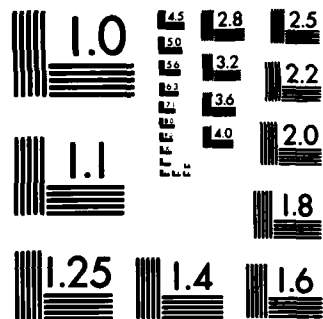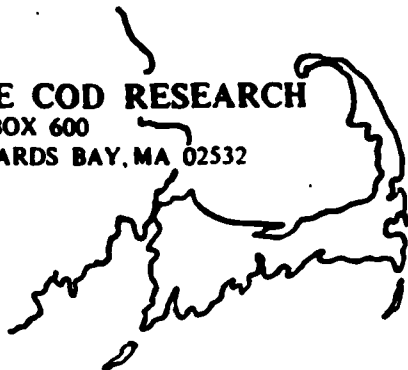MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

CAPE COD RESEARCH
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AD-A144 775

FINAL TECHNICAL REPORT

ARPA ORDER NO.: 4941/9-21-83   PROGRAM CODE NO.: 2Y145

CONTRACTOR: CAPE COD RESEARCH, INC.

CONTRACT NO.: N00014-84-C-0056 /ONR CONTRACT AMOUNT: $49,999.00

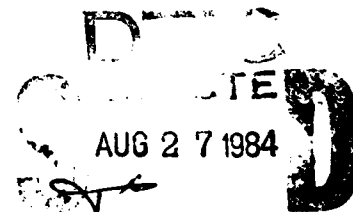EFFECTIVE DATE OF CONTRACT: 15 NOV 1983

EXPIRATION DATE OF CONTRACT: 14 MAY 1984

PRINCIPAL INVESTIGATOR: Dr. Myles Walsh

TELEPHONE NO.: (617) 759-5911

SHORT TITLE OF WORK: "Sea Water Rope Batteries"

REPORTING PERIOD: 15 November 1983 to 15 May 1984

AUG 2 7 1984

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EXECUTIVE SUMMARY

This research demonstrated the feasibility of supplying approximately 1 watt of electrical power for one year on the sea bed with a novel battery, the rope battery. The proposed battery would look very much like a small diameter wire rope, possibly hundreds of feet long. This unusual shape permits the rope battery to take full advantage of the vastness of the ocean floor and permits at great pressure the steady diffusion of reaction products away from the battery itself.

A sea water battery is described consisting of an inner bundle of coated wires which slowly corrode and an outer layer of fine wires which simultaneously provides strength, armor and surface area for slow hydrogen evolution. Two variations are examined. The fuse utilizes magnesium wires and burns slowly from the end. The rope utilizes lithium-zinc alloys and is slowly consumed along its entire length.
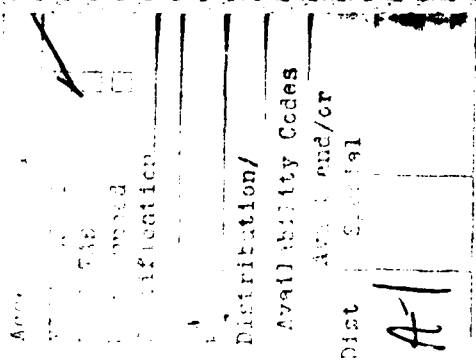
Ocean tests of sea water rope batteries are recommended.

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1.0 INTRODUCTION

This program explored the feasibility of supplying electrical power to devices on the sea bed for long periods of time with a novel sea water battery, the rope battery.

The proposed battery would look very much like a small diameter wire rope. This unusual shape permits the rope battery to take full advantage of the vastness of the ocean floor. When uncoiled, the rope battery allows for the steady diffusion of products of reaction away from reaction sites, thereby avoiding the many problems associated with more compact geometries.

The following design goals resulted from detailed discussions of battery requirements[   ]with NOSC, San Diego:

> Energy Out - One watt-year from converter at 4 V.
>
> Total Weight - 100# Maximum.
>
> Cost - $1,000 Maximum.
>
> Life - Ten year shelf life.
>
> Rating - 1.25 watts out of battery at end of life.
>
> Decay -After one year, voltage exceeds 0.65 V.
>
> Duty Cycle - Steady drain.
>
> Volume - Must be compact on storage.

