these living organism existing in the presence of the electrodeposition process.

6.2.2. Fifteen gallon aquaria were used, supplied with water at a rate of approximately two (2) gallons per minute. Test samples were constructed in the same manner as those used in the closed system experiments, (Figure 31, Photo 38). The power supply was again a 0-100V, 0-10A capacity transformer coupled with a Variac. The water sources were:

- direct deep water
- phytoplankton-rich deep water
- effluent mollusk water



SAMPLE MOLLUSK EFFLUENT
WATER POWER OFF 11:45
8/18

Photo 3

Two series of tests were run, limited in number by the fact that the phytoplankton culture pools were out of commission for several days at the time the tests were scheduled. Both tests ran for three days, after which material samples (Tables 15, 16) were taken for analysis by X-Ray diffraction. Total alkalinity, pH, temperature, voltage, and amperage were monitored by the same methods and equipment as outlined in the previous section to insure that the initial conditions of the electrolytes remained fairly constant.

6.2.3. Small changes in the electrolytes occured with respect to the parameters monitored. Temperature increased slightly, but this can not be attributed particularly to electrical current input. Minimum pH was 7.5 for the effluent mollusk water, 7.2 for the direct deep water, and 7.75 for the phytoplankton rich deep water. Total alkalinity never dropped more than 5-10 mg/l for all electrolytes.

Analysis of deposited material sampled after both 3 - day test series showed the following compound percentages:

Table 15: X-Ray Diffraction Analysis

	Series One (power input: .25Amps/4-5.5Volts)				
Sample	Electrolyte	% Brucite	% Aragonite	% Calcite	% Halite
19	phyto-plankton rich deep water	83%	12%	1%	4%
20	effluent water	50%	15%	5%	trace

Table 16: X-Ray Diffraction Analysis

	Series Two (power input: 2Amps/5-7Volts)				
Sample	Electrolyte	% Brucite	% Aragonite	% Calcite	% Halite
47	phyto-plankton rich deep water	80%	4%	trace	trace
49	effluent water	65%	5%	trace	trace
46	deep water	68%	5%	3%	8%

While the X-Ray Diffraction analysis did show percentage differences of the compounds between the deposited materials in different electrolytes, futher investigation must be done to be conclusive. Generally, the samples from the phytoplankton-rich deep water showed more brucite (80-83%) than the others. Also, when the amperage was higher (2 Amps vs. 0.25 Amps), a slight decrease in aragonite occurred for all material samples. This may be due to the fact that less of the compound deposited was well crystalized, and therefore, was less pronounced in the X-Ray diffraction analysis.

7. Cubes for mechanical testing, (University of Texas Marine Science Institute Port Aransas).

This experiment was devised in order to perform mechanical tests determining the psi (pounds per square inch) load capacity of electrodeposited materials with wire mesh reinforcement and the psi of electrodeposited materials with wire mesh reinforcement after phasing.

The experiment is divided into three parts:

1. Electrodeposition and testing of three (3) test cubes (procedure 1).
2. Electrodeposition, phasing, and subsequent testing of 3 test cubes (procedure 2).
3. Electrodeposition of one preassembled test cube and subsequent testing (procedure 3).

7.1.1. Procedure 1. Three (3) test sets of seven (7) cubes each of galvanized 1/8" wire mesh with gradated side lengths between 1/2" and 3 1/2" (Figure 40) were submerged between 2" and 36" of seawater in a concrete tank with a flow rate of 3 1/2 gal./min. from a settling tank (Photo 39). Each cube is connected to a cathode wire, two lead anodes are placed between 1' - 0" and 3' - o" from the cubes.

Direct electrical current is supplied by a regulated power supply. All electrical readings are taken with a Micronta 22-204A meter. Ambient water temperature ranges between 68°F and 74°F.

After an electrodeposited mineral layer of 1/4" on the surfaces of the cubes has been achieved, cube 1 will be positioned in cube 2 (Figure 40, Step 1) in order to merge the accretion layers of cube 1 and 2. After this has been achieved, the entity cube 1 and 2 will be positioned in cube 3, and so forth, until the seven cubes form a structural entity with 4" side length. Then structural testing can commence.

