

AD-A070 860

CIVIL ENGINEERING LAB (NAVY) PORT HUENEME CA
DEVELOPMENT OF SUPERCORRODING ALLOYS FOR USE AS TIMED RELEASES --ETC(U)
MAR 79 S A BLACK
CEL-TN-1550

F/G 11/6

UNCLASSIFIED

NL

1 OF 1
AD
A070860



END
DATE
FILMED

8-79
DDC

LEVEL II

12

Technical



Note

TN no. N-1550

title: DEVELOPMENT OF SUPERCORRODING ALLOYS FOR USE AS
TIMED RELEASES FOR OCEAN ENGINEERING APPLICATIONS

author: S. A. Black

date: March 1979

sponsor: NAVAL MATERIAL COMMAND
Washington, DC 20360

program nos: ZF61-512-001-078

DDC
R
JUL 6 1979
D

A 070860

DDC FILE COPY



CIVIL ENGINEERING LABORATORY

NAVAL CONSTRUCTION BATTALION CENTER
Port Hueneme, California 93043

Approved for public release; distribution unlimited.

79 07 05 087

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TN-1550	2. GOVT ACCESSION NO. DN887002	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DEVELOPMENT OF SUPERCORRODING ALLOYS FOR USE AS TIMED RELEASES FOR OCEAN ENGINEERING APPLICATIONS		5. TYPE OF REPORT & PERIOD COVERED Final; Oct 1977 - Sep 1978
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) S. A. Black		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS CIVIL ENGINEERING LABORATORY Naval Construction Battalion Center Port Hueneme, California 93043		10. PROGRAM ELEMENT PROJECT TASK AREA & WORK UNIT NUMBERS 62766N; ZF61-512-001-078
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Material Command Washington, D.C. 20360		12. REPORT DATE March 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) CEL-TN-155A		13. NUMBER OF PAGES 36
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. (12) 40p.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) (9) Final rept. Oct 77 - Sep 78		
18. SUPPLEMENTARY NOTES (16) F61512 / (17) ZF61512401		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Corrosion, magnesium, seawater reaction, gas generators, buoyancy gas generators, hydrogen generators, heat source, corrodable links.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → A family of supercorroding magnesium alloys that react spontaneously and vigorously with seawater have been developed at CEL. Supercorroding alloys are so named because of their high corrosion rate in seawater. Investigations of several different alloy formulations show that the alloys can be useful for generation of hydrogen for ocean buoyancy, fuel for thermodynamic engines and fuel cells, production of heat for divers and as self- → (continued)		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

391 111

JOB

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Continued

destructing links for retrieval of oceanographic instruments.

Supercorrodng alloys with magnesium as the anode material and with several different cathode materials were fabricated and tested to determine mechanical and corrosive characteristics. Alloys with 5 atomic percent iron cathode produce 950 ml of hydrogen per gram of alloy and 13.3 K joules of heat per gram. One gram is over 90% reacted within one minute from immersion. Compacting and sintering produces samples with 9 ksi shear and tensile strengths. Corrosion rates for sintered samples are approximately 9×10^{-3} inches per hour. Alloys with other cathode materials and different levels of cathode content were fabricated and tested. Sufficient data is available on several different formulations of supercorrodng alloys to permit preliminary selection for specific applications.

.009

Library Card

Civil Engineering Laboratory
DEVELOPMENT OF SUPERCORRODING ALLOYS FOR USE
AS TIMED RELEASES FOR OCEAN ENGINEERING APPLI-
CATIONS (Final), by S. A. Black
TN-1550 36 pp illus March 1979 Unclassified

1. Corrosion 2. Seawater reaction I. ZF61-512-001-078

A family of supercorrodng magnesium alloys that react spontaneously and vigorously with seawater have been developed at CEL. Supercorrodng alloys are so named because of their high corrosion rate in seawater. Investigations of several different alloy formulations show that the alloys can be useful for generation of hydrogen for ocean buoyancy, fuel for thermo-dynamic engines and fuel cells, production of heat for divers and as self-destructing links for retrieval of oceanographic instruments.

Supercorrodng alloys with magnesium as the anode material and with several different cathode materials were fabricated and tested to determine mechanical and corrosive characteristics. Alloys with 5 atomic percent iron cathode produce 950 ml of hydrogen per gram of alloy and 13.3 K joules of heat per gram. One gram is over 90% reacted within one minute from immersion. Compacting and sintering produces samples with 9 ksi shear and tensile strengths. Corrosion rates for sintered samples are approximately 9×10^{-3} inches per hour. Alloys with other cathode materials and different levels of cathode content were fabricated and tested. Sufficient data is available on several different formulations of supercorrodng alloys to permit preliminary selection for specific applications.

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Table of Contents

	<u>Page</u>
INTRODUCTION.....	1
BACKGROUND.....	1
SUPERCORRODING ALLOY FORMATION.....	3
TEST PROGRAM.....	4
Test Procedure.....	6
RESULTS.....	9
Powdered Samples.....	9
Sintering and Compaction.....	12
Alternate Cathode Compacts.....	20
Surface Corrosion Rate.....	24
Discussion.....	25
APPLICATIONS.....	28
SUMMARY AND CONCLUSIONS.....	29
REFERENCES.....	30

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or special
A	

INTRODUCTION

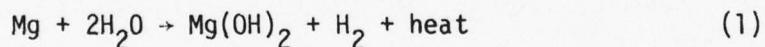
The Civil Engineering Laboratory (CEL) has developed a family of supercorroding magnesium alloys that react spontaneously and vigorously in seawater. The alloys predictably self-destruct by corrosion processes and produce usable quantities of heat and hydrogen gas. This research was performed with Independent Exploratory Development funds and conducted during FY-78.

Discovery of the alloys evolved during research aimed at utilizing the accelerated corrosion of magnesium in the form of a short-circuited seawater battery to produce heat for military divers¹. Although the alloys were originally² conceived as an efficient heat and hydrogen gas source, early research² indicated other potential applications. The research described herein was conducted to provide further information on the mechanical strength, corrosion properties, and self-destructing predictability of the alloys in compacted powder form for possible use as oceanographic timing and activating devices. Such devices, usually referred to as corrodable links, are useful for recovery of ocean installed instruments, shedding of protective shrouds, delayed activation of mechanical or electrical functions, and scuttling or discarding appendages underwater.

Various cathodic materials in powdered form were mechanically alloyed with magnesium, and evaluated to determine the reaction rate in seawater. Samples of each of the powdered alloys were compacted, sintered and tested to determine their mechanical properties and corrosion characteristics. The goal was to obtain preliminary information on the alloys for use in the design of underwater corroding links.

BACKGROUND

In general, magnesium reacts with seawater according to the formula:



The reaction has a theoretical energy density of 14.9 kJ/kg (1885 W-hr/lb)³ and produces 1.0 liter of hydrogen gas per gram of magnesium (14.8 ft³/lb) at STP.

By itself, magnesium corrodes slowly in seawater because of low local potential differences within the magnesium. When a suitable cathodic material is brought into close proximity and electrically connected to the magnesium, an electrochemical cell (battery) is formed, and the corrosion reaction proceeds rapidly. The dual-plate cell shown in Figure 1 represents this configuration. When the electrical load is replaced by a short circuit, the reaction proceeds even more rapidly, and the cell efficiently produces heat and hydrogen gas. The rate of reaction has been shown to be a function of (1) electrolyte temperature, pH, salinity, and density, (2) anode-cathode

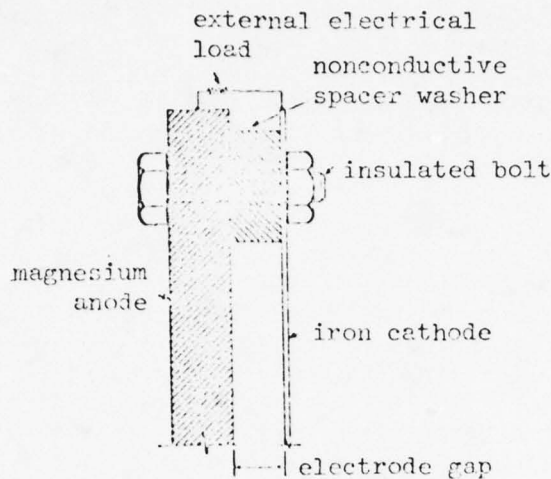


Figure 1. Dual Plate Cell Arrangement. For maximum heat or hydrogen gas production the electrical load is replaced by a short circuit.

plate spacing, and (3) ambient pressure^{1,3}. The basic problem with the dual plate cell is that the power decays as magnesium is consumed. That is, as the magnesium plate becomes thinner the electrode gap increases, and subsequently the internal cell resistance increases and power decays.

Supercorrodng alloys were conceived as a potential solution to eliminate the dual plate power decay. In the early developmental stage powdered metal mini-cells were fabricated by ball-milling (using lightweight ceramic balls) a mixture of iron and magnesium powders. The milling produced composite powdered particles with iron bonded to the magnesium surface.^{3,4,5,6}

Tests showed that rapid corrosion rates were achieved with the mini-cells, but that the reaction efficiency (percentage completion) was low. The accelerated reaction rate was attributed to the close proximity of the anode-cathode pairs and the relatively large cathode surface area. The low efficiency was attributed to poor electrical contact and low mechanical strength of the Mg-Fe particle bond.³ Hydrogen bubble formation in gaps at the bond surface between the iron and magnesium particles coupled with weak bond strength resulted in many of the bonds breaking before the magnesium particle was completely reacted.

A process called mechanical alloying has been used to develop new materials which overcome the problems that limited the mini-cell's efficiency. The process was developed by the International Nickel Company (INCO) for forming alloys not possible by conventional

techniques.⁷ For example, using conventional alloying methods less than 1% iron can be dissolved in magnesium; the INCO process can alloy* virtually any amount of iron that is desired. Samples of powdered alloys have been fabricated with as much as 20% iron content. Tests have shown that magnesium-based alloys from this process react several orders of magnitude faster and more efficiently than the mini-cells.² Because of their extremely rapid corrosion rate and high reaction efficiency these materials were named supercorroding alloys.

SUPERCORRODING ALLOY FORMATION

Supercorroding mechanical alloys in powdered form are produced from powdered constituents using a high energy ball mill. The mill containing the powders consists of a vertical cylindrical drum with a series of internal horizontal impellers. The impellers are attached to a shaft which is turned externally by an electric motor. Turning the impellers agitates steel balls inside the drum. Every time steel balls collide, powder particles are trapped between them. The force of impact creates atomically clean surfaces on the trapped particles and welds them together. An inert atmosphere (CO₂) prevents reoxidation of the surfaces. By repeated flattening, fracturing and rewelding supercorroding alloys are formed.

The tendency of powdered particles to cold-weld together predominates during the early stage of the process. As milling continues, the particles get harder and more brittle. Eventually a balance results between welding and particle fracturing. Continued milling refines the particles' characteristic layered structure. An example of this structure is shown in the photomicrograph in Figure 2. The gray areas are iron; the thickness of each layer in the composite particle decreases from repeated impacts. A more complete description of the INCO process for fabricating mechanical alloys is given in reference 7.

*The term alloy or supercorroding alloy used herein denotes a homogeneous mixture of minute galvanic cell particles which have strong bonds between micro-cell constituents and intimate atomic-level electrical contact.

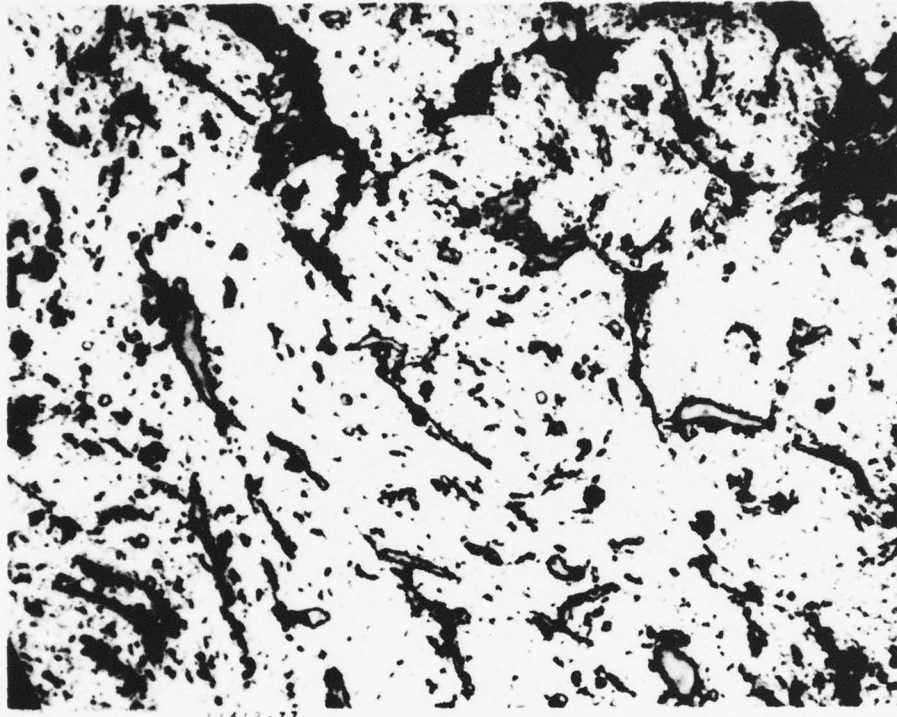


Figure 2. Photo micrograph of mechanically alloyed magnesium-iron particle magnified 500x contains 5 atomic percent Fe. Iron appears as the dark gray areas within the magnesium matrix.