No available battery meets all of these requirements. The better available choice is probably a lithium thionyl chloride battery which for this mission would cost between $5,000 and $10,000. The size of this battery would pose a safety hazard, especially in the event of fire or accidental damage to the pressure case.

This research was funded through the 1983 DoD SBIR program which is structured in three phases:

> I. A three-quarter man-year effort over a four month period to determine, insofar as possible, the scientific feasibility of the sea water rope battery design concept,
>
> II. A two man-year effort over a period of eighteen months to evaluate prototypes in the ocean, and
>
> III. A non-Federal program to pursue commercial applications of this R&D.

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This report summarizes the Phase I research performed to demonstrate the feasibility of the proposed approach.

2.0 BACKGROUND

An intensive literature search by DTIC failed to disclose any references to low-drain, long-life sea water batteries. The entire thrust of the R&D efforts in this area appear to be focused on high-drain, short-life batteries.

In the absence of literature, the following general conclusions were reached after discussions with NOSC:

-Although multicell configurations without an inverter are a possible approach to the problem, the primary thrust of the effort is to develop a single cell sea water battery.

-Preliminary testing should be in filtered natural sea water rather than in ASTM sea salt mixed in deionized water.

-Effects which are normally negligible may be important. Of special concern are the effects of hydrogen embrittlement on the structural integrity of the operating anode, chunking and the negative difference effect.

-Pure zinc, aluminum and magnesium look like a good place to start the search for an anode material which meets the program goals.

-Tests at about $4^\circ C$ and $20^\circ C$ should be sufficient for this feasibility demonstration.

3.0 DESIGN CONCEPTS

Storage considerations and design simplicity dictated that only batteries with a constant cross section were considered.

Two design concepts were explored; for simplicity, they were called the fuse and the rope.

The "fuse" electrochemically burns from the bitter end at high local current density towards the device being powered. Here, the metal is sealed on the sides by a coating which protects the sides from the chemical corrosion of humid air for at least ten years and protects the metal on immersion in salt water for at least a year. The feasibility of this approach hinged on discovering a mechanism for rapidly destroying this coating as a direct result of the electrochemical consumption of the metal.

The "rope" electrochemically burns along the entire battery length at very low local current density. Here, the metal wire, ribbon, or bundle of wires is only partially protected from the salt water

by an insulating polymer coating. The feasibility of this approach hinged on developing an alloy with a unique combination of high coulombic efficiency in salt water at low current density (less than 1 mA/cm^2) and output voltage at this current density versus a hydrogen evolution cathode of in excess of 0.6V.

4.0 THE CATHODE

Elementary calculations of the weights of the traditional sea water battery cathode materials suggest the use of surfaces which consume any available oxygen and then evolve hydrogen. This design choice results in the simplest, cheapest, and lightest possible cathode for this application.

In order to permit the quantitative prediction of the performance of rope battery cathodes of arbitrary shape, a mathematical model was developed which accurately and quantitatively predicts the performance of long thin supported metal surfaces performing electrochemical reactions in cold sea water.

The model assumes that locally the electrochemical reaction is of the general form:

$$\text{Current Density} = i_o \sinh(V/E_o)$$

where i_o and E_o can be directly measured on small surfaces immersed in sea water. For a long thin cathode structure of uniform cross sectional area A, electrical conductivity K, and perimeter P, the current collected at one end due to this electrochemical reaction was predicted as:

$$\text{Current Collected} = 2(Pi_o E_o AK)^{1/2} \sinh(C/2E_o)$$

where C is the cathode polarization. The total length of the structure does not appear in this expression because it has been assumed that the length squared exceeds $KE_o A/i_o P$.