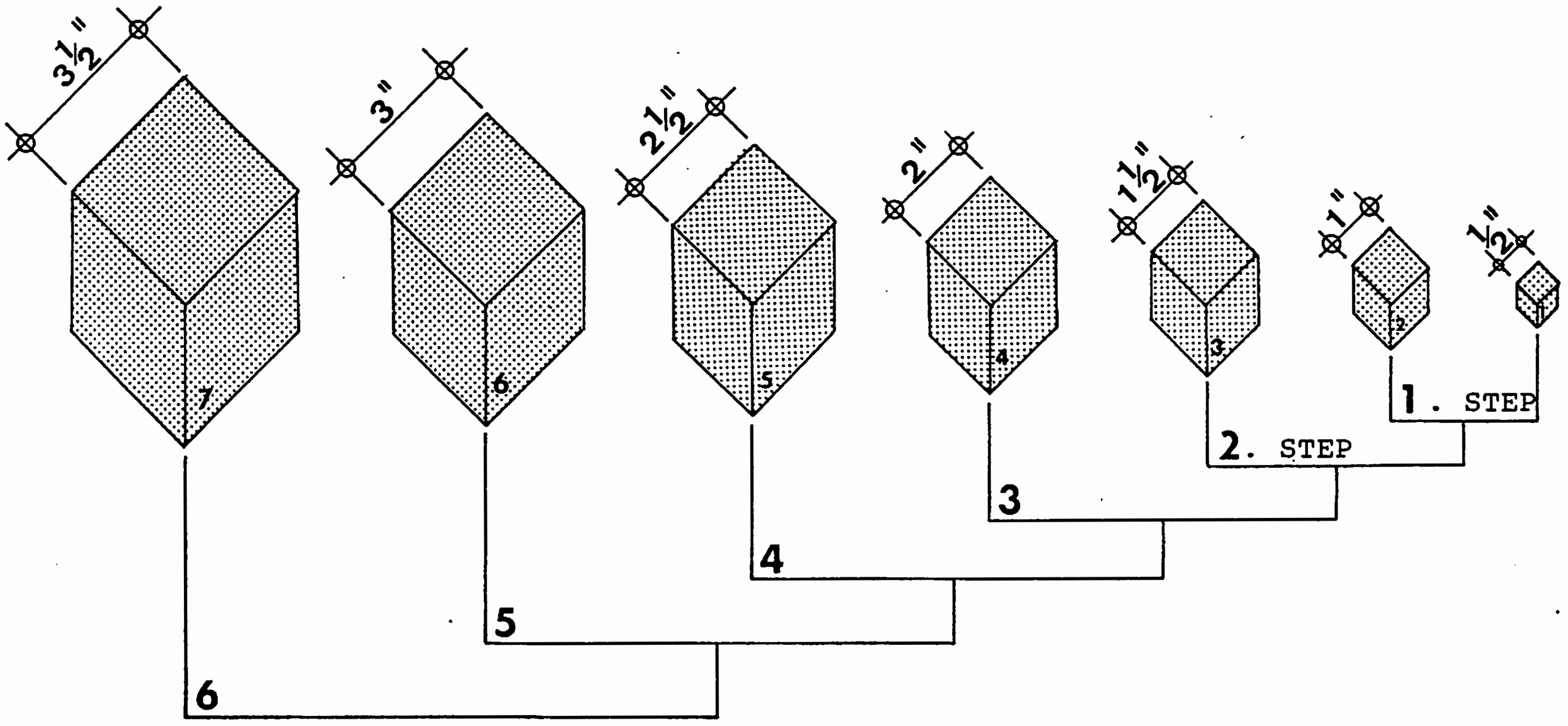
7.1.2. All cubes were coated with electrodeposited material with a thickness of 1/8" 504 hours after submersion. For this no other data are available at this time.

7.1.3. A discussion of this project is not yet possible. This will be furnished in the forthcoming addendum to this report.

7.2.1. Procedure 2. This procedure uses the same methods and materials as outlined in 7.2.1.(Procedure 1) with the exception that before steps 1 - 6 (Figure 40) are taken the 3 sets of seven cubes each will be subjected to 720 hours of phasing at a depth of 2' - 0" in the ship channel under the pier laboratory of the University of Texas M.S.I. at Port Aransas.

7.2.2. Same results as outlined under 7.3.1.

7.2.3. A discussion of this project is not yet possible. This will be furnished in the forthcoming addendum to this report.