TEST PROGRAM

The compositions of the alloys used to fabricate test samples and for subsequent evaluation were selected from the results of previous research.² The objective of this selection process was to obtain a range of reaction rates from hours to minutes. Prior to the manufacture of the final powdered alloys, one specific alloy was produced using several different milling parameters (e.g., milling time and milling energy). These samples of this particular alloy were then tested to determine which set of milling parameters produced the optimum (most rapid) reaction rate and highest reaction efficiency. Because resources did not allow a similar investigation to be conducted for each of the other alloys, this set of milling parameters was used in the manufacture of all the remaining powdered alloys. The list of powdered alloys thus produced is presented in Table 1.

Table 1. Characteristics of Prepared Magnesium Based Supercorroding Alloy Powders.

<u>Cathode Material</u>	<u>Cathode Content (Atomic Percent)</u>	<u>Apparent Density (g/cc)</u>
Fe	.7	.63
Fe	1.6	.63
Fe	4.3	.69
Fe	9.8	.79
Fe	19.0	.90
Ni	4.4	.70
Ti	4.6	.66
Cu	4.3	.71
C	4.3	.59

After fabrication of these powders, samples of the Mg-9.8 Fe* alloy were compacted in the form of barstock (1.07 cm square by 6.5 cm long) and discs (1.27 cm dia by .32 cm thick). The compaction was performed at four different pressures. Several of the 550 M pascal (40 TSI) compacted samples were sintered under various conditions of time and temperature. Testing of these Mg-9.8 Fe samples was used to determine the sintering conditions for optimum reaction rate and efficiency and also the effect of compaction pressure on the reaction. Optimum sintering conditions and 550 M pascal (40 TSI) compaction pressure were then used to prepare barstock and disc samples from the alloys listed in Table 1.

Final testing of the alloys shown in Table 1 was conducted as shown below:

	<u>Reaction Rate</u>	<u>Reaction Efficiency</u>	<u>Time to Failure</u>	<u>Surface Corrode Rate</u>	<u>Mechanical Strength</u>
Powders	x	x			
Barstock			x	x	x
Discs	x	x			

*Mg-9.8 Fe represents a supercorroding alloy with magnesium as the anode material and 9.8 atomic percent iron as the cathode material.

Test Procedure

The corrosion performance of supercorroding alloys was evaluated by collecting the hydrogen produced from the seawater reaction (equation 1) of both powders and disc samples and comparing the results to theoretical gas production. The theoretical volume of hydrogen liberated in the reaction for each gram of magnesium consumed is approximately 1.0 liter at 23.7°C and one atmosphere (15.9 ft³/lb. mg at 75°F).

The experimental arrangement for powdered alloy and compacted disc tests is shown in Figure 3. Test samples were weighed on an analytical balance and placed in a reaction flask in a constant temperature bath. Fifty milliliters of seawater were transferred from a second flask to the reaction flask. The hydrogen produced by the reaction was then collected in an inverted graduated cylinder. Hydrogen evolved as a function of time was visually observed as water displaced in the graduated cylinder. All data were manually recorded.

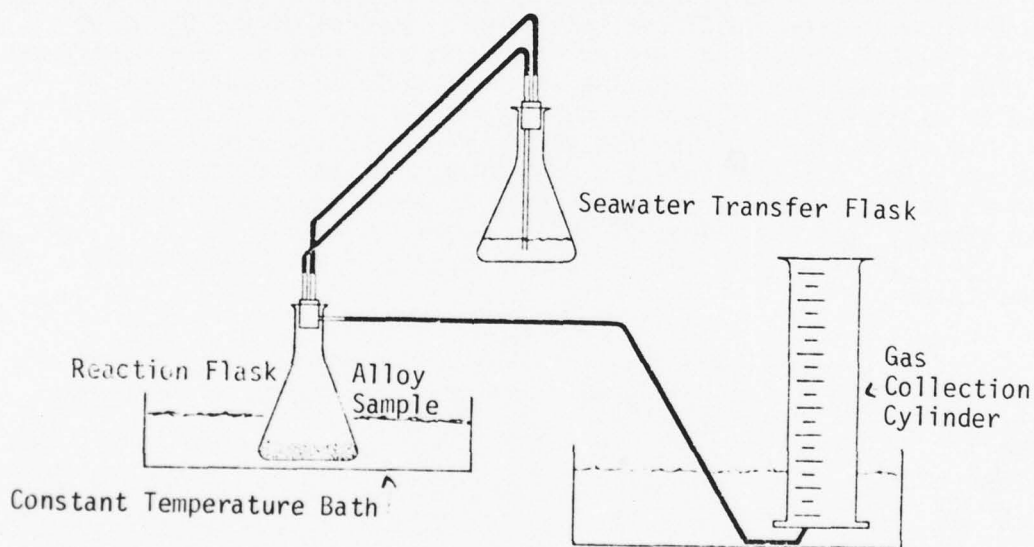


Figure 3. Apparatus for measuring hydrogen produced by powdered and disc samples of supercorroding alloys. The dual hoses between reaction and seawater flasks allow transfer of fluid between flasks.

Barstock samples were tested by INCO to determine transverse rupture (tensile strength) and shear strength. Transverse rupture tests were performed in accordance with ASTM specification B 578-70 except that the specimen thickness was 1.07 cm instead of .64 cm. Shear strength was determined according to ASTM specification B 565-72.

Barstock samples were tested to determine the time to corrosion failure under a fixed tensile load. The samples were drilled at each end to accept nylon fishing line. Except for a .6 cm wide circumferential strip about the center of each bar the surfaces were coated with epoxy cement to preclude seawater contact. A prepared sample is shown in Figure 4. Each sample was placed in a seawater tank with a 5.33 kg tensile load applied to the bar through the fishing line via a weight and a series of pulleys as shown in Figure 5. A trip line, which would activate when the bar corroded through and the ends separated, was attached to an electrical switch on a clock. The clock was manually started when the bar was immersed in seawater and stopped automatically when the ends of the bar separated. In this manner the time to failure was recorded.

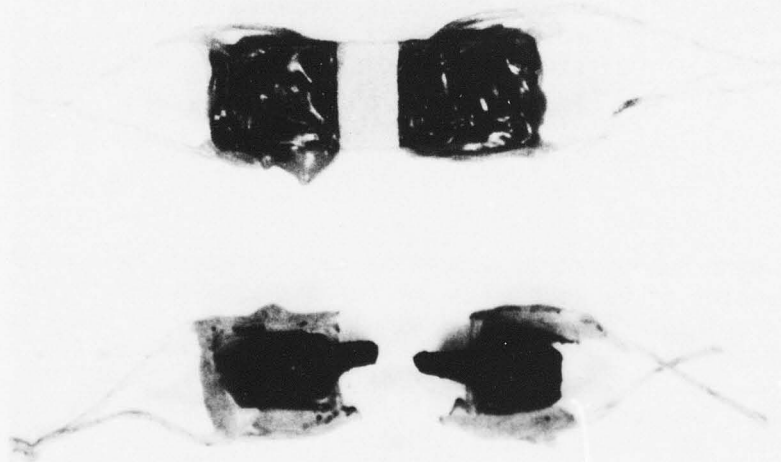


Figure 4. Samples of barstock 3.2 cm long, with a .6 cm square cross-section were prepared as shown above. A weight of 5.33 kg was suspended from the sample which was immersed in seawater. The failed sample is shown above.

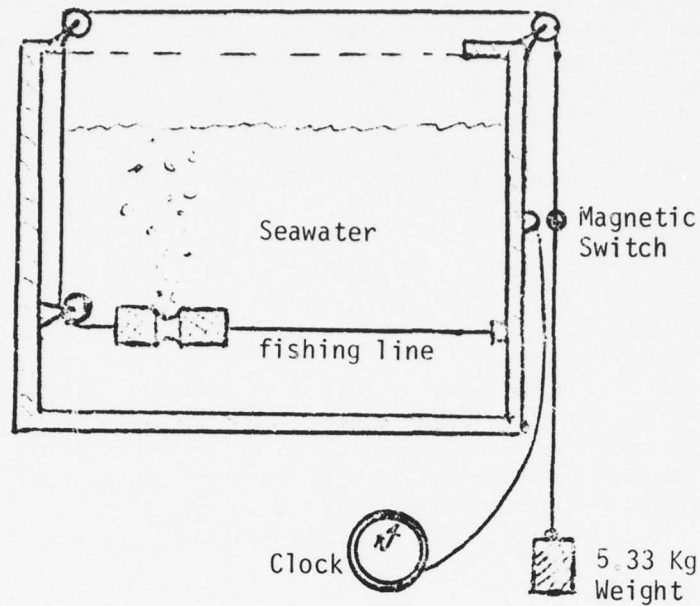


Figure 5. Arrangement for determining time-to-failure of barstock samples prepared as shown in Figure 4. When the sample breaks the weight moves downward and the magnetic switch is opened thus stopping the clock.

Tests were conducted to determine the corrosion rate of a flat surface. Samples of barstock were coated with epoxy cement on all surfaces except for one end. The sample was placed in seawater with the uncoated surface facing up. Measurements of the depth of corrosion were made at regular intervals (out of water) using a micrometer depth gauge. The surface was lightly scraped to remove loose corrosion products prior to taking data.

RESULTS

Powdered Samples

Samples of the Mg-9.8 Fe alloy powder which were fabricated using different milling parameters* were tested to determine reaction rate and reaction efficiency. The test results (Figure 6) clearly show that milling parameters affect reaction characteristics and that optimum performance can be achieved by selecting the appropriate parameters. The milling parameters used in the preparation of sample "A" were selected for manufacture of the remaining alloys.

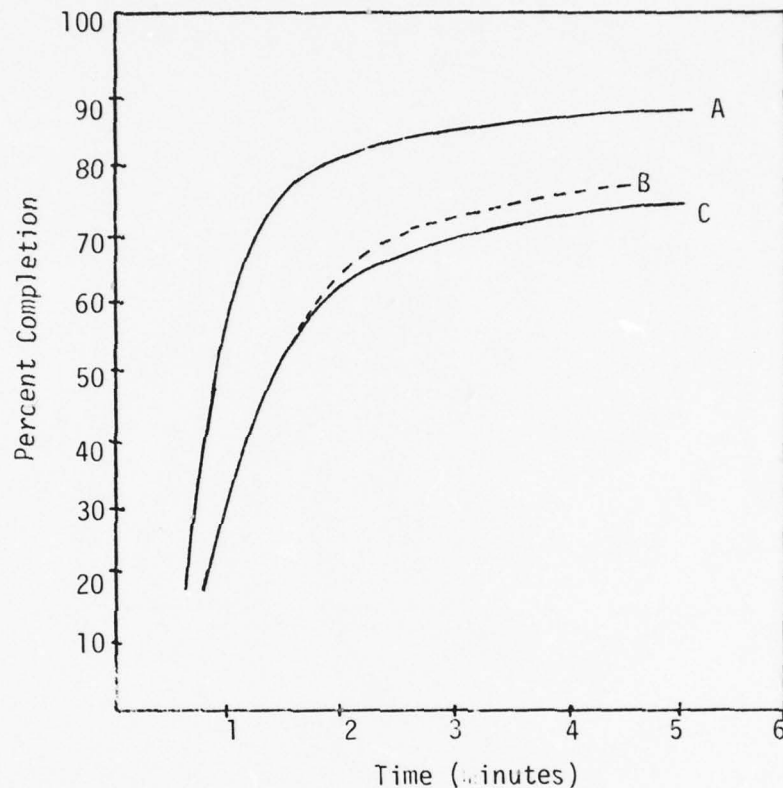


Figure 6. Samples A, B, and C of Mg-9.8 Fe alloy were prepared using different milling parameters such as speed of mill, ball-to-powder ratio and time in mill. Parameters of sample "A" were used for preparation of the remaining alloys.

*Milling parameters included: time of milling; speed of the mill; and ball-to-powder ratio.

Figure 7 presents the results of corrosion tests of magnesium powders with different amounts of iron cathode. Increasing the cathode content results in an increase in the reaction rate.

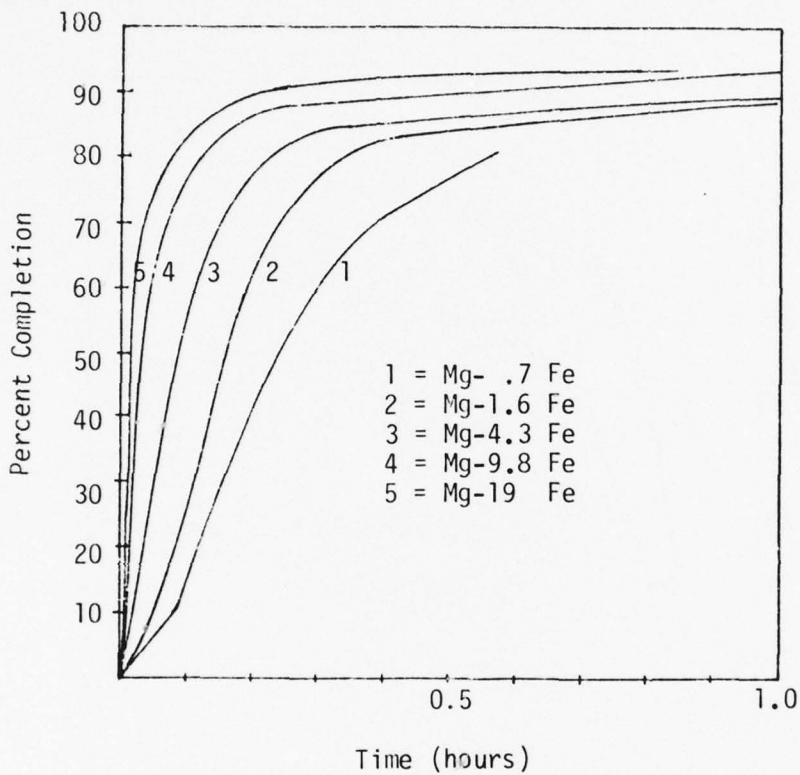


Figure 7. Reaction characteristics for powdered alloys with increasing iron content.