Experiments were performed to demonstrate the validity of the assumptions and the predictions resulting from this model. The structure chosen for this demonstration was a very fine·nickel wire (0.127mmD) whose surface had been activated by immersion in acidic palladium chloride.
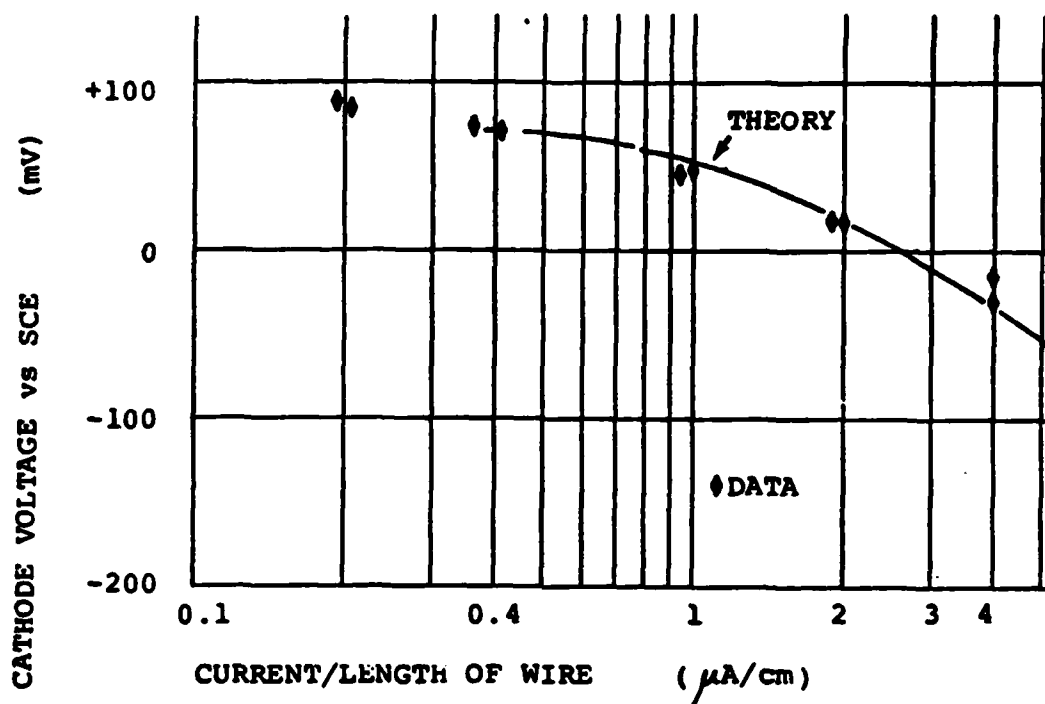
Assuming that the performance curve is of the form:

Current/Length = Pi_o sinh(V/E_o)

where for this case of oxygen consumption in 5°C natural sea water on 0.127mm palladized nickel wire the data on a 32cm long section of wire best fit:

Current/Length = 3.5μA/cm sinh(V/120mV)

where V = Local Polarization = +88mV -(Voltage vs SCE)

FIGURE 1 - Calibration Data for Oxygen Consumption on Wire Cathode

Figure 1 illustrates that in cold natural sea water, oxygen
consumption at this wire cathode locally follows a rate law which
closely approximates the assumed form. (Oxygen consumption rather
than hydrogen evolution takes place in cold surface sea water at
low drain rates.) These data permit quantitative prediction of the
behavior of longer wire cathodes. Specifically the model
predicted that for wires with this performance level and geometry
that for lengths longer than 7.5m the current produced should be
independent of further length increases and that:

$$\text{Current Collected} = 2.6\text{mA } \sinh(C/240\text{mV})$$

In order to check these two predictions, thirty meters of 0.24cm
in diameter AZ 61A wire were stretched in a straight line about 30
cm below the surface of natural sea water whose temperature was
4°C. This wire served as the anode for the catalyzed wire
cathode which consumed dissolved oxygen at low current densities.

The performance of this fine wire was measured by connecting one
end through an ammeter and a variable resistor to one end of the
magnesium wire. The voltage of the cathode at the connection
point and at the bitter end were measured with respect to standard
calomel electrodes (SCEs).

The wire cathode was stretched parallel and approximately 10cm
from the anode. Experimental independent variables were typically
wire length and current.

For a constant 3mA current, the voltages at the ends of the wire
cathode varied as follows with wire length:

Wire Length, m	2.3	5.0	8.6	15	24
Cathode Voltage,mV	-99	-56	-56	-56	-56
End Voltage,mV	-63	+03	+35	+49	+75

These data illustrate that fine wires can generate substantial
currents and that ohmic losses in the wire restrict the effective
useful length of the wire. They further illustrate that the model
prediction for these conditions of an effective length of 7.5m is
not unreasonable.