TEST CUBES

Fig. 40

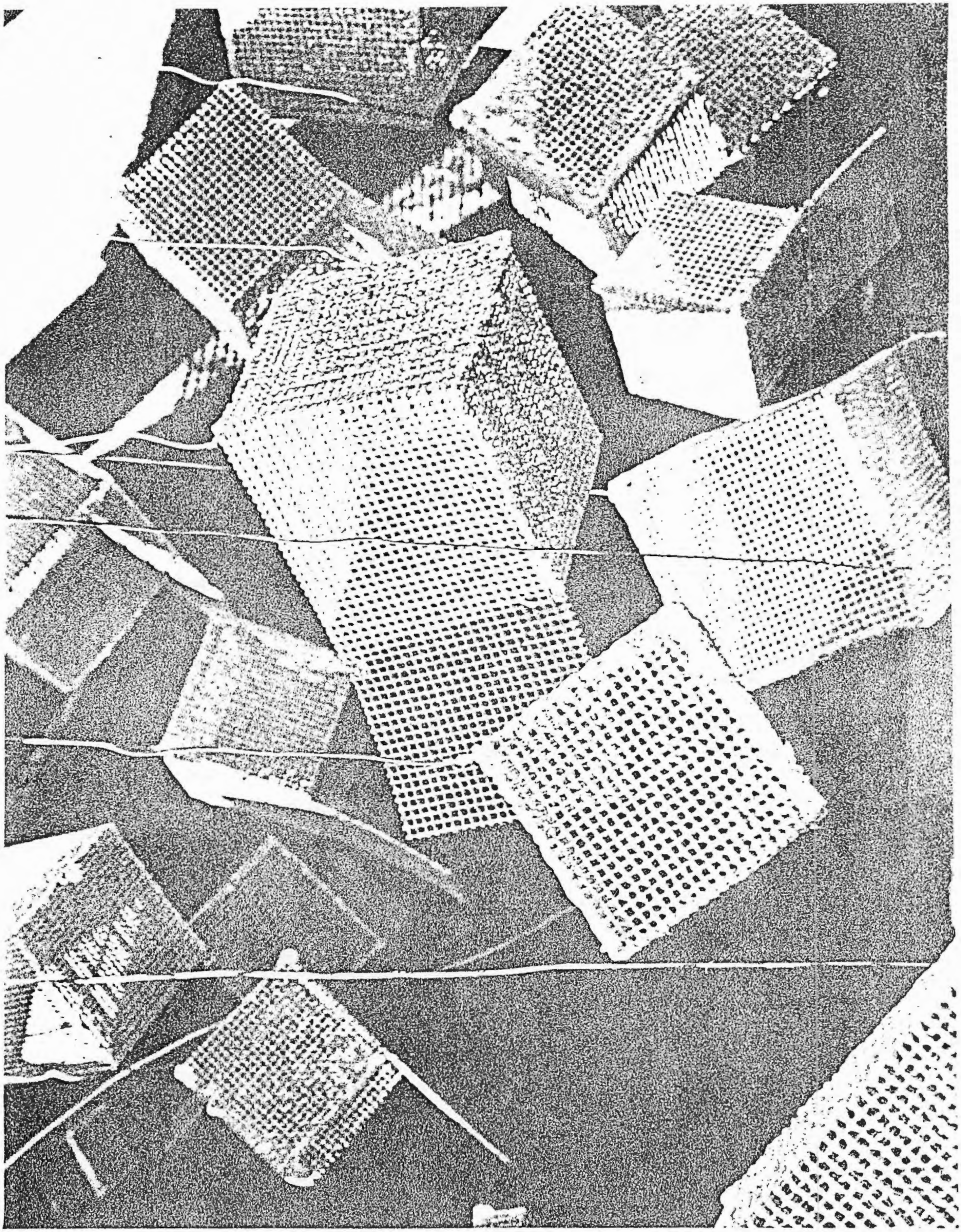


Photo 3

7.3.1. Procedure 3. One (1) test set of 7 cubes consisting of galvanized 1/8" wire mesh with gradated side lengths between 1/2" and 3 1/2" (Figure 41), was submerged in 6" of seawater in a concrete tank with a flow rate of 3 1/2 gal./min. from a settling tank. Each cube is connected to a cathode wire, one lead anode is placed 1' - 0" from the cube assembly. The individual cubes are held in position by nylon string and are equally spaced to avoid touching of the wire mesh surfaces. After cube 1 has been coated with a mineral layer of 1/4" thickness, cube 2 will be activated as a cathode until an electrodeposited layer of 1/4" is achieved, and so forth until a solid cube with a sidelength of 4" has been formed. Then structural testing can commence.