As shown in Figure 8, the reaction rate is a strong function of cathode content up to 10 atomic percent. Increasing the cathode content above 10% only slightly increases the reaction rate. Similar results can be expected for alloys with other cathode materials.

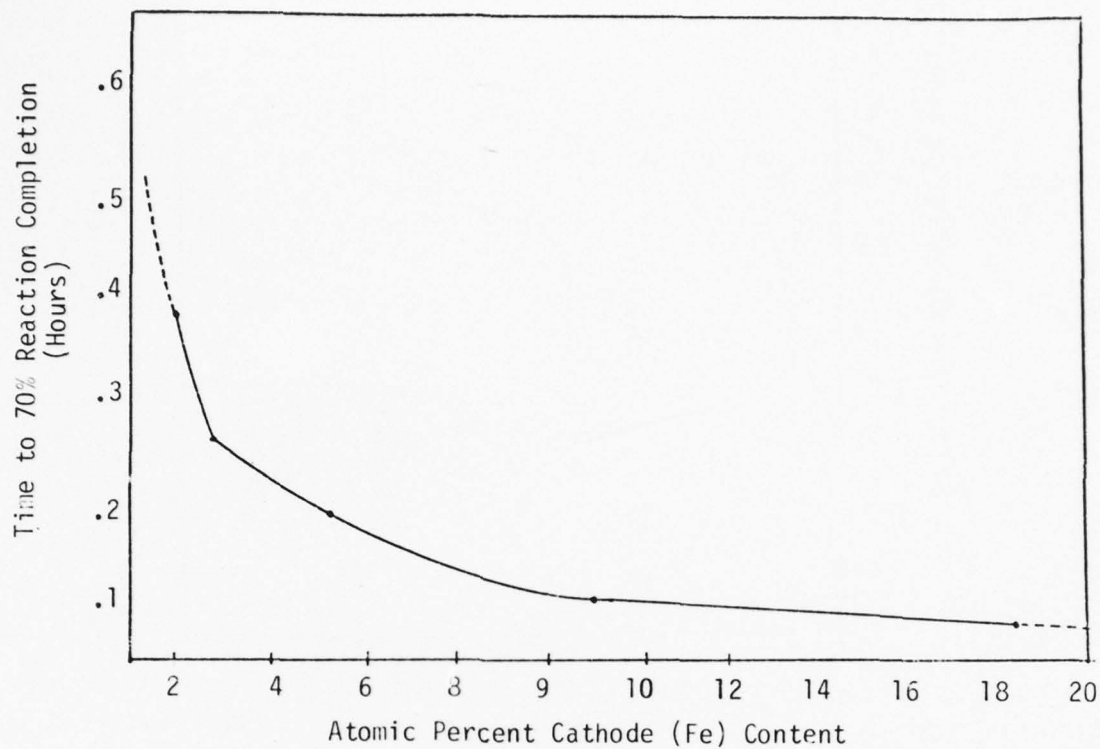


Figure 8. This plot of the time required for alloy powders with different iron content shows the trend of increasing reaction rate for increasing cathode content.

Figure 9 shows the results of tests with the powdered alloys of different cathode material, and approximately the same atomic percent cathode content. The nickel alloy reacted slightly faster than the iron alloy while copper, carbon and titanium (in decreasing order) reacted slower. Note that the iron alloy attained the highest efficiency of the alloys tested. It is expected that the efficiency of the other alloys would be improved by optimization of their milling parameters.

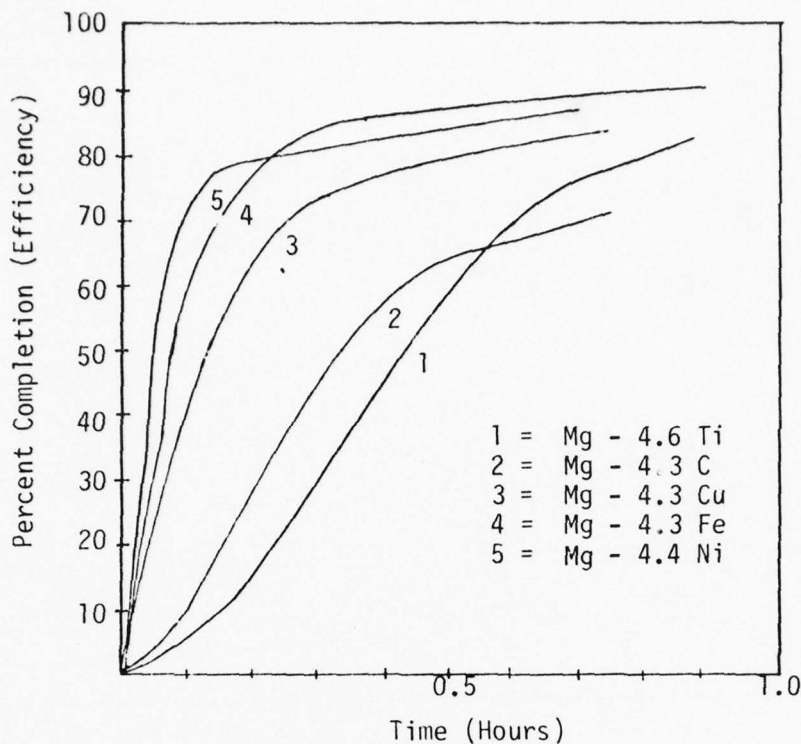


Figure 9. Reaction characteristics for supercorroding alloys with different cathode materials and approximately the same level of atomic percent cathode content. Nickel reacted fastest; iron was most efficient, and carbon reacted slowest.

Sintering and Compaction

Mechanical properties of the Mg-9.8 Fe alloy which was compacted to 550 M pascals and sintered at various conditions are listed in Table 2. Tensile strength (transverse rupture) increases slightly with increasing sinter temperature, while shear strength "peaks" near 700°F. Time of sintering does not seem to appreciably affect the mechanical properties. Since the optimum mechanical strength is a desirable parameter for a mechanical linkage, the sinter conditions of 700°F and one hour duration were selected for preparation of the remaining samples.

Table 2. Properties of Compacted* and Sintered Alloys with 9.8% Fe

<u>Sintering Condition</u>	<u>Sintered Density (g/cc)</u>	<u>Transfer Rupture Strength M pascals (kpsi)</u>	<u>Shear Strength M pascals (kpsi)</u>
600 ⁰ F/3 h/CO ₂	2.11	79.2 (11.5)	71 (10.3)
600 ⁰ F/1 h/CO ₂	2.11	77.9 (11.3)	71 (10.3)
700 ⁰ F/3 h/CO ₂	2.11	88.2 (12.8)	77.2 (11.2)
700 ⁰ F/1 h/CO ₂	2.12	85.4 (12.4)	84.1 (12.2)
800 ⁰ F/1 h/CO ₂	2.10	88.2 (12.8)	69.6 (10.1)

*Compacting pressure - 550 M pascals (40 TSI)

Effects of sintering conditions on corrosion rate of the Mg-9.8 Fe alloy are presented in Figures 10 and 11. Time to failure of the barstock samples for the sinter conditions is presented in Figure 12. The results clearly show that the reaction rate decreases with both increasing time and increasing temperature of sinter.

Mechanical properties of the Mg-9.8 Fe alloy specimens which were compacted at different pressures and sintered at 700⁰F for one hour are presented in Table 3. As seen in Figure 13, shear strength and tensile strength both increase with compaction pressure.

Table 3. Properties of Compacted and Sintered* Mg-9.8 Fe Powder.

<u>Compacting Pressure M pascals (TSI)</u>	<u>Sintered Density (g/cc)</u>	<u>Transverse Rupture Strength M pascals (kpsi)</u>	<u>Shear Strength M pascals (kpsi)</u>
70 (5)	1.51	2.8 (.4)	11.7 (1.7)
140 (10)	1.83	22.1 (3.2)	32.4 (4.7)
280 (20)	1.99	40 (5.8)	40.0 (7.1)
420 (30)	2.07	62.7 (9.1)	49.6 (7.2)
550 (40)	2.10	71.7 (10.4)	66.8 (9.7)

*Sintered 700⁰F/1 hr/CO₂

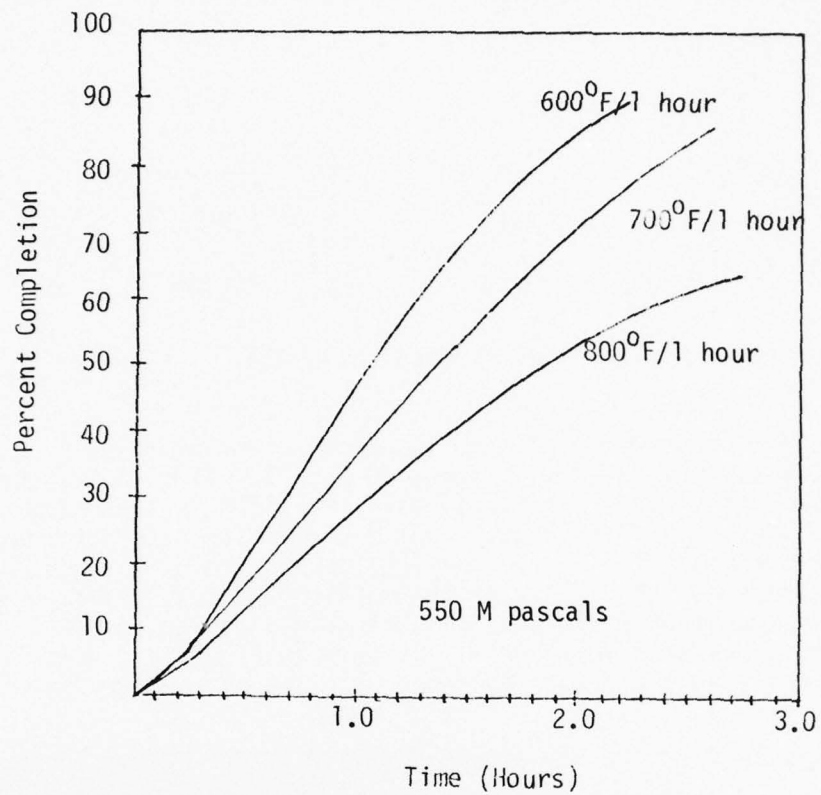


Figure 10. Reaction Characteristics for sample of the Mg-9.8 Fe alloy which were compacted to 550 M pascal (40 TSI) and sintered at the indicated temperatures for one hour in a CO_2 atmosphere. Reaction rate decreases with increasing sinter temperature.

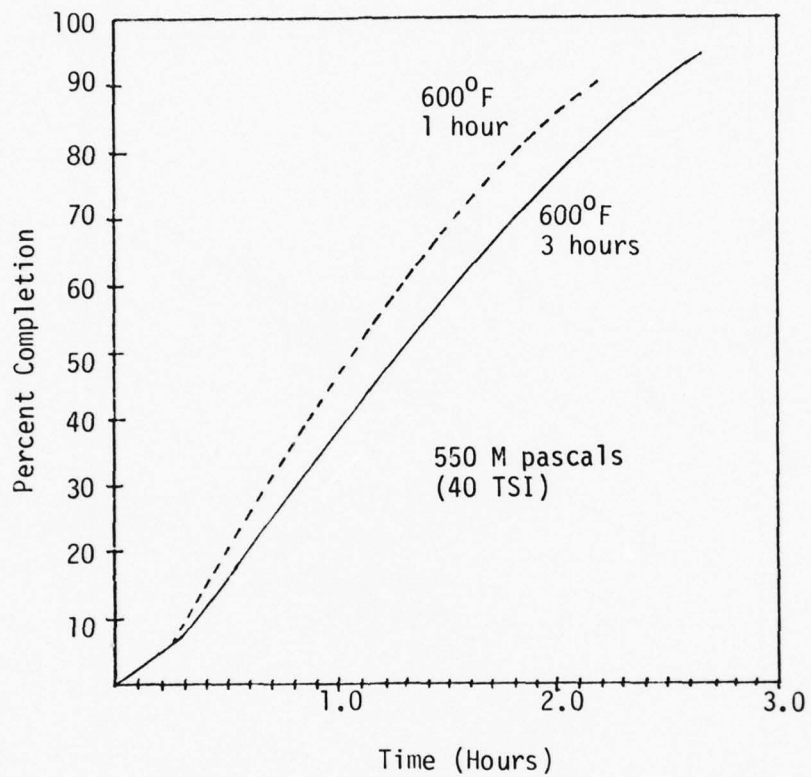


Figure 11. Mg-9.8 Fe alloys were sintered at 600°F for one and three hours. Reaction rate decreases with time of sinter.