Performance curves for the wire cathode extended 8.6, 15 and 24m
were taken. These data are shown in Figure 2 and compared with
the a priori prediction of the model. Based on the excellent
agreement between theory and experiment, we believe that we can
use these relationships to accurately predict the performance and
decay of rope battery cathodes of uniform cross section but
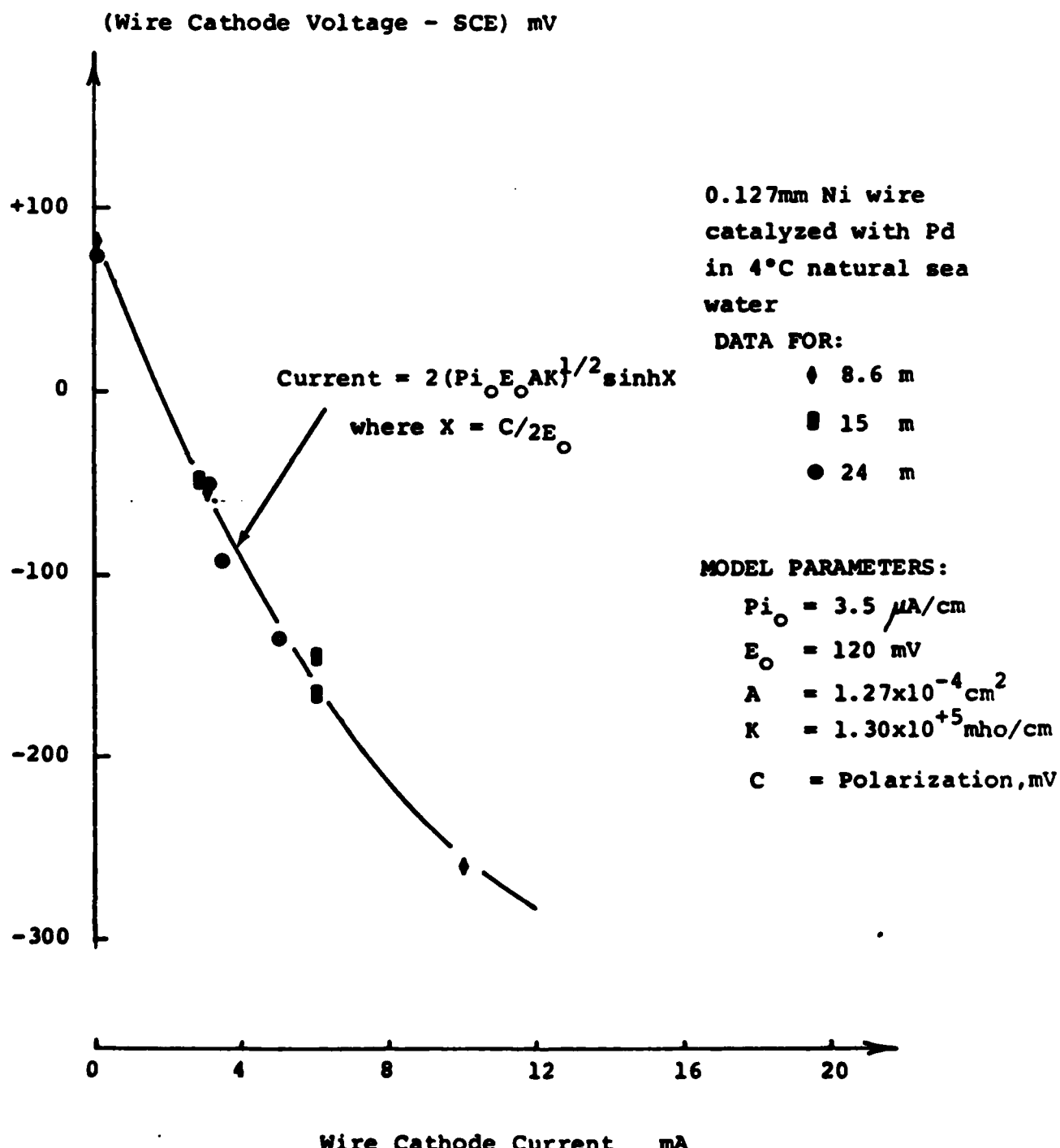arbitrary shape.

