Accelerated Corrosion of Copper-Nickel Piping

National Materials Advisory Board

Commission on Sociotechnical Systems

NMAB-343

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

14

1. REPORT NUMBER
NMAB-343

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

6

4. TITLE (and Subtitle)
Accelerated Corrosion of Copper-Nickel Piping.

9

5. TYPE OF REPORT & PERIOD COVERED
Final Rep[redacted]t.

6. PERFORMING ORG. REPORT NUMBER
NMAB-343

7. AUTHOR(s)
NMAB Committee on Accelerated Corrosion of Copper-Nickel Piping

15

8. CONTRACT OR GRANT NUMBER(s)
N00014-77-C-0251

9. PERFORMING ORGANIZATION NAME AND ADDRESS
National Materials Advisory Board
National Academy of Sciences
Washington, D.C. 20418

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
12 39p.

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research Resident
Representative, George Washington Univ.
2110 G Street, N.W., Washington, D.C. 20037

11

12. REPORT DATE
Dec[redacted]77

13. NUMBER OF PAGES
36

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Naval Sea Systems Command
Washington, D.C. 20362

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Ammonia	Erosion
Cavitation	Passivity
Corrosion	Sulphide
Cupro-Nickel	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Unexpectedly severe corrosion occurred in cupro-nickel piping in seawater cooling systems aboard ships built in one location. A workshop ~~was~~ convened to discuss the problem, with the findings incorporated in this report, along with conclusions reached by the National Academy of Sciences committee.

Among other findings, the workshop identified turbulence as a major contributing factor, and the practice of running the seawater loop wide open while throttling the fresh-water loop as contributory to the turbulence.

over

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

405 114

20. ABSTRACT Contd.

cont.

Recommendations of the committee were: (1) reduce the velocity of flow in the pipes; (2) use long radius elbows whenever possible; and (3) conduct research or development to evaluate the following remedial measures-- (a) suitability of alternate materials; (b) determination of the significance of the iron content in alloy 706 (90Cu-10Ni); (c) investigation of the relative corrosion rate when a negative potential is applied to the system, using the cupro-nickel piping as a cathode; (d) control of seawater pH to a value of about 9.0; and (e) use of electrochemical probes to detect changes in corrosion rates.

The committee, in commenting on the Navy's research program, felt that the turbulence aspect had been given inadequate attention, that the role of ammonia had not been given adequate consideration, that the design of the shore-based simulation test did not sufficiently resemble the installed conditions, and that more should be done on characterizing reaction product films.

ACCELERATED CORROSION OF COPPER-NICKEL PIPING

Report of

THE COMMITTEE ON ACCELERATED CORROSION OF
COPPER-NICKEL PIPING

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council

Publication NMAB-343
National Academy of Sciences
Washington D.C.
1977

NOTICE

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competence and with regard to appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, National Academy of Engineering, and the Institute of Medicine.

This study of the cause and prevention of accelerated corrosion of copper-nickel piping in ship systems by the National Materials Advisory Board was conducted under Contract No. N00014-77-C-0251 with the U.S. Navy, Office of Naval Research.

This report is for sale by the National Technical Information Service, Springfield, Virginia 22151.

Printed in the United States of America.

NATIONAL MATERIALS ADVISORY BOARD
COMMITTEE ON ACCELERATED CORROSION OF COPPER-NICKEL PIPING

Chairman

MICHAEL J. PRYOR, Director, Metals Research Laboratories, Olin Corporation, New Haven, Connecticut

Members

FRANKLIN H. COCKS, Professor of Mechanical Engineering and Materials Science, School of Engineering, Duke University, Durham, North Carolina

FREDERICK G. HAMMIT, Professor, Department of Mechanical Engineering, University of Michigan, Ann Arbor

LLOYD A. HELDT, Professor of Metallurgy, Department of Metallurgical Engineering, Michigan Technological University, Houghton

DANA R. KESTER, Professor of Oceanography, Graduate School of Oceanography, University of Rhode Island, Kingston

DONALD M. McCUE, Manager, Tube Sales, TIMET, Division of Titanium Metals Corp. of America, Pittsburgh, Pennsylvania

FREDERIC W. PEMENT, Materials Science Division, Nuclear Materials Department, Research and Development Center, Westinghouse Electric Corporation, Pittsburgh, Pennsylvania

E. NEVILLE PUGH, Professor of Metallurgy, Department of Metallurgy and Mining Engineering, University of Illinois, Urbana

ELLIS D. VERINK, JR., Chairman, Department of Materials Science and Engineering, University of Florida, Gainesville

Liaison Representatives

UGO BERTOCCI, Corrosion and Electrodeposition Section, Materials Building, National Bureau of Standards, Washington, D.C.

PHILIP A. CLARKIN, Office of Naval Research, Arlington, Virginia

GEORGE DANEK, Naval Ship Research and Development Center, Annapolis, Maryland

HARVEY P. HACK, Naval Ship Research and Development Center, Annapolis, Maryland

RODNEY JOSEPH, Manager of Copper, Lead, Zinc Program, Bureau of Domestic Commerce, Department of Commerce, Washington, D.C.