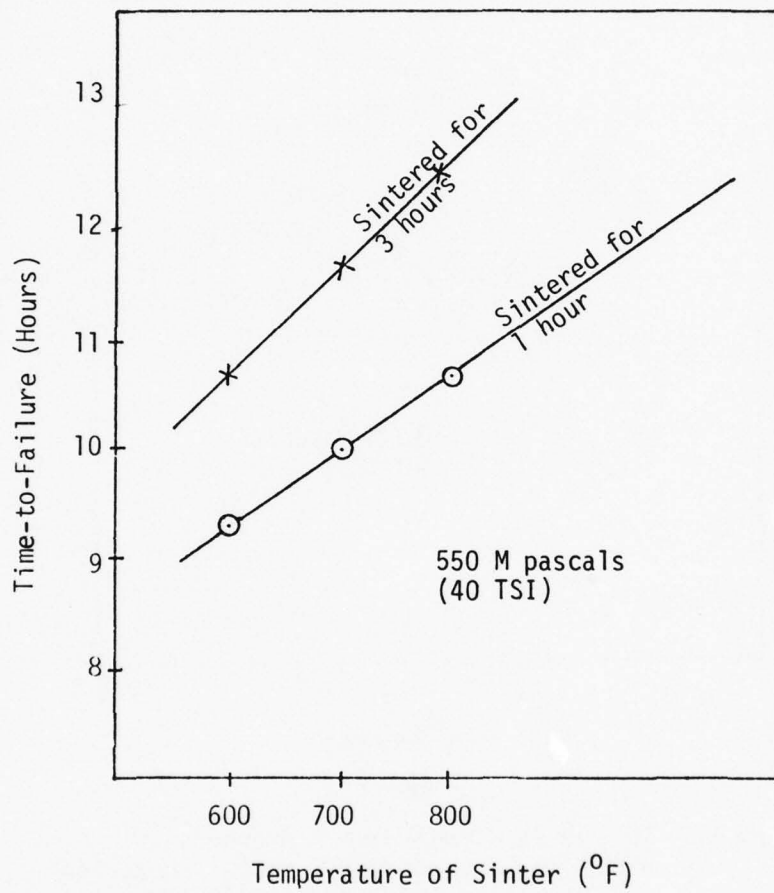


Figure 12. Increasing the time and temperature of sinter effects the time to failure for Mg-9.8 Fe alloys as shown above.

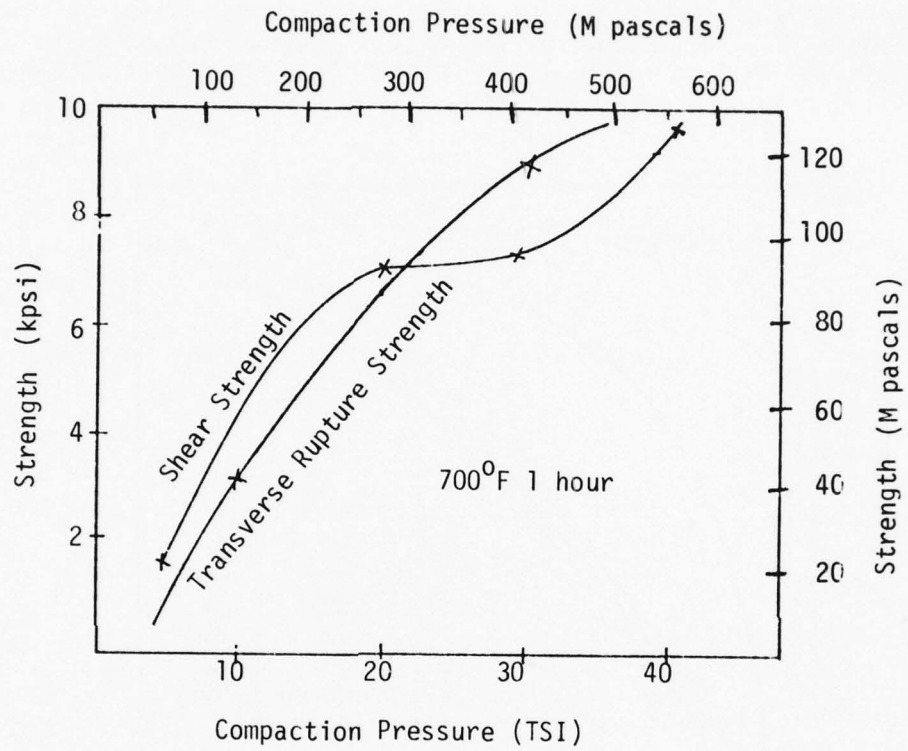


Figure 13. Mechanical strength characteristics for Mg-9.8 Fe alloy samples which were compacted at different pressures and sintered at 700°F for one hour are shown above.

Results of the corrosion tests with discs of each compaction pressure are presented in Figure 14. Powdered sample results are included for reference. The 70 M pascal (5 TSI) sample crumbled immediately on immersion in the seawater and reacted almost as rapidly as the powder sample. Reaction rate decreases with increasing compaction pressure up to approximately 420 M pascals and continues to decrease slightly for increasing compaction pressure between 420 M pascals and 550 M pascals (30-40 TSI). These findings were confirmed by the barstock time to failure tests results as shown in Figure 15. Increasing the compaction pressure beyond 550 M pascals (40 TSI) is not expected to significantly affect either the reaction rate or time to failure.

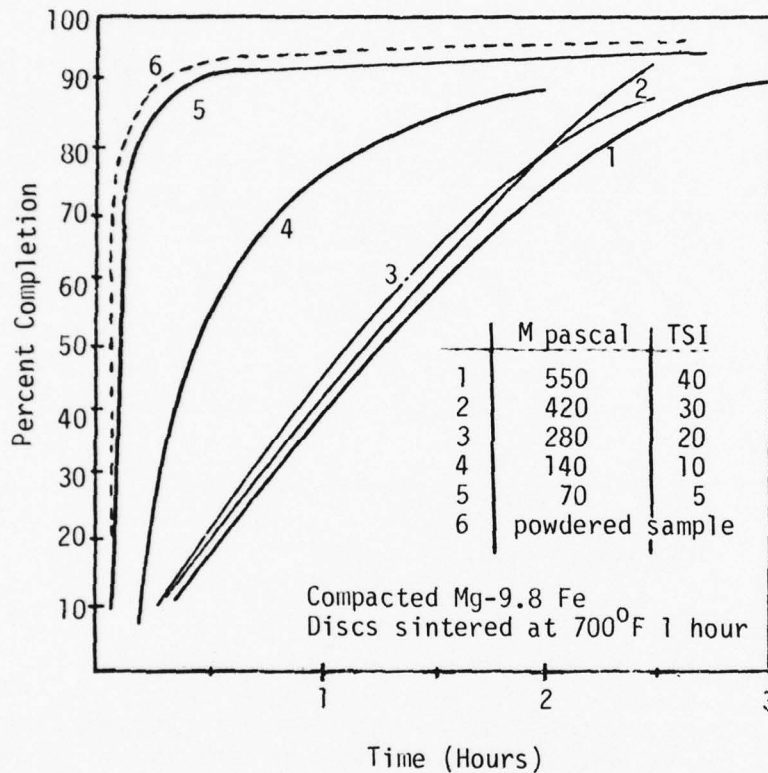


Figure 14. Reaction rate decreases as compaction pressure increases as shown above. The 5 TSI sample reacted almost as rapidly as the powdered sample (dashed line).

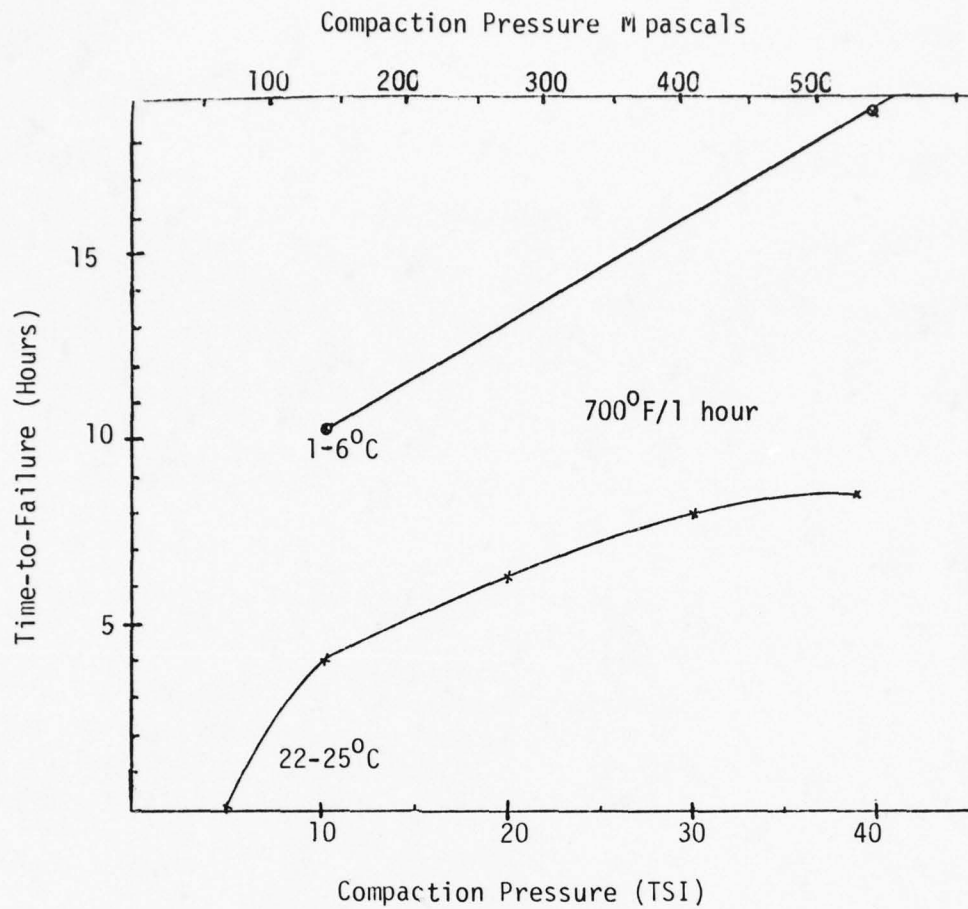


Figure 15. Time to failure for Mg-9.8 Fe barstock samples compacted at different pressures also shown are the results of tests at lower ambient temperature.

Also shown in Figure 15 are the results of two time to failure tests performed at lower ambient temperatures. The tests were conducted by using refrigerated seawater and surrounding the reaction vessel with ice. Starting temperature was approximately 1°C, and at termination the seawater was approximately 6°C. The results show that the time to failure is substantially increased (decreased reaction rate) by lowering the temperature.

Alternate Cathode Compacts

The alloys with different amounts of iron cathode content (iron series) and those with other cathode materials were compacted into disc and barstock form at 550 M pascals (40 TSI). All specimens were sintered at 700⁰F for one hour in a CO₂ atmosphere. Mechanical properties of these alloys are shown in Table 4. Mechanical strength does not vary uniformly with increasing iron content. The fact that the Mg-9.8 Fe sample is slightly stronger than the others iron series alloys is attributed to optimization of its milling parameters of the prepared samples tested, the Mg-4.6 Ti was strongest with carbon, nickel, iron and copper following in decreasing order of strength.

Table 4. Properties of Compacted* and Sintered* Alloys.

Alloy	PM No.	Sintered Density (g/cc)	Transverse Rupture Strength M pascals (kpsi)	Shear Strength M pascals (kpsi)
Mg- .7 Fe	1311	1.79	68.9 (10)	61.3 (8.9)
Mg-1.6 Fe	1308	1.81	64.8 (9.4)	59.3 (8.6)
Mg-4.3 Fe	1309	1.93	61.3 (8.9)	63.4 (9.2)
Mg-9.8 Fe	1306	2.10	71.7 (10.4)	66.8 (9.7)
Mg-19 Fe	1310	2.42	67.5 (9.8)	68.2 (9.9)
Mg-4.3 Cu	1312	1.87	44.1 (6.4)	50.3 (7.3)
Mg-4.4 Ni	1313	1.94	74.1 (10.8)	66.8 (9.7)
Mg-4.3 C	1314	1.78	88.9 (12.9)	65.5 (9.5)
Mg-4.6 Ti	1315	1.89	93.7 (13.6)	80.6 (11.7)

*Compacting Pressure - 550 M pascals (40 TSI)

Sintered 700⁰F/1 hr/CO₂

Disc corrosion test results for the iron series are presented in Figure 16. Time to failure for the barstock is shown in Figure 17. As expected from the results of the powder tests, the reaction rate increases significantly with higher cathode content.