(Wire Cathode Voltage - SCE) mV

Current = $2(Pi_oE_oAK)^{1/2}sinhX$

where $X = C/2E_o$

0.127mm Ni wire
catalyzed with Pd
in 4°C natural sea
water

DATA FOR:

◆ 8.6 m

▮ 15 m

● 24 m

MODEL PARAMETERS:

Pi_o = 3.5 μA/cm

E_o = 120 mV

A   = $1.27 \times 10^{-4} cm^2$

K   = $1.30 \times 10^{+5}$ mho/cm

C   = Polarization, mV

Wire Cathode Current   mA

FIGURE 2 - Comparison of Cathode Theoretical Model With Data

5.0 ANODE MATERIALS AND ELECTROCHEMICAL RESULTS

The mass and volume of anode material required to achieve the mission goal of 1.25 watt-years is fixed by thermodynamic, physical and electrochemical factors. The results of calculations using typical and optimistic values for these factors produced the following table:

Alloy Type	Required Mass, kg		Required Volume, l	
	Minimum	Maximum	Minimum	Maximum
Zinc	18	22	2.5	3.0
Aluminum	5	8	2.5	4.2
Magnesium	6	10	3.4	5.6

These calculated estimates are in line with earlier estimates by NOSC and demonstrate that the proposed battery, if compactly stored, could occupy a volume of about 4 liters. That this result is independent of choice of anode material is an accident and does not result from any fundamental principle.

The following table summarizes the predicted length and diameter of a rope battery in which the metal occupies about 60% of the volume of the structure.

Length, m	10	20	40
Diameter, cm	2.9	2.1	1.5

Because this battery would contain numerous wires, each carrying a fraction of the total current of about one ampere, the ohmic losses in the metal are negligible. For the worst case of a "fuse" configuration using zinc, this loss amounts to only 3mV for a ten meter battery.

6.0 ANODE CHOICES

The limited nature of this Phase I effort greatly restricted the experimental latitude to readily available alloys and to a very limited number of lithium-zinc mixtures which were made pyrometallurgically.

Tests on magnesium alloys were limited to MTA (magnesium with 7%Tl and 5% Al), 99.98% magnesium and AZ 61A (magnesium with 6%Al and 1%Zn).

Tests on aluminum were confined to 99.998% aluminum wire.

Numerous tests were made in natural sea water both at atmospheric pressure and at pressures up to 1.5 MPa.

In general, these results confirmed the experimental work of others. In summary, it appears that the magnesium alloys are

suitable only for the "fuse" configuration where the burning of
the end continuously exposes more of the magnesium. In a fuse
battery the sludge is left behind because the reaction is locally
performed at high rate. MTA produces a sludge which is much more
basic than pure magnesium or AZ 61A. None of these alloys appear
to be especially ductile and this will restrict the diameter of
the spool on which the rope battery can be coiled to greater than
a meter.

Pure aluminum performs very poorly at low current density and in
the absence of a source of base. Aluminum could only be used in
cold natural sea water if it were alloyed with an alkali metal.
Our attempts to make Li-Al alloys were unsuccessful because of the
high eutectic temperature and the very corrosive nature of lithium
vapors above 700°C. However, there is, in principle, no reason
that these alloys could not be made and tested.

Zinc alloys have the advantage of great stability for long periods
of time in cold sea water, have soluble discharge products and are
sufficiently ductile to be formed into wire ropes. However, the
output voltage of pure zinc/hydrogen evolution batteries is not
likely to exceed 0.6V. This places a large burden on the
converter circuitry. Thus, the feasibility of alloying zinc with
small amounts of lithium in order to achieve somewhat higher
voltages without loss of the advantages of zinc alloys was
studied.