7.3.2. Cubes 1, 2 and 3 were solidly covered by electrodeposited material after 504 hours of continuous operation.

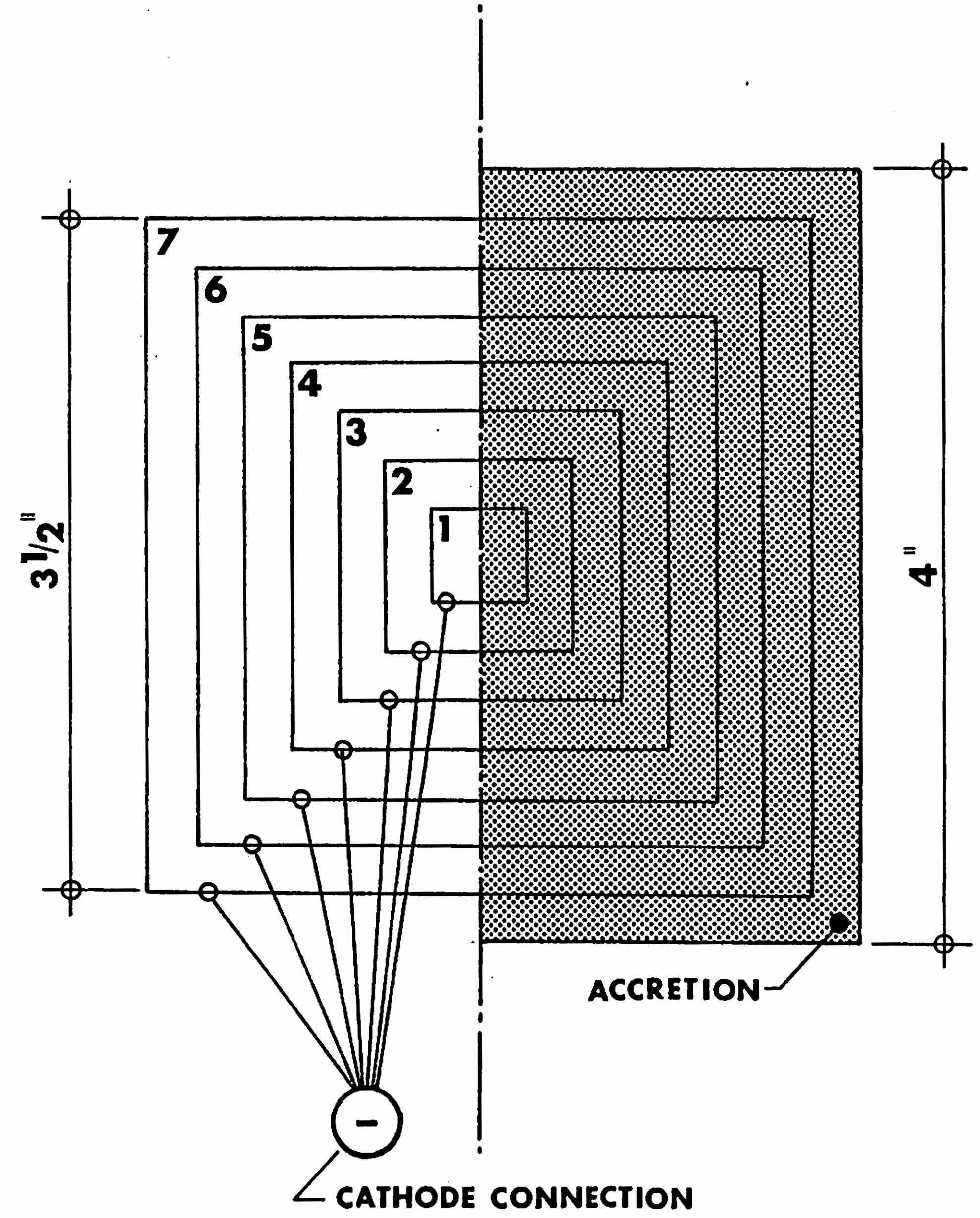
7.3.3. A discussion of this project is not yet possible. This will be furnished in the forthcoming addendum to this report.

8. Data Reduction and Acquisition System (DARS).

At present, the DARS, as illustrated in Figure 42, is not yet completely debugged. It is being calibrated at the Symbiotic Processes Laboratory, U.T. Austin, Texas. The analog input channels being calibrated are: pH, temperature (seawater), temperature (cathode), conductivity, voltage (reference), voltage (total), amperage, magnesium ion concentration, calcium ion concentration, chloride ion concentration, and ten resistivity probes. As soon as the DARS is operating with little degree of error, it will be possible to conduct analyses of the electrochemical reactions occurring in a controlled situation to provide a standard as outlined in the grant proposal.

8.1. During the calibration period, it has been possible to design and construct a more sophisticated reference electrode than previously outlined. Figure 43 illustrates the design and operation. As layers of minerals are accreted, the resistance of the resistance leaps (R_n) will increase, thus allowing the DARS to pin-point precisely three important factors: rate of growth, resistance of the material, and porosity as a possible function of resistance. One fourth inch (1/4") platinum wire (.025" diameter) was soldered to the tip of each copper lead wire, to be exposed through holes bored at 1 mm every quarter turn in a 6.99 cm x 1.85 cm plexiglass cylinder. Once the probes were placed, acrylic resin was poured into the cylinder to seal the platinum/copper connections. The last input lead (#30) acts as the reference electrode to maintain constant amperage or constant voltage. Figure 44 illustrates graphically the operation of the reference probe while electrochemical reactions are taking place. The resistance of the electrolytic cell is equal to the resistance of the water plus the resistance of the accreted material according to:

$$R = R_E + R_a = \rho_E \left(\frac{D_E}{A}\right) + \rho_a \left(\frac{a}{A}\right) = \frac{V}{I} \qquad \text{(Equation 1)}^{9}$$