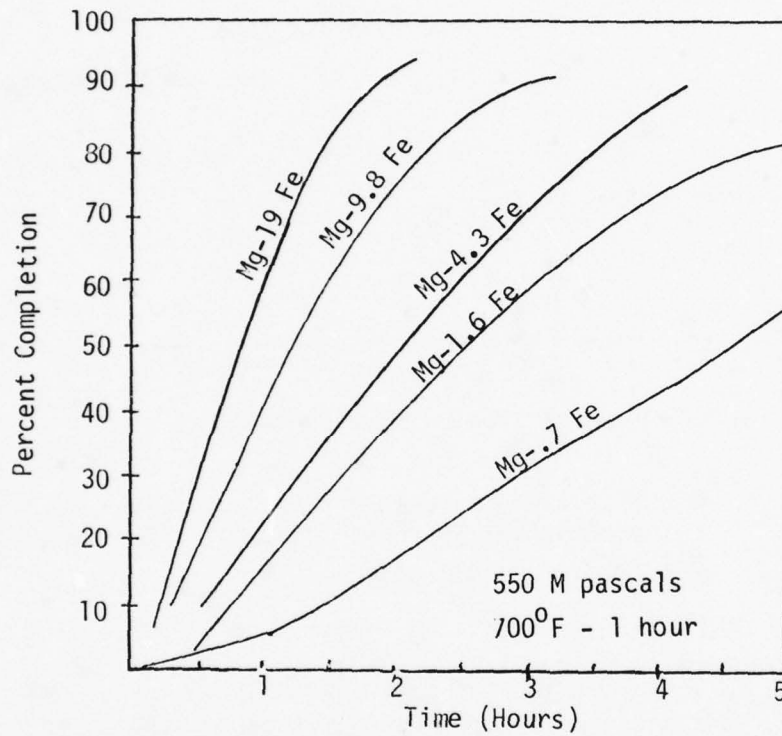


Figure 16. Reaction rate for the iron series alloys discs compacted to 550 M pascals increases with increasing cathode content.

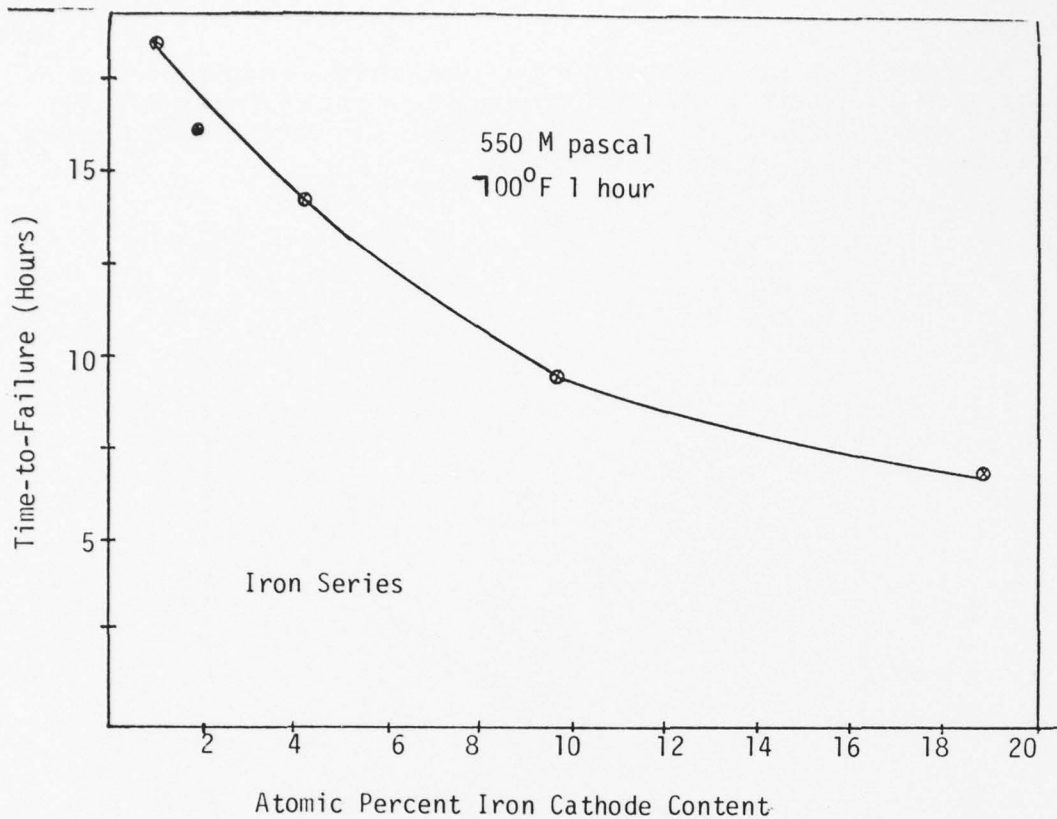


Figure 17. Barstock time-to-failure decreases with increasing cathode content as shown above for the iron series alloys.

The corrosion performance of alloy discs of different cathode materials is shown in Figure 18. Nickel reacted more rapidly with iron a close second. Titanium, copper and carbon in decreasing order reacted slowest. In the barstock time to failure tests (Figure 19) the nickel alloy reacted faster with the titanium alloy second. Iron, copper and carbon alloys reacted slowest.

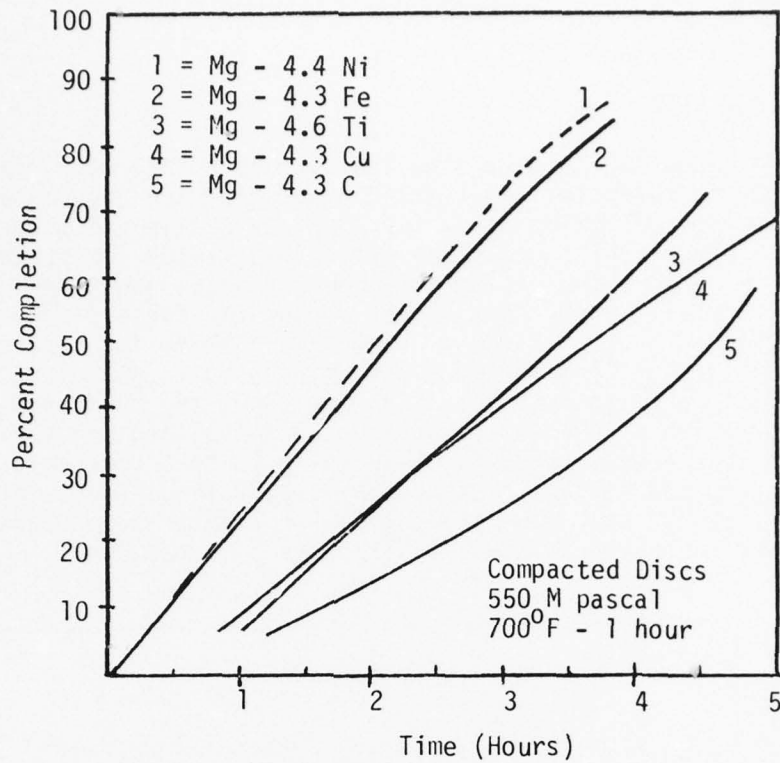


Figure 18. Reaction rate for compacted discs with different cathode materials is shown above.

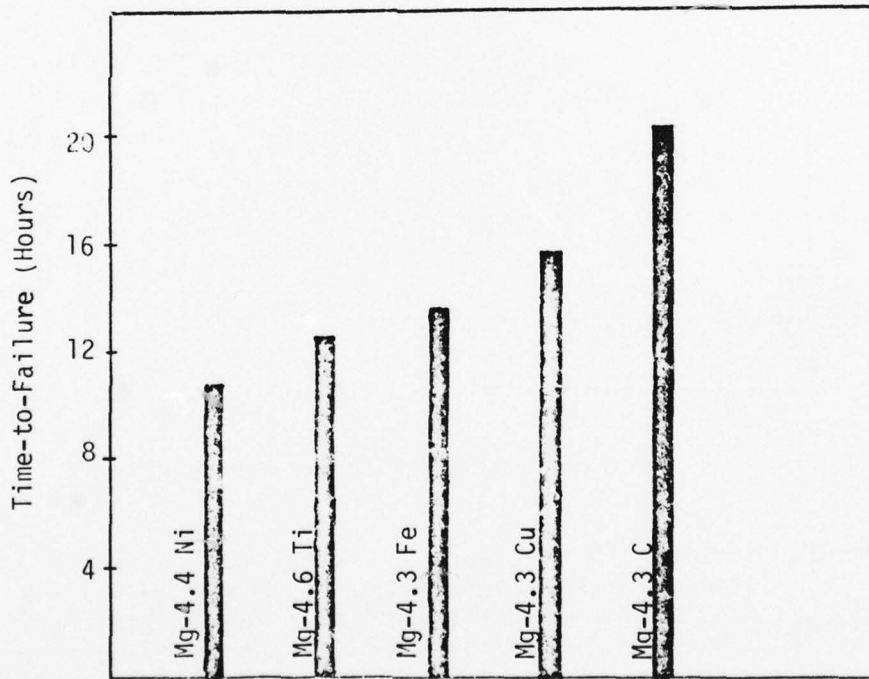


Figure 19. Time-to-failure for barstock samples of alloys with different cathode materials.

Surface Corrosion Rate

Tests were conducted to determine the corrosion rate of a flat surface. The number of tests conducted was limited because of the unavailability of samples. Surface corrosion rates for the iron series alloys are plotted in Figure 20. The corrosion rates for all alloys tested are presented in Figure 21. Note that two different corrosion rates are given. It was found that the alloys corroded slower during the first six hours of immersion (dashed line of Figures 20 and 21) than during the remaining test hours (20 hours). The difference was attributed to changing conditions on the test specimen wetted surface. On immersion, the surface was smooth. As corrosion proceeded the surface became pitted and consequently the exposed surface area increased. Eventually (3 to 6 hours after immersion) the exposed surface area became relatively constant and corrosion proceeded at a steady rate. The solid lines in Figures 20 and 21 represent the steady state corrosion rate after six hours of immersion.

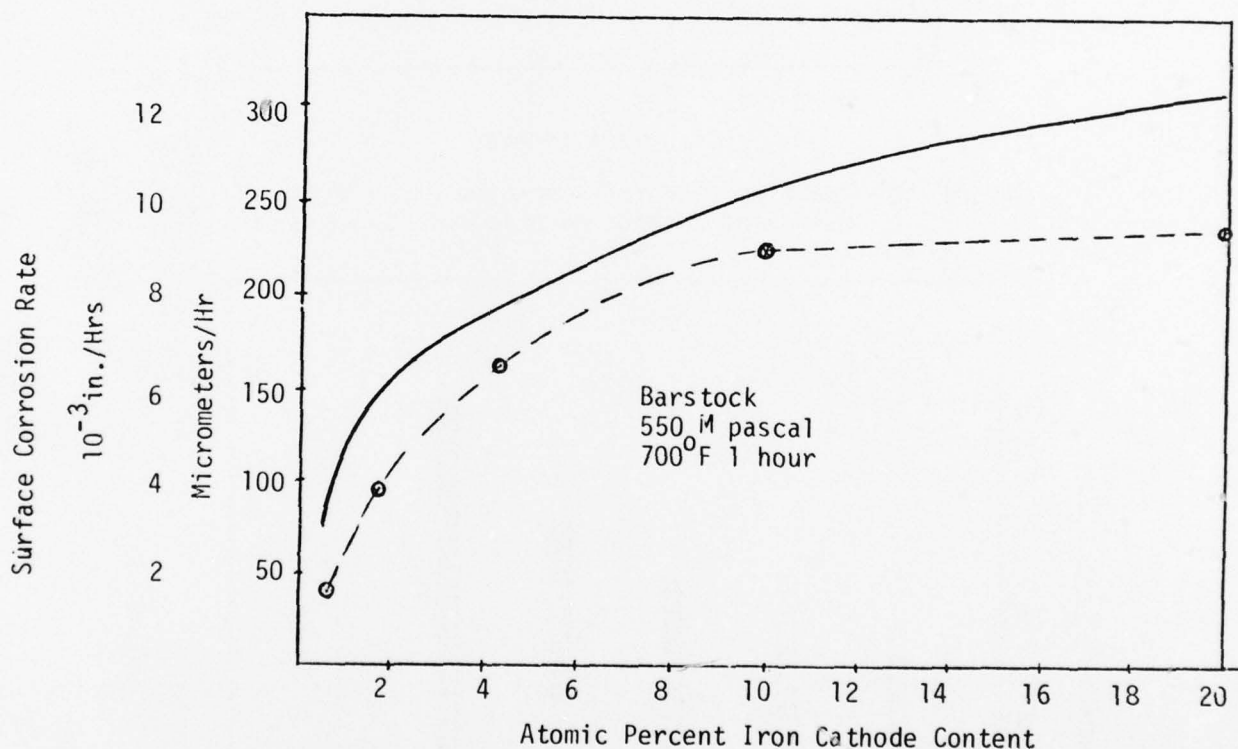


Figure 20. Surface corrosion rate for alloys with different percent iron cathode content. Corrosion decreases with decreasing cathode content. The dashed line indicates the corrosion rate during the first 6 hours and the solid line the corrosion rate from 6 to 20 hours.