MURRAY ROSEN, U.S. Bureau of Mines, Corrosion and Electrometallurgy Group, College Park Metallurgy Research Center, College Park, Maryland

NMAB Staff

JOSEPH R. LANE, Staff Metallurgist

Participants in the July 12-13, 1977

Workshop on
Accelerated Corrosion of Copper-Nickel Piping

WALTER K. BOYD, Battelle Memorial Institute, Columbus, Ohio

B. FLOYD BROWN, Chemistry Department, American University, Washington, D.C.

LOUIS CARUSO, Phelps Dodge Brass Company, East Brunswick, New Jersey

JAMES E. CASTLE, Metallurgy Section, Department of Materials Science, Pennsylvania State University, University Park

RONALD M. LATANISION, Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge

KENNETH R. LAWLESS, Materials Science Department, University of Virginia, Charlottesville

WALTER B. LAWRENCE, Project Engineer, Bechtel Power Corporation, San Francisco, California

T. S. LEE III, Francis LaQue Corrosion Laboratories, Wrightsville Beach, North Carolina

FLORIAN B. MANSFELD, Rockwell International Science Center, Thousand Oaks, California

OLIVER OSBORNE, Lake Jackson, Texas

JAMES M. POPPLEWELL, Olin Corporation, New Haven, Connecticut

DONALD E. WHITE, United Engineers and Constructors, Inc., Philadelphia, Pennsylvania

ACKNOWLEDGMENTS

The members of the committee and the task groups would like to express their sincere appreciation to Messrs. Danek and Hack of the Navy for their conscientious and largely successful efforts to obtain the voluminous information required by various task groups over and above what was provided in the briefings.

PRECEDING PAGE BLANK-NOT FILMED

CONTENTS

ABSTRACT

Unexpectedly severe corrosion occurred in cupro-nickel piping in seawater cooling systems aboard ships built in one location. A workshop was convened to discuss the problem, with the findings incorporated in this report, along with conclusions reached by the National Academy of Sciences commitee.

Among other findings, the workshop identified turbulence as a major contributing factor, and the practice of running the seawater loop wide open while throttling the fresh-water loop as contributory to the turbulence.

Recommendations of the committee were:

1. Reduce the velocity of flow in the pipes.

2. Use long radius elbows whenever possible.

3. Conduct research or development to evaluate the following remedial measures:

   a. suitability of alternate materials;

   b. determination of the significance of the iron content in alloy 706 (90Cu-10Ni);

   c. investigation of the relative corrosion rate when a negative potential is applied to the system, using the cupro-nickel piping as a cathode;

   d. control of seawater pH to a value of about 9.0;

   e. use of electrochemical probes to detect changes in corrosion rates.

The committee, in commenting on the Navy's research program, felt that the turbulence aspect had been given inadequate attention, that the role of ammonia had not been given adequate consideration, that the design of the shore-based simulation test did not sufficiently resemble the installed conditions, and that more should be done on characterizing reaction product films.

Chapter 1

INTRODUCTION

A. BACKGROUND

Since March of 1974, certain ships being fitted up in an East Coast shipyard developed leaks in the 90/10 cupro-nickel piping in seawater cooling systems. Perforation of the heavy wall piping has been extremely rapid, taking place in as little as four months. Vessels that have been repiped also have failed a second and even a third time during the approximately three- to four-year fitting up period.

Analysis of the corrosion problem was conducted over a period of some three years at the David W. Taylor Naval Ship Research and Development Center. Figure 1 is a photograph of the inside of a corroded pipe. The phenomenology of the deterioration is as follows:

1. The majority of the damage occurred downstream from M bronze fittings and elbows (containing around 6% Sn, 1.5% Pb, 4% Zn, 0.5% Ni, balance essentially copper). These fittings caused turbulent flow at the pitted locations. There were occasional examples of erosion or localized attack as far as 2 to 3 feet from the elbows and flanges. These occurrences were limited. Pitting rarely occurred upstream of elbows or flanges.

2. The appearance of the corrosion product film in the pitted region was quite different from the normal dark brown adherent cuprous oxide coating that forms on CDA*706 (90/10 copper-nickel) in clean seawater. Instead, the films in the sites of localized attack were black or brown and were accompanied by flaky films that exhibited green, black or sometimes red colors.

3. Corroded areas generally were deep and sharply scalloped and exhibited symmetrical features. Erosion of the downstream edges of the pits was sometimes observed.

---

* Alloy numbers used are those specified by the Copper Development Association Inc. The terms copper-nickel and cupro-nickel have been used interchangeably in this report.

FIGURE 1 Typical Appearance of Corroded Inside Surface of Cupro-Nickel Piping. (Courtesy of U.S. Naval Ship Research and Development Center.)

4. The flow velocity in the cupro-nickel piping was not high enough to produce erosion-corrosion of 706 under those conditions of exposure to clean seawater where 706 piping had been generally quite satisfactory over the years.

5. Somewhat similar attack has been experienced on CDA 715 (70/30 cupro-nickel) but the depth of attack was substantially less than in the case of CDA 706.

In view of the foregoing circumstances, the David W. Taylor Naval Ship R & D Center performed an extensive investigation of the causes for failure of the copper-nickel piping on the downstream side of the M bronze elbows, flanges, and fittings. At the outset of the Navy investigation, it was realized that sulfide (HS^- ion) and the ammonium ion could be responsible for lowering the erosion-corrosion resistance of 706 and could give rise to the severe pitting in areas of turbulent flow. Much of the early work was directed toward detecting the presence of sulfide in the water at the shipyard. This proved difficult because of the limited sensitivity of the standard chemical analysis, which becomes indefinite