TEST CUBE

Fig. 41

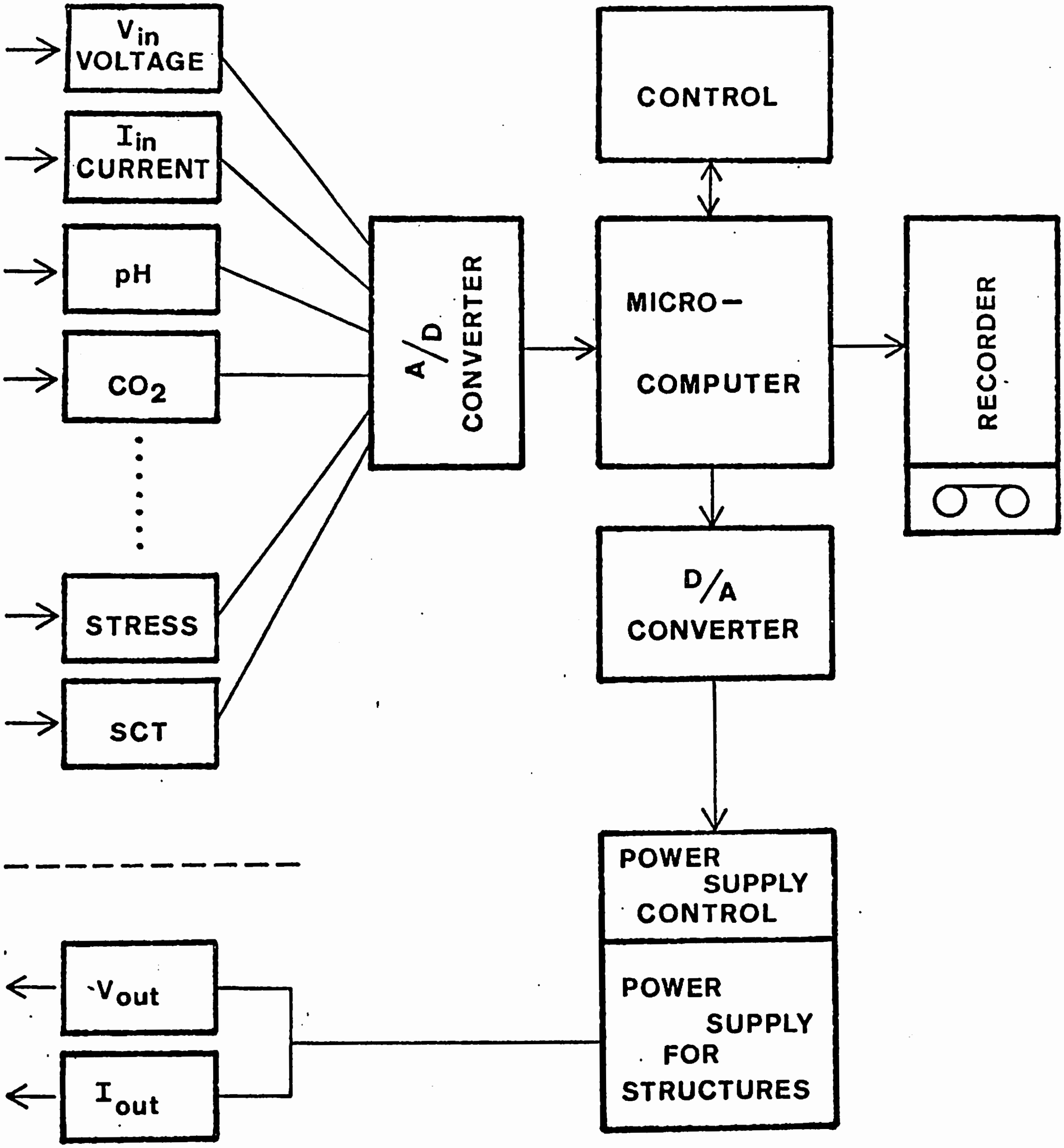
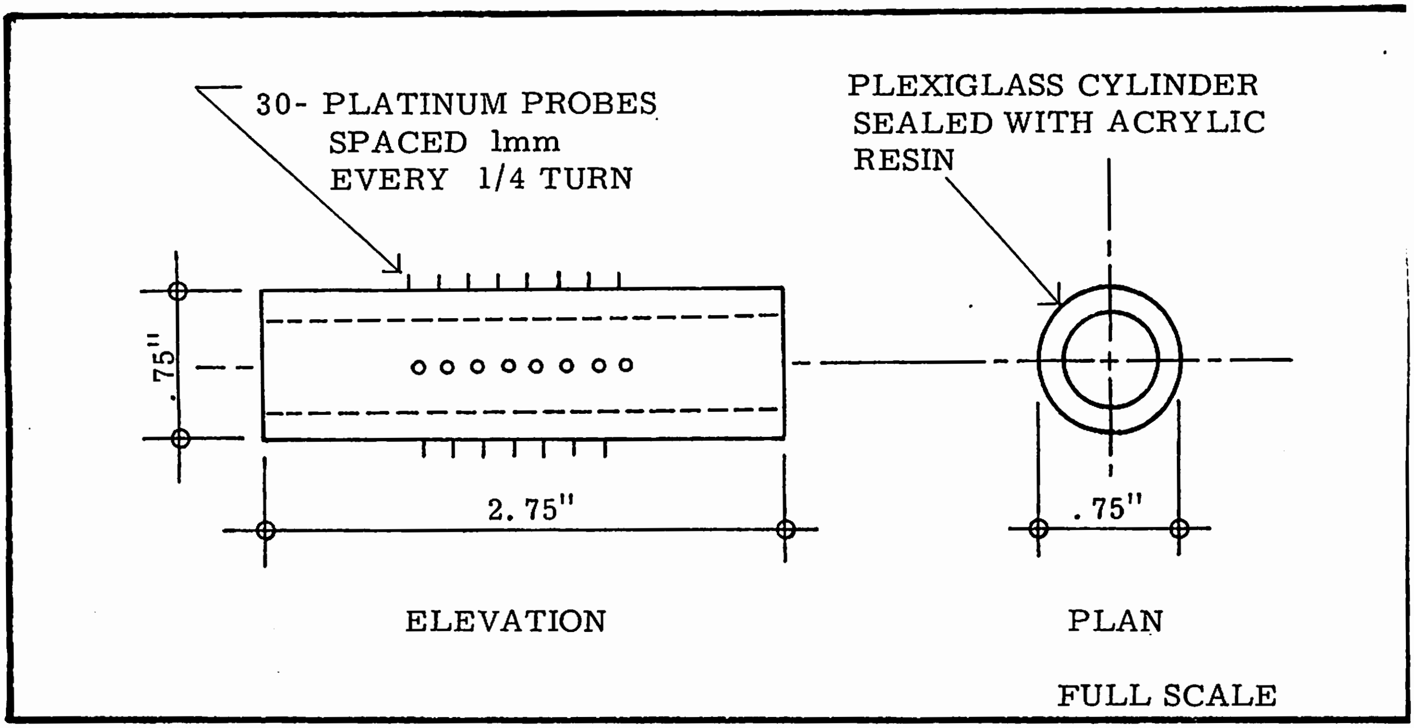