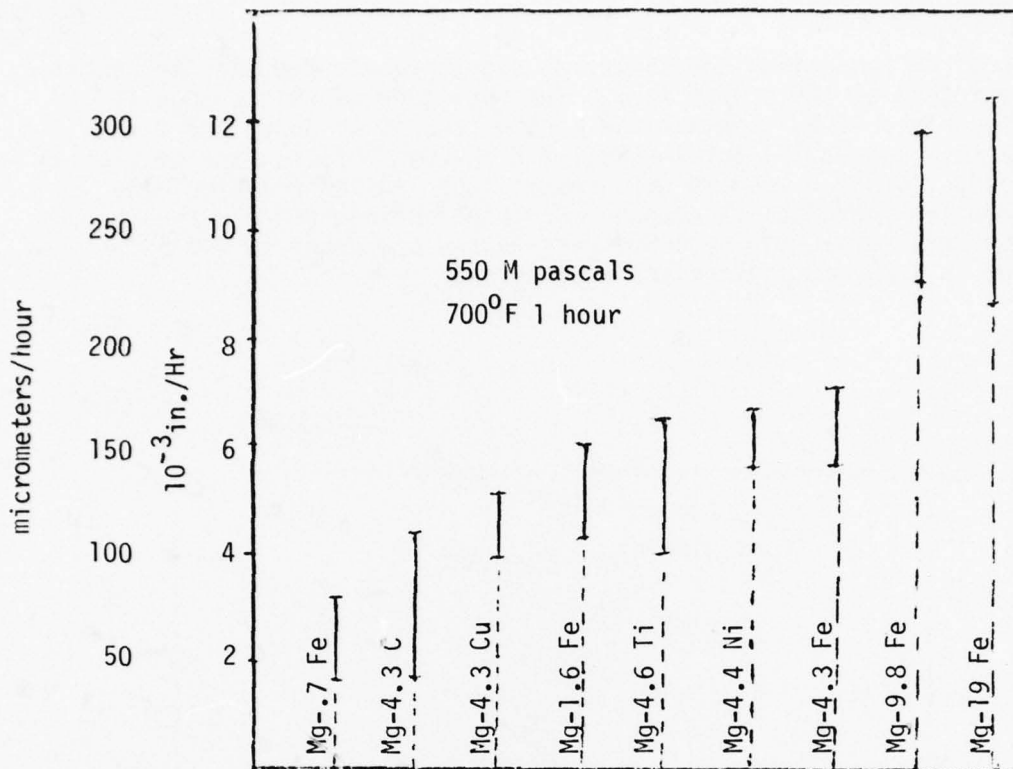


Figure 21. Summary of surface corrosion ratio for all samples tested. The dashed line indicates corrosion rate during the first 6 hours and solid line the corrosion from 6 to 20 hours.

As expected, from the results of previous tests, the surface corrosion rate increased with increased cathode content and the general order of ranking (Fe, Ni, Ti, Cu and C) remained unchanged from the results of disc tests.

Discussion

Results of tests with the Mg-9.8 Fe powder as shown in Figure 6 demonstrated that alloy corrosion performance was affected by manufacturing parameters. The optimum manufacturing parameters for each alloy (in terms of reaction efficiency and strength) are probably unique for that alloy.

An investigation of the milling parameters for each alloy tested would result in a faster reaction rate and higher reaction efficiency. The effect of milling parameters on mechanical strength, time to failure for barstock and surface corrosion rate is not known at this time.

Combined compacting and sintering significantly reduces the reaction rate over that of the powder form. The magnitude of this change is shown in Figure 22 by a comparison of the results of powder and disc samples (550 M pascals) for the Mg-4.3 Fe alloy. Reducing the compaction pressure below 550 M pascals will result in increased reaction rate and decreased mechanical strength. For applications where strength is important, compacting to 550 M pascals and sintering to 700^oF for one hour in a CO₂ atmosphere are recommended.

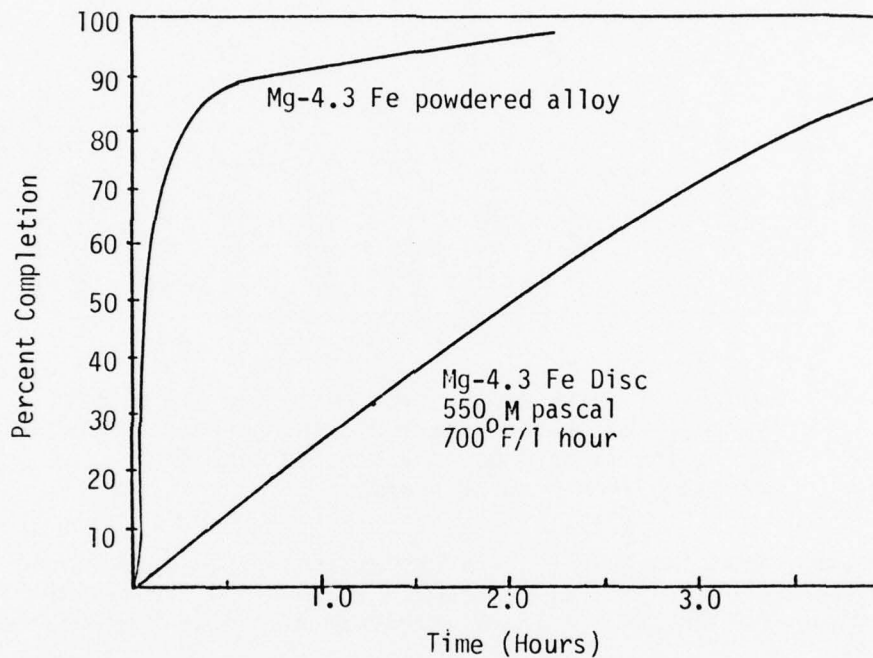


Figure 22. Shown is a comparison of the reaction rate for the disc and powdered samples for the Mg-4.3 Fe alloy. Compacting greatly reduces the reaction rate.

In addition to milling, compacting, and sintering, alloy corrosion performance is a function of the amount and type of cathode material present. Figure 23 summarizes the results of powder, disc and barstock tests for the iron series alloys. The reaction rate increases with cathode content up to 20 atomic percent. Increasing the cathode content over 20 percent will not result in a significant change in the reaction rate. Similar results are expected for other cathode materials.

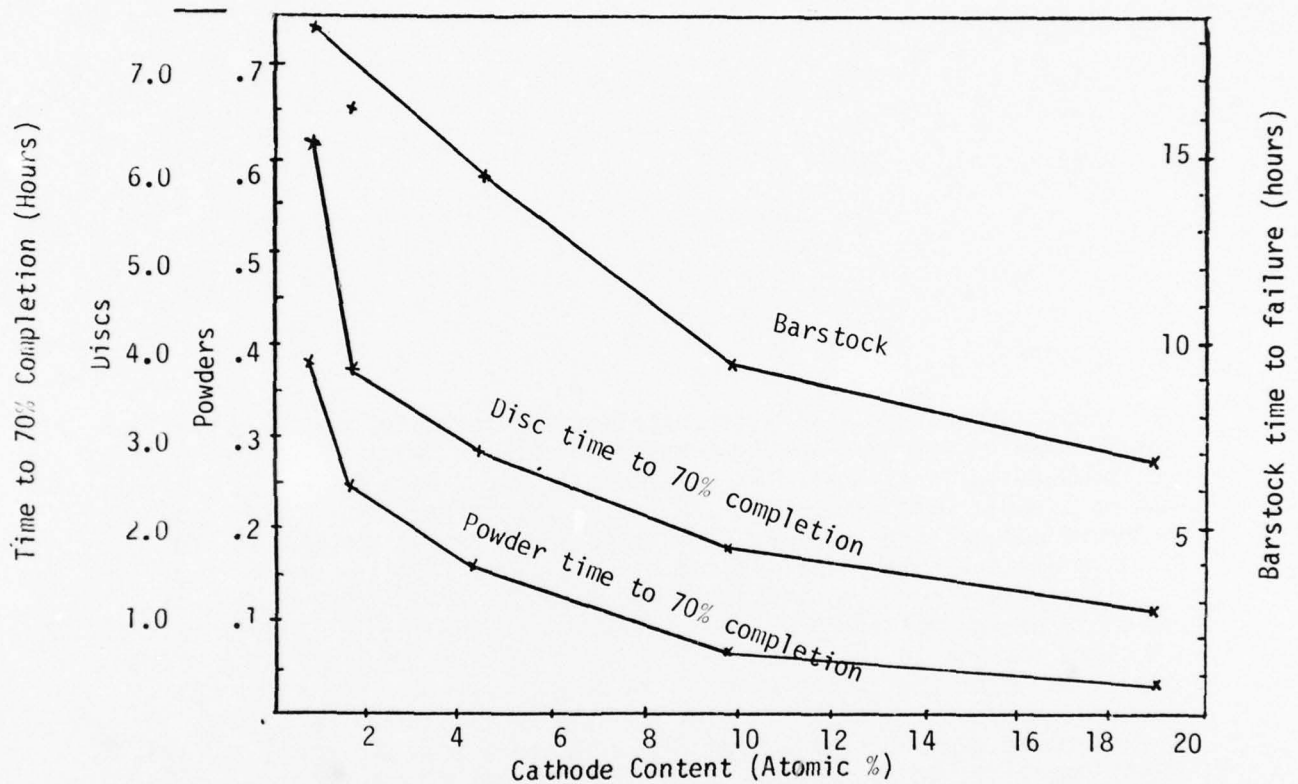


Figure 23. A summary of the results of powder, disc and barstock samples for the iron series shows the effect of cathode content on reaction rate.

Reaction rate, time to failure, surface corrosion rate, and mechanical strength of the alloys tested also depend on the cathode type. Ranking for the different cathode materials tested is summarized in Table 5.

Magnesium with titanium as the cathode formed the strongest alloy tested while magnesium with nickel reacted fastest.

Table 5. Order of Ranking for Materials Listed.

<u>Fast</u>	<u>Powder</u>	<u>Disc</u>	<u>Barstock Failure</u>	<u>Surface Corrosion</u>
	Ni	Ni	Ni	Fe
	Fe	Fe	Ti	Ni
	Cu	Ti	Fe	Ti
↓	C	Cu	Cu	Cu
<u>Slow</u>	Ti	C	C	C

APPLICATIONS

Supercorrodng alloys were conceived as sources of heat and hydrogen gas for use in remote areas such as in the ocean. Heat and hydrogen gas production is discussed in reference 2. As a heat source, the alloys can be used to warm divers or melt ice in arctic regions. The hydrogen produced can be used to power fuel cells and internal combustion engines, or to provide buoyancy for lifting heavy objects from the ocean floor.

The research discussed herein was selected to generate information which is useful for applying the technology to the design of self-destructing linkages for use in the ocean. The link could be in the form of a round pin which holds the object to be released to an anchor or instrument package. Another useful form for a corrodable link would be that of a flat round disc one surface of which is exposed to the ambient seawater. Upon immersion the surface would corrode and the disc eventually fail. The failure could be used to facilitate flooding and scuttling or to activate other mechanical and electrical functions.

Desirable failure time for corrodable linkage devices varies depending on the application. For example, it may be desired to retrieve a sampling device within one to eight hours of deployment. In another application, it may be desirable to scuttle a surface float such as a sonobuoy after eight to ten days of operation.

The present method of design for corrodable linkages is to form galvanic couples of dissimilar metals, the anode of which serves as the destructing link. This type of linkage has been generally unreliable because of the need for a reliable low resistance connection between the anode and cathode materials. Even a slight degradation of this connection can result in a significant change of the activation or release time.

Supercorrodable alloys offer a solution to the difficulties experienced with presently used corrodable links. With supercorrodable alloys the anode (magnesium) and cathode (iron, nickel, etc.) are combined to form a material which self-destructs on immersion in seawater. The destruction time depends on several factors such as cross sectional area of the link, cathode material, percent of cathode material present and surrounding temperature. The data presented herein provides a baseline by which a preliminary assessment of alloy performance and applicability for use in a particular application can be determined. Further refinement of the technology can be tailored once a specific application is defined.

SUMMARY AND CONCLUSIONS

Alloys of magnesium and various cathodic materials were fabricated by the International Nickel Company (INCO) and tested by the Civil Engineering Laboratory (CEL) to determine their corrosion properties. In both powdered and solid form, the alloys were found to have a high reaction efficiency. In powdered form, the alloys corrode rapidly and the rate of corrosion depends on both the cathode type and cathode content. Magnesium with either a nickel or iron cathode corrode most rapidly. Compacting and sintering the alloys produces solid forms that have significant shear and tensile properties which can be useful as self-destructing linkages and timing mechanisms for use in the ocean. The activation or failure time of the linkage can be tailored by selection of the cathode content and cross-section dimensions. In this manner, it is expected that activation times from minutes to days can be reliably achieved.

The preliminary data provided in this report can be used to determine the applicability of supercorrodable alloys in a particular application.

Final selection of the alloy cathode and level of cathode present depends upon the end use. Prior to manufacturing a particular alloy a study of the effect of milling parameters on corrosion performance should be performed. This study will insure optimum corrosion performance, mechanical strength and uniformity of the final product.

REFERENCES

1. Civil Engineering Laboratory. Technical Note N-1315, "Preliminary Development of an Electrochemical Heat Source for Military Diver Heating," by S.A. Black, et al., November 1973.
2. Civil Engineering Laboratory. Technical Memorandum 43-78-02, "Development and Evaluation of Supercorroding Alloys," by S.A. Black and S.S. Sergev, November 1977.
3. Civil Engineering Laboratory. Technical Note N-1501, "A Self-Contained Experimental Diver Heater," by S.A. Black and S.S. Sergev, September 1977.
4. U.S. Navy Patent No. 3,942,511, "Sandwiched Structure for Production of Heat and Hydrogen Gas," by S.A. Black, et al., March 1976.
5. U.S. Navy Patent No. 3,993,577, "Method for Production of Heat and Hydrogen Gas," by S.A. Black, et al., November 1976.
6. U.S. Navy Patent No. 4,017,414, "Powdered Metal Source for Production of Heat and Hydrogen Gas," by S.A. Black, et al., April 1977.
7. Benjamin, J.S., "Mechanical Alloying," Scientific American, May 1976, Vol. 234, No. 5, pp. 40-48.