The following alloys were made pyrometallurgically and tested with
respect to a SCE in room temperature, natural sea water:

| Alloy Composition in Weight % Li | Voltage vs SCE in 19 C sea water at | | | |
	0 mA/cm^2	0.1 mA/cm^2	0.5 mA/cm^2	1.0 mA/cm^2
0.00 initial	-1022mV	-1010mV	-1004mV	- 994mV
0.00 final	-1022mV	-1000mV	-1002mV	- 996mV
0.50 initial	-1366mV	-1355mV	-1354mV	-1348mV
0.50 steady	-1366mV	-1356mV	-1320mV	-1254mV
1.50 initial	-1418mV	-1417mV	-1406mV	-1400mV
1.50 steady	-1368mV	-1360mV	-1280mV	-1250mV

These data illustrate that the addition of small amounts of
lithium to zinc greatly improves the energy density of the couple
at low current density. The design operating current density of a
zinc rope battery to produce 1.4A for a year is about 0.5mA/cm2

Thus these results are extremely promising and should be followed
up with more detailed tests in any future effort requiring low
current densities for long periods of time in natural sea water.

The 0.5% and the 1.5% alloys show remarkable stability in cold sea

water. At current densities of above 1mA/cm^2 the surface becomes covered with a thin white film of what is probably magnesium hydroxide. This film does not form in 3%NaCl. This film tends to passivate the surface and performance above 1mA/cm^2 in natural sea water appeared no better than that achieved with pure zinc. 3.0% and 5.0% lithium alloys were also made but the performance was actually worse than the 1.5% alloy. These alloys were much less stable in natural sea water and a film of hydrogen appeared to cover the exposed surface of the 5.0% alloy.

These results lead to the following two conclusions:

-pure zinc wire could be employed for preliminary ocean tests of the rope concept, with the understanding that output voltages in the future can be substantially raised by purchasing, on special order, zinc-lithium alloy wire.

-and magnesium AZ61 is the better choice of the active alloys for preliminary ocean tests of the fuse concept, because it is commercially available in wire form and because it is electrochemically very active at high drain.

7.0 FEASIBILITY DEMONSTRATION FOR THE ROPE

On paper, the rope battery appears quite feasible, especially if the performance of zinc can be raised slightly through alloying.

Consider a 7x7 wire rope composed of forty nine 3.2 mm zinc wires, each 10 meters long. Each of these wires is insulated from the next by braided fiberglass sleeving. Bundles of seven of these insulated wires are protected by catalyzed tinned copper tubular braid (MIL QQ-B-575) which has a nominal ID of 11/64". These seven bundles are wound together into a wire rope.

The braid also serves as the cathode. Experiments were performed on a commercial braid of this type (Belden #8661) and the parameters for the cathode model directly measured as:

$$AK = 2.1 \times 10^{+4} \text{mho-cm}$$
$$Pi_o = 0.03 \text{ mA/cm of braid}$$
$$E_o{}^o = 50 \text{ mV}$$

The cathode model predicts that for seven strands of cathode surface area the current collected should be:

$$\text{Current Collected} = 2.5A \sinh(C/100mV)$$

The zinc surface area for this 10 meter battery will begin life at about 5000 cm^2 and end life at about 1000cm^2. Thus current densities will never exceed 2 mA/cm^2. At this low current density, a performance level of -1.0V vs SCE is anticipated. The predicted battery performance becomes:

$$\text{Battery Voltage} = 0.760V - (\text{Battery Current})(0.04 \text{ ohms})$$

This battery has a predicted life of over one year at a steady drain of 1.25 watts.

8.0 FEASIBILITY DEMONSTRATION OF THE FUSE

The fuse is attractive because magnesium alloys are already well developed to operate at high local current density at potentials well below 1V. Their use, however, required the development of a a composite coating which protects the metal but rapidly disintegrates as a result of the electrochemical reactions at the end.

Figure 3 illustrates the concept developed after much trial and error for solving this problem. Essentially the magnesium wire is masked lengthwise with precision slit tape (Bishop Graphics, Inc.) and then coated with two coats of epoxy-polyamide varnish designed to meet MIL-C-22750C (Versamid 115-173 by Henkel Corporation). The dry coating is about two mils thick and withstands cold sea water for periods greater than one year. The precision slit tape is now peeled away to leave a narrow strip of exposed magnesium. This surface is roughened by etching and then filled with silicone rubber monomer dissolved in acetone. The acetone evaporates and the silicone rubber bonds to the exposed magnesium but not to the epoxy-polyamide.