V_{in}
VOLTAGE
I_{in}
CURRENT
pH
CO_2
STRESS
SCT
A/D
CONVERTER
CONTROL
MICRO-
COMPUTER
RECORDER
D/A
CONVERTER
POWER
SUPPLY
CONTROL
POWER
SUPPLY
FOR
STRUCTURES
V_{out}
I_{out}

Fig. 42


30- PLATINUM PROBES
SPACED 1mm
EVERY 1/4 TURN
PLEXIGLASS CYLINDER
SEALED WITH ACRYLIC
RESIN
.75"
2.75"
.75"
ELEVATION
PLAN
FULL SCALE

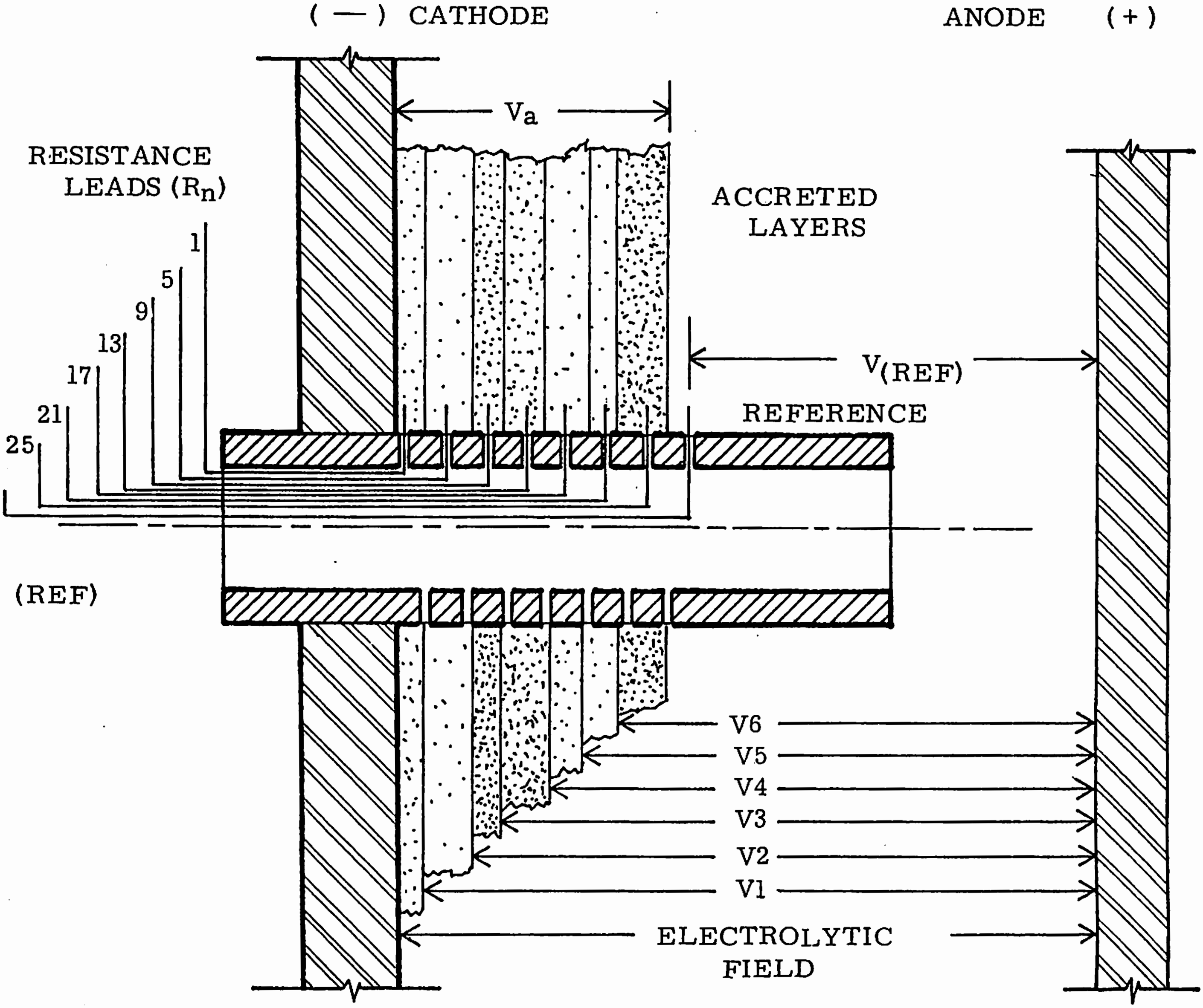

(—) CATHODE
ANODE (+)
Va
RESISTANCE
LEADS (Rn)
1
5
9
13
17
21
25
ACCRETED
LAYERS
V(REF)
REFERENCE
(REF)
V6
V5
V4
V3
V2
V1
ELECTROLYTIC
FIELD