DISTRIBUTION LIST

AFB CESCH, Wright-Patterson; MAC/DET (Col. P. Thompson) Scott, IL; Stinfo Library, Offutt NE
ARCTICSUBLAB Code 54T, San Diego, CA
ARMY BMDSC-RE (H. McClellan) Huntsville AL; ERADCOM Tech Supp Dir. (DELS-D) Ft. Monmouth, NJ
ARMY COASTAL ENGR RSCH CEN Fort Belvoir VA; R. Jachowski, Fort Belvoir VA
ARMY CORPS OF ENGINEERS MRD-Eng. Div., Omaha NE; Seattle Dist. Library, Seattle WA
ARMY CRREL A. Kovacs, Hanover NH
ARMY ENG WATERWAYS EXP STA Library, Vicksburg MS
ARMY ENGR DIST. Library, Portland OR
ARMY ENVIRON. HYGIENE AGCY Water Qual Div (Doner), Aberdeen Prov Ground, MD
ARMY MATERIALS & MECHANICS RESEARCH CENTER Dr. Leno, Watertown MA
ARMY MOBIL EQUIP R&D COM Mr. Cevasco, Fort Belvoir MD
ARMY TRANSPORTATION SCHOOL MAJ T Sweeney, Code ATSP CD-TE Fort Eustis VA
ARMY-PLASTEC Picatinny Arsenal (A M Anzalone, SMUPA-FR-M-D) Dover NJ
ASST SECRETARY OF THE NAVY Spec. Assist Energy (P. Waterman), Washington DC; Spec. Assist Submarines,
Washington DC
BUREAU OF RECLAMATION Code 1512 (C. Selander) Denver CO
CINCLANT Civil Engr. Supp. Plans. Ofr Norfolk, VA
CNO Code NOP-964, Washington DC; Code OP 323, Washington DC; Code OP 987 Washington DC; Code OPNAV
09B24 (H); Code OPNAV 22, Wash DC; Code OPNAV 23, Wash DC; OP987J (J. Boosman), Pentagon
COMCBPAC Operations Off, Makalapa HI
COMNAVBEACHPHIBREFTRAGRU ONE San Diego CA
COMOCEANSYSPAC SCE, Pearl Harbor HI
COMSUBDEVGRUONE Operations Ofr, San Diego, CA
DEFENSE DOCUMENTATION CTR Alexandria, VA
DEFENSE INTELLIGENCE AGENCY Dir., Washington DC
DMAHC Code LAL Washington DC
DOE Dr. Cohen
DTNSRDC Code 1706, Bethesda MD; Code 172 (M. Krenzke), Bethesda MD
DTNSRDC Code 284 (A. Ruffolo), Annapolis MD; Code 522 (Library), Annapolis MD
GSA Fed. Sup. Serv. (FMBP), Washington DC
HEDSUPPACT PWO, Taipei, Taiwan
MARINE CORPS BASE PWO Camp Lejeune NC
MCAS Facil. Engr. Div. Cherry Point NC; CO, Kaneohe Bay HI; J. Taylor, Iwakuni Japan
MILITARY SEALIFT COMMAND Washington DC
NAS Code 18700, Brunswick ME; Dir. Util. Div., Bermuda; ENS Buchholz, Pensacola, FL; Lead. Chief, Petty Ofr,
PW/Self Help Div, Beeville TX; PW (J. Maguire), Corpus Christi TX; PWO Key West FL; PWO, Glenview IL;
SCE Norfolk, VA
NATL RESEARCH COUNCIL Naval Studies Board, Washington DC
NAVACT PWO, London UK
NAVAEROSPREGMEDCEN SCE, Pensacola FL
NAVCOASTSYS LAB CO, Panama City FL; Code 713 (J. Quirk) Panama City, FL; Code 715 (J. Mittleman) Panama
City, FL; Library Panama City, FL
NAVCOMMAREAMSTRSTA SCE Unir J Naples Italy
NAVCOMMSTA Code 401 Nea Makri, Greece; PWO, Exmouth, Australia
NAVEDTRAPRODEVCCEN Tech. Library
NAVELEXSYSCOM Code PME-124-61, Washington DC
NAVENVIRHLTHCEN CO, Cincinnati, OH
NAVEODFAC Code 605, Indian Head MD
NAVFAC PWO, Barbados; PWO, Centerville Bch, Ferndale CA; PWO, Guam
NAVFACENGCOM Code 043 Alexandria, VA; Code 044 Alexandria, VA; Code 0451 Alexandria, VA; Code 0453 (D.
Potter) Alexandria, VA; Code 0454B Alexandria, VA; Code 04B3 Alexandria, VA; Code 04B5 Alexandria, VA;
Code 101 Alexandria, VA; Code 10133 (J. Leimanis) Alexandria, VA; Code 1023 (T. Stevens) Alexandria, VA; LT
Parisi, Code PC-2 Alexandria, VA; Morrison Yap, Caroline Is.; P W Brewer Alexandria, VA; PL-2 Ponce P.R.
Alexandria, VA

NAVFACENGCOCM - CHES DIV. Code FPO-1 Wash, DC; FPO-1 (Spencer) Wash, DC; FPO-1 Wash, DC; Scheessele, Code 402, Wash, DC
 NAVFACENGCOCM - LANT DIV.; Eur. BR Deputy Dir, Naples Italy; RDT&ELO 102, Norfolk VA
 NAVFACENGCOCM - NORTH DIV. (Boretsky) Philadelphia, PA; CO; Code 09P (LCDR A.J. Stewart); Code 1028, RDT&ELO, Philadelphia PA; Design Div. (R. Masino), Philadelphia PA; ROICC, Contracts, Crane IN
 NAVFACENGCOCM - PAC DIV. Code 402, RDT&E, Pearl Harbor HI; Commander, Pearl Harbor, HI; PC-2 Alexandria, VA
 NAVFACENGCOCM - SOUTH DIV. Code 90, RDT&ELO, Charleston SC
 NAVFACENGCOCM - WEST DIV. Code 04B; 09P/20; RDT&ELO Code 2011 San Bruno, CA
 NAVFACENGCOCM CONTRACT Eng Div dir. Southwest Pac, Manila, PI; OICC, Southwest Pac, Manila, PI; ROICC Off Point Mugu, CA
 NAVHOSP LT R. Elsbernd, Puerto Rico
 NAVNUPWRU MUSE DET Code NPU-30 Port Hueneme, CA
 NAVOCEANO Code 1600 Bay St. Louis, MS; Code 3432 (J. DePalma), Bay St. Louis MS
 NAVOCEANSYSCEN Code 409 (D. G. Moore), San Diego CA; Code 4473 Bayside Library, San Diego, CA; Code 52 (H. Talkington) San Diego CA; Code 5204 (J. Stachiw), San Diego, CA; Code 5214 (H. Wheeler), San Diego CA; Code 5224 (R. Jones) San Diego CA; Code 6565 (Tech. Lib.), San Diego CA; Code 7511 (PWO) San Diego, CA
 NAVPGSCOL D. Leipper, Monterey CA; E. Thornton, Monterey CA; J. Garrison Monterey CA
 NAVPHIBASE CO, ACB 2 Norfolk, VA; Code S3T, Norfolk VA; Harbor Clearance Unit Two, Little Creek, VA; OIC, UCT ONE Norfolk, Va
 NAVREGMEDCEN SCE (D. Kaye); SCE, Guam
 NAVSCOLCECOFF C35 Port Hueneme, CA
 NAVSEASYSOCM Code 00C-DB DiGeorge, Washington, DC; Code OOC (LT R. MacDougal), Washington DC; Code SEA OOC Washington, DC
 NAVSEC Code 6034 (Library), Washington DC
 NAVSHIPREPFAC Library, Guam; SCE Subic Bay
 NAVSHIPYD; Code 202.4, Long Beach CA; Code 202.5 (Library) Puget Sound, Bremerton WA; Code 440 Portsmouth NH; Code 440.4, Charleston SC; Salvage Supt, Phila., PA; Tech Library, Vallejo, CA
 NAVSTA CO Naval Station, Mayport FL; CO Roosevelt Roads P.R. Puerto Rico; Maint. Cont. Div., Guantanamo Bay Cuba; PWD (LTJG P.M. Motolenich), Puerto Rico; PWO Midway Island; PWO, Keflavik Iceland; PWO, Mayport FL; SCE, Guam; SCE, Subic Bay, R.P.; Utilities Engr Off. (LTJG A.S. Ritchie), Rota Spain
 NAVSTA BISHOPS POINT Harbor Clear. Unit one, Pearl Harbor, HI
 NAVSUPPACT Code 413, Seattle WA; LTJG McGarran, Vallejo CA; Security Offr, San Francisco, CA
 NAVSURFWPCEN PWO, White Oak, Silver Spring, MD
 NAVTECHTRACEN SCE, Pensacola FL
 NAVWPCEN Code 2636 (W. Bonner), China Lake CA
 NAVWPNSTA EARLE Code 092, Colts Neck NJ; PW Office (Code 09C1) Yorktown, VA; PWO, Seal Beach CA
 NAVWPNSUPPCEN Code 09 Crane IN
 NCBU 405 OIC, San Diego, CA
 NCBC CEL AOIC Port Hueneme CA; Code 10 Davisville, RI; Code 155, Port Hueneme CA; Code 156, Port Hueneme, CA
 NOAA Library Rockville, MD
 NORDA Code 410 Bay St. Louis, MS; Code 440 (Ocean Rsch Off) Bay St. Louis MS
 NRL Code 8400 Washington, DC; Code 8441 (R.A. Skop), Washington DC; Rosenthal, Code 8440, Wash, DC
 NSD SCE, Subic Bay, R.P.
 NTC Code 54 (ENS P. G. Jackel), Orlando FL
 NAVOCEANSYSCEN Hawaii Lab (D. Moore), Hawaii
 NUCLEAR REGULATORY COMMISSION T.C. Johnson, Washington, DC
 NUSC Code 131 New London, CT; Code EA123 (R.S. Munn), New London CT; Code S332, B-80 (J. Wilcox); Code SB 331 (Brown), Newport RI, Code TA131 (G. De la Cruz), New London CT
 OCEANAV Mangmt Info Div., Arlington VA
 OCEANSYSLANT LT A.R. Giancola, Norfolk VA
 ONR (Dr. E.A. Silva) Arlington, VA; BROFF, CO Boston MA; Code 221, Arlington VA; Code 481, Arlington VA; Code 481, Bay St. Louis, MS; Code 700F Arlington VA; Dr. A. Laufer, Pasadena CA
 PHIBCB I P&E, Coronado, CA
 PMTC Code 3331 (S. Opatowsky) Point Mugu, CA; EOD Mobile Unit, Point Mugu, CA; Pat. Counsel, Point Mugu CA

PWC CO Norfolk, VA; CO, Great Lakes IL; Code 120C (Library) San Diego, CA; Code 200, Great Lakes IL; Code 220.1, Norfolk VA; Code 400, Pearl Harbor, HI; Code 400, San Diego, CA; Code 700, San Diego, CA; OIC CBU-405, San Diego CA
 UCT TWO OIC, Port Hueneme CA
 U.S. MERCHANT MARINE ACADEMY Kings Point, NY (Reprint Custodian)
 US DEPT OF INTERIOR Bureau of Land MNGMNT - Code 733 (T.E. Sullivan) Wash, DC
 US GEOLOGICAL SURVEY Off. Marine Geology, Piteleki, Reston VA
 US NATIONAL MARINE FISHERIES SERVICE Highlands NY (Sandy Hook Lab-Library)
 US NAVAL FORCES Korea (ENJ-P&O)
 USCG (G-ECV) Washington Dc; (G-ECV/61) (Burkhart) Washington, DC; (G-MP-3/USP/82) Washington Dc; G-EOE-4/61 (T. Dowd), Washington DC
 USCG ACADEMY LT N. Stramandr, New London CT
 USCG R&D CENTER CO Groton, CT; D. Motherway, Groton CT; Tech. Dir. Groton, CT
 USNA Ch. Mech. Engr. Dept Annapolis MD; Ocean Sys. Eng Dept (Dr. Monney) Annapolis, MD; Oceanography Dept (Hoffman) Annapolis MD; PWD Engr. Div. (C. Bradford) Annapolis MD
 AMERICAN CONCRETE INSTITUTE Detroit MI (Library)
 AMERICAN UNIVERSITY Washington DC (M. Norton)
 CALIF. DEPT OF FISH & GAME Long Beach CA (Marine Tech Info Ctr)
 CALIF. DEPT OF NAVIGATION & OCEAN DEV. Sacramento, CA (G. Armstrong)
 CALIF. MARITIME ACADEMY Vallejo, CA (Library)
 CALIFORNIA INSTITUTE OF TECHNOLOGY Pasadena CA (Keck Ref. Rm)
 CALIFORNIA STATE UNIVERSITY LONG BEACH, CA (CHELAPATI); LONG BEACH, CA (YEN); LOS ANGELES, CA (KIM)
 CATHOLIC UNIV. Mech Engr Dept. Prof. Niedzwecki, Wash., DC
 COLORADO STATE UNIV., FOOTHILL CAMPUS Fort Collins (Nelson)
 CORNELL UNIVERSITY Ithaca NY (Serials Dept, Engr Lib.)
 DAMES & MOORE LIBRARY LOS ANGELES, CA
 DUKE UNIV MEDICAL CENTER B. Muga, Durham NC; DURHAM, NC (VESIC)
 FLORIDA ATLANTIC UNIVERSITY BOCA RATON, FL (MC ALLISTER); Boca Raton FL (Ocean Engr Dept., C. Lin)
 FLORIDA ATLANTIC UNIVERSITY Boca Raton FL (W. Tessin)
 FLORIDA ATLANTIC UNIVERSITY W. Hartt, Boca Raton FL
 FLORIDA TECHNOLOGICAL UNIVERSITY ORLANDO, FL (HARTMAN)
 GEORGIA INSTITUTE OF TECHNOLOGY Atlanta GA (School of Civil Engr., Kahn); Atlanta GA (B. Mazanti)
 INSTITUTE OF MARINE SCIENCES Morehead City NC (Director)
 IOWA STATE UNIVERSITY Ames IA (CE Dept, Handy)
 LEHIGH UNIVERSITY BETHLEHEM, PA (MARINE GEOTECHNICAL LAB., RICHARDS); Bethlehem PA (Fritz Engr. Lab No. 13, Beedle); Bethlehem PA (Linderman Lib. No.30, Flecksteiner)
 LIBRARY OF CONGRESS WASHINGTON, DC (SCIENCES & TECH DIV)
 MAINE MARITIME ACADEMY (Wyman) Castine ME; CASTINE, ME (LIBRARY)
 MICHIGAN TECHNOLOGICAL UNIVERSITY Houghton, MI (Haas)
 MIT Cambridge MA; Cambridge MA (Rm 10-500, Tech. Reports, Engr. Lib.); Cambridge MA (Whitman); Cambridge, MA (Harleman)
 NATL ACADEMY OF ENG. ALEXANDRIA, VA (SEARLE, JR.)
 NORTHWESTERN UNIV Z.P. Bazant Evanston IL
 UNIV. NOTRE DAME Katona, Notre Dame, IN
 OREGON STATE UNIVERSITY (CE Dept Grace) Corvallis, OR; CORVALLIS, OR (CE DEPT. BELL); Corvallis OR (School of Oceanography)
 PENNSYLVANIA STATE UNIVERSITY STATE COLLEGE, PA (SNYDER); State College PA (Applied Rsch Lab); UNIVERSITY PARK, PA (GOTOLSKI)
 PURDUE UNIVERSITY Lafayette IN (Leonards); Lafayette, IN (Altschaeffl); Lafayette, IN (CE Engr. Lib)
 SAN DIEGO STATE UNIV. I. Noorany San Diego, CA; Dr. Krishnamoorthy, San Diego CA
 SCRIPPS INSTITUTE OF OCEANOGRAPHY LA JOLLA, CA (ADAMS)
 SEATTLE U Prof Schwaegler Seattle WA
 SOUTHWEST RSCH INST King, San Antonio, TX; R. DeHart, San Antonio TX
 STANFORD UNIVERSITY Engr Lib, Stanford CA; STANFORD, CA (DOUGLAS)
 STATE UNIV. OF NEW YORK Buffalo, NY; Fort Schuyler, NY (Longobardi)
 TEXAS A&M UNIVERSITY College Station TX (CE Dept. Herbich); W.B. Ledbetter College Station, TX