Preliminary testing of this concept shows that magnesium wire coated in this manner burns from the end at an angle of about 15°. While further work is needed to study long term stability of this composite coating, this approach is feasible.

Design of a fuse battery would be very similar to that of a rope battery. The 7x7 configuration using composite coated AZ 61A instead of zinc would appear to be a good starting point. This fuse battery for 1.25 watt-years of life would also be about 10 meters long and would weigh about 70 pounds (30kg).

9.0 CONCLUSIONS AND RECOMMENDATIONS

Relatively inexpensive, reliable sea water batteries for deep sea surveillance and autonomously powered fiber optic repeaters appear feasible, but further ocean testing is needed to verify predicted performance levels and to better define the problems associated with the real environment.

While a wire rope about ten meters long appears to be the optimum shape, thinner ropes up to seventy meters long may be easier to rapidly uncoil over the side.

Two approaches are recommended for future testing; namely, a fuse

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based on AZ 61A coated with a composite coating and a rope based on zinc wire.

It is further recommended that Zn-Li-Pb alloys be studied for use as low-drain, long-life anode materials. A substantial improvement in output voltage is possible and these alloys appear to have considerable stability in natural sea water.

Improvements in the efficiency of the hydrogen evolution surface would be most desirable. Further work, especially with Ni-Mo coatings, is recommended.
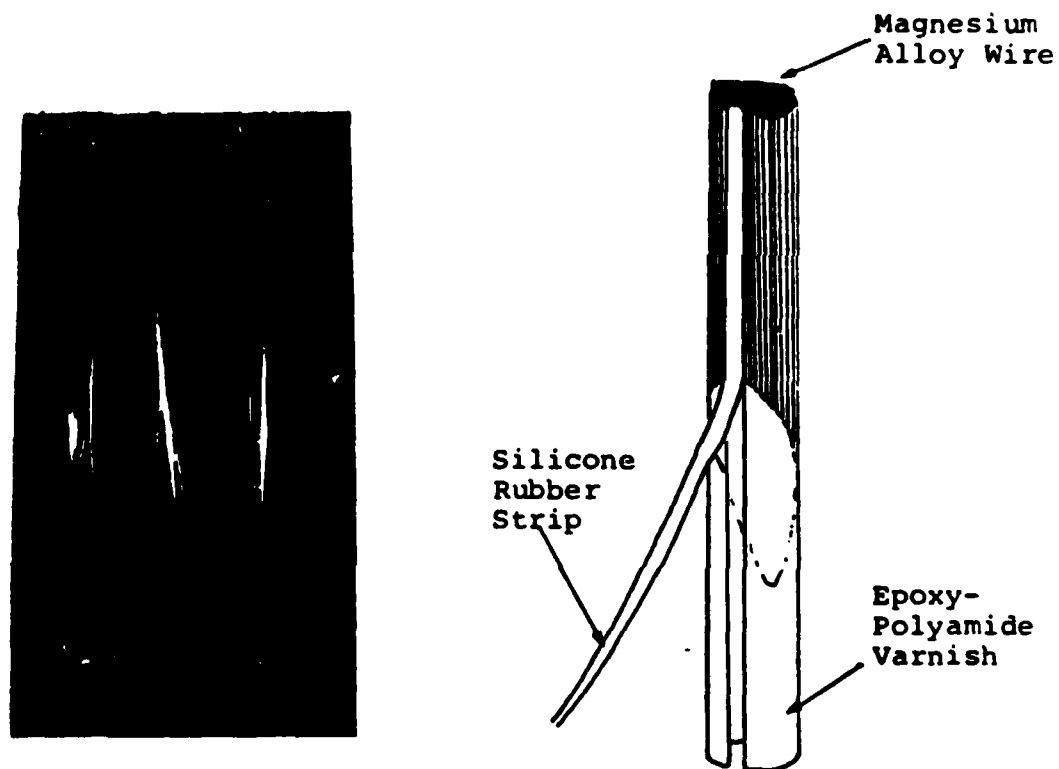

FIGURE 3 - Composite Coating for Fuselike Behavior

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