Fig. A

Fig 43

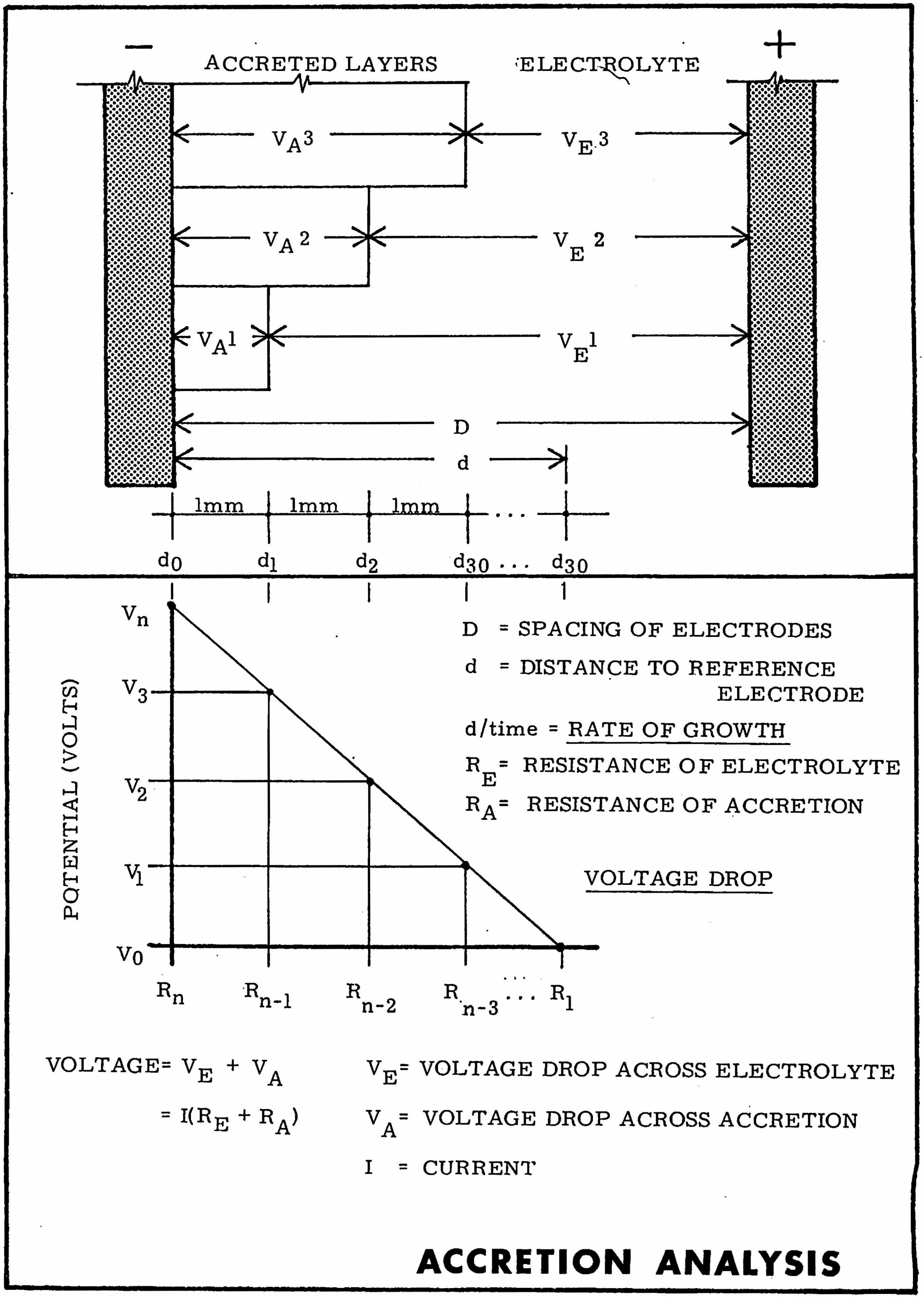

−
ACCRETED LAYERS
ELECTROLYTE
+
VA3
VE3
VA2
VE2
VA1
VE1
D
d
1mm
1mm
1mm
d0
d1
d2
d30 . . .
d30
Vn
V3
V2
V1
V0
POTENTIAL (VOLTS)
Rn
Rn-1
Rn-2
Rn-3 . . .
R1
D = SPACING OF ELECTRODES
d = DISTANCE TO REFERENCE ELECTRODE
d/time = RATE OF GROWTH
RE = RESISTANCE OF ELECTROLYTE
RA = RESISTANCE OF ACCRETION
VOLTAGE DROP
VOLTAGE = VE + VA
= I(RE + RA)
VE = VOLTAGE DROP ACROSS ELECTROLYTE
VA = VOLTAGE DROP ACROSS ACCRETION
I = CURRENT
ACCRETION ANALYSIS

Fig. 44

where R_E = Resistance electrolyte, R_a = resistance accreted materials, $_E$ = resistivity seawater, ρ_a = resistivity accreted material, A = area of current path, D_E = distance from cathode to anode, V = voltage, I = amperage, and a = thickness of accreted material.

The resistance of the cell over a period of time will be analyzed according to:

$$R(t) = \frac{V_E\ (t) + V_a\ (t)}{I} \approx \rho_E \left(\frac{D_E - a}{A}\right) + \rho_a (a) + \frac{a\ (t)}{A} \quad \text{(Equation 2)}^9$$

where V_E = voltage drop across seawater (electroyte) and V_a = voltage across accreted materials. Central to the DARS is the 6800 Motorola microprocessor which contains at present 1K memory, adequate to acquire and reduce the analog parameters previously discussed. The hardware was designed to accept more memory to total 64K to increase control over the electrochemical reactions through the voltage/amperage output. Software and other possible servo-controlled catalysts will be continually modified as we achieve greater understanding of present and potential electrochemical reactions.

9. Conclusion.

One major retarding circumstance must be mentioned: the Data Acquisition and Reduction System could not be built in time and is only now undergoing test runs for operation.

The feasibility of using electrodeposition on wire mesh formations in shallow water to construct artificial reefs was clearly proven, although forthcoming reports on observations by a marine biologist would establish this fact beyond doubt.

X-Ray diffraction analyses of more recent material samples of the architectural components and data obtained from mechanical tests for structural properties of electrodeposited materials are needed to assess the feasibility of the electrodeposition process to generate large architectural components.

Data from material test samples taken during the next year from all structures undergoing phasing processes will conclusively prove or disprove the feasibility to use phasing in order to achieve material properties suited for architectural and engineering applications.

During January 1977, further material samples for analyses from structures submerged in St. Croix will be taken and observations made. This report was written during the grant period. A forthcoming supplement will present further results and discussions.

X-Ray Diffraction Analysis of Chemical Compounds
Present in Samples Produced by
Electrolysis of Seawater

	Compounds and Percentages					
Sample #	Brucite $Mg(OH)_2$	Calcite $CaCO_3$	Aragonite $CaCO_3$	Halite NaCl	Quartz SiO_2	Other
1	80	T	12	T	--	8
2	60	7	17	5	7	4
3	58	2	7	3	4	26
4	40	1	8	2	2	47
5	69	1	24	5	1	--
7	44	T	18	15	--	23
10	77	6	5	12	--	--
11	57	3	25	10	5	--
17	79	T	15	5	--	1
19	83	1	12	4	--	--
20	50	T	15	T	T	35
21	60	3	6	15	--	16
22	50	T	6	T	--	44
23	60	T	5	T	--	35
24	70	9	7	14	--	--
25	45	T	16	--	1	38
26	90	T	10	T	T	--
27	70	T	15	15	--	--
28	73	T	7	20	--	--
30	65	4	18	11	2	--
31	61	1	5	20	T	13
32	40	1	3	2	T	54
33	50	4	10	--	1	35
34	80	2	10	2	1	5
35	35	1	15	4	2	43
36	79	3	5	2	--	11
37	70	1	15	10	1	3
38	50	3	26	8	--	13
42	50	1	25	--	T	24
44	40	4	17	5	1	33
46	68	3	5	8	1	15
47	80	T	4	T	T	16
49	65	T	5	--	--	30
54	80	5	6	2	1	6
60	61	2	10	12	1	14
66	60	3	4	10	--	23
67	68	5	12	4	4	7
73	70	4	25	--	--	1
79	79	3	18	--	--	--
82	88	4	3	5	T	--
86	69	--	20	10	--	1
87	50	4	32	2	3	9
88	89	T	8	3	--	--

Quantitative and Qualitative
Analysis Continued

Compounds and Percentages

Sample #	Brucite $Mg(OH)_2$	Calcite $CaCO_3$	Aragonite $CaCO_3$	Halite $NaCl$	Quartz SiO_2	Other
92	80	1	19	T	T	--
93	50	3	10	5	T	32
94	58	2	9	8	1	22
95	98	T	2	T	T	--
96	51	1	13	3	T	32
97	70	1	3	1	--	25
98	80	1	8	8	3	--
99	70	2	22	T	T	6
100	25	T	5	15	T	55
101	90	T	7	T	T	3

The figures above represent 100% of the sample. It should be noted, however, that there is an error factor of approximately ± 10%. More accurate testing is being conducted to provide an error factor of no more than ± 5%. Tests to date have been conducted on a Philips X-Ray Diffractometer, Chemical Eng. Lab, Dr. Steinfink, Director, Univ. of Texas at Austin. In the above analysis, T represents Trace element, or less than one percent.

11. References

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