UNIVERSITY OF ALASKA Marine Science Inst. College. AK
 UNIVERSITY OF CALIFORNIA BERKELEY, CA (CE DEPT, GERWICK); BERKELEY, CA (CE DEPT, MITCHELL); Berkeley CA (B. Bresler); Berkeley CA (Dept of Naval Arch.); Berkeley CA (E. Pearson); DAVIS, CA (CE DEPT, TAYLOR); La Jolla CA (Acq. Dept, Lib. C-075A); SAN DIEGO, CA, LA JOLLA, CA (SHEROCK)
 UNIVERSITY OF CONNECTICUT Groton CT (Inst. Marine Sci, Library)
 UNIVERSITY OF DELAWARE Newark, DE (Dept of Civil Engineering, Chesson)
 UNIVERSITY OF HAWAII HONOLULU, HI (SCIENCE AND TECH. DIV.); Honolulu HI (Dr. Szilard)
 UNIVERSITY OF ILLINOIS Metz Ref Rm, Urbana IL; URBANA, IL (DAVISSON); URBANA, IL (LIBRARY); URBANA, IL (NEWMARK)
 UNIVERSITY OF MASSACHUSETTS (Heronemus), Amherst MA CE Dept
 UNIVERSITY OF MICHIGAN Ann Arbor MI (Richart)
 UNIVERSITY OF NEBRASKA-LINCOLN Lincoln, NE (Ross Ice Shelf Proj.)
 UNIVERSITY OF NEW HAMPSHIRE DURHAM, NH (LAVOIE)
 UNIVERSITY OF PENNSYLVANIA PHILADELPHIA, PA (SCHOOL OF ENGR & APPLIED SCIENCE, ROLL)
 UNIVERSITY OF RHODE ISLAND KINGSTON, RI (PAZIS); Narragansett RI (Pell Marine Sci, Lib.)
 UNIVERSITY OF SO. CALIFORNIA Univ So. Calif
 UNIVERSITY OF TEXAS Inst. Marine Sci (Library), Port Arkansas TX
 UNIVERSITY OF WASHINGTON Seattle WA (M. Sherif); Dept of Civil Engr (Dr. Mattock), Seattle WA; SEATTLE, WA (APPLIED PHYSICS LAB); SEATTLE, WA (MERCHANT); SEATTLE, WA (OCEAN ENG RSCH LAB, GRAY); SEATTLE, WA (PACIFIC MARINE ENVIRON. LAB., HALPERN); Seattle WA (E. Linger)
 UNIVERSITY OF WISCONSIN Milwaukee WI (Ctr of Great Lakes Studies)
 URS RESEARCH CO. LIBRARY SAN MATEO, CA
 VIRGINIA INST. OF MARINE SCI. Gloucester Point VA (Library)
 AGBABIAN ASSOC. C. Bagge, El Segundo CA
 ALFRED A. YEE & ASSOC. Honolulu HI
 AMETEK Offshore Res. & Engr Div
 AMSCO Dr. R. McCoy, Erie, PA
 ARCAIR CO. D. Young, Lancaster OH
 ARVID GRANT OLYMPIA, WA
 ATLANTIC RICHFIELD CO. DALLAS, TX (SMITH)
 BECHTEL CORP. SAN FRANCISCO, CA (PHELPS)
 BELGIUM HAECON, N.V., Gent
 BETHLEHEM STEEL CO. Dismuke, Bethelhem, PA
 BOUW KAMP INC Berkeley
 BRANDINDUS SERV INC. J. Buehler, Hacienda Heights CA
 BRITISH EMBASSY Sci. & Tech. Dept. (J. McAuley), Washington DC
 BROWN & CALDWELL E M Saunders Walnut Creek, CA
 BROWN & ROOT Houston TX (D. Ward)
 CANADA Can-Dive Services (English) North Vancouver; Library, Calgary, Alberta; Lockheed Petro. Serv. Ltd, New Westminster B.C.; Lockheed Petrol. Srv. Ltd., New Westminster BC; Mem Univ Newfoundland (Chari), St Johns; Nova Scotia Rsch Found. Corp. Dartmouth, Nova Scotia; Surveyor, Nenninger & Chenevert Inc., Montreal; Trans-Mnt Oil Pipe Lone Corp. Vancouver, BC Canada; Warnock Hersey Prof. Srv Ltd, La Sale, Quebec
 CF BRAUN CO Du Bouchet, Murray Hill, NJ
 CHEVRON OIL FIELD RESEARCH CO. LA HABRA, CA (BROOKS)
 COLUMBIA GULF TRANSMISSION CO. HOUSTON, TX (ENG. LIB.)
 CONCRETE TECHNOLOGY CORP. TACOMA, WA (ANDERSON)
 CONTINENT OIL CO O. Maxson, Ponca City, OK
 DILLINGHAM PRECAST F. McHale, Honolulu HI
 DIXIE DIVING CENTER Decatur, GA
 DRAVO CORP Pittsburgh PA (Wright)
 NORWAY DET NORSKE VERITAS (Library), Oslo
 EVALUATION ASSOC. INC KING OF PRUSSIA, PA (FEDELE)
 EXXON PRODUCTION RESEARCH CO Houston TX (A. Butler Jr); Houston, TX (Chao)
 FORD, BACON & DAVIS, INC. New York (Library)
 FRANCE Dr. Dutertre, Boulogne; L. Pliskin, Paris; P. Jensen, Boulogne; Roger LaCroix, Paris
 GOULD INC. Shady Side MD (Ches. Inst. Div., W. Paul)
 GRUMMAN AEROSPACE CORP. Bethpage NY (Tech. Info. Ctr)

HALEY & ALDRICH, INC. Cambridge MA (Aldrich, Jr.)
 ITALY M. Caironi, Milan; Sergio Tattoni Milano
 MAKAI OCEAN ENGRNG INC. Kailua, HI
 KOREA Korea Rsch Inst. Ship & Ocean (B. Choi), Seoul
 LAMONT-DOHERTY GEOLOGICAL OBSERV. Palisades NY (McCoy); Palisades NY (Selwyn)
 LIN OFFSHORE ENGRG P. Chow, San Francisco CA
 LOCKHEED MISSILES & SPACE CO, INC. L. Trimble, Sunnyvale CA; Mgr Naval Arch & Mar Eng Sunnyvale.
 CA: Sunnyvale CA (Ryniewicz); Sunnyvale, CA (K.L. Kerr)
 LOCKHEED OCEAN LABORATORY San Diego CA (F. Simpson)
 MARATHON OIL CO Houston TX (C. Seay)
 MARINE CONCRETE STRUCTURES INC. MEFAIRIE, LA (INGRAHAM)
 MC CLELLAND ENGINEERS INC Houston TX (B. McClelland)
 MEXICO R. Cardenas
 MOBIL PIPE LINE CO, DALLAS, TX MGR OF ENGR (NOACK)
 NEWPORT NEWS SHIPBLDG & DRYDOCK CO. Newport News VA (Tech. Lib.)
 NORWAY A. Torum, Trondheim; DET NORRSKE VERITAS (Roren) Oslo; I. Foss, Oslo; J. Creed, Ski; Norwegian
 Tech Univ (Brandtzaeg), Trondheim
 OCEAN ENGINEERS SAUSALITO, CA (RYNECKI)
 OCEAN RESOURCE ENG. INC. HOUSTON, TX (ANDERSON)
 PACIFIC MARINE TECHNOLOGY Long Beach, CA (Wagner)
 PORTLAND CEMENT ASSOC. SKOKIE, IL (CORLEY; SKOKIE, IL (KLIEGER); Skokie IL (Rsch & Dev Lab.
 Lib.)
 PRESCON CORP TOWSON, MD (KELLER)
 PUERTO RICO Puerto Rico (Rsch Lib.), Mayaguez P R
 R J BROWN ASSOC (McKeehan), Houston, TX
 RAND CORP. Santa Monica CA (A. Laupa)
 RAYMOND INTERNATIONAL INC. E Colle Soil Tech Dept, Pennsauken, NJ
 RIVERSIDE CEMENT CO Riverside CA (W. Smith)
 SANDIA LABORATORIES Library Div., Livermore CA
 SCHUPACK ASSOC SO. NORWALK, CT (SCHUPACK)
 SEATECH CORP. MIAMI, FL (PERONI)
 SHELL DEVELOPMENT CO, Houston TX (C. Sellars Jr.); Houston TX (E. Doyle)
 SHELL OIL CO, HOUSTON, TX (MARSHALL); Houston TX (R. de Castongrene); I. Boaz, Houston TX
 SOUTH AMERICA N. Nouel, Valencia, Venezuela
 SWEDEN GeoTech Inst; VBB (Library), Stockholm
 TECHNICAL COATINGS CO Oakmont PA (Library)
 TIDEWATER CONSTR. CO Norfolk VA (Fowler)
 TRW SYSTEMS CLEVELAND, OH (ENG. LIB.); REDONDO BEACH, CA (DAI)
 UNITED KINGDOM A. Denton, London; British Embassy (Info. Offr), Washington DC; Cement & Concrete Assoc
 Wexham Springs, Slough Bucks; Cement & Concrete Assoc. (Library), Wexham Springs, Slough; Cement &
 Concrete Assoc. (Lit. Ex), Bucks; D. Lee, London; D. New, G. Maunsell & Partners, London; J. Derrington,
 London; Library, Bristol; R. Browne, Southall, Middlesex; R. Rudham Oxfordshire; Shaw & Hatton (F. Hansen),
 London; Taylor, Woodrow Constr (014P), Southall, Middlesex; Taylor, Woodrow Constr (Stubbs), Southall,
 Middlesex; Univ. of Bristol (R. Morgan), Bristol
 WATT BRIAN ASSOC INC, Houston, TX
 WESTINGHOUSE ELECTRIC CORP. Annapolis MD (Oceanic Div Lib, Bryan)
 WESTINTRUCORP Egerton, Oxnard, CA
 WISS, JANNEY, ELSTNER, & ASSOC Northbrook, IL (D.W. Pfeifer)
 WM CLAPP LABS - BATTELIE DUXBURY, MA (LIBRARY); Duxbury, MA (Richards)
 WOODWARD-CLYDE CONSULTANTS (A. Harrigan) San Francisco; PLYMOUTH MEETING PA (CROSS, III)
 ADAMS, CAPT (RET) Irvine, CA
 AL SMOOTS Los Angeles, CA
 ANTON TEDESKO Bronxville NY
 BRAHTZ La Jolla, CA
 BULLOCK La Canada
 F. HEUZE Boulder CO
 LAYTON Redmond, WA
 R.F. BESIER Old Saybrook CT

R.Q. PALMER Kaitua, HI
T.W. MERMEL Washington DC
WM TALBOT Orange CA
CEC Parisi, Anthony M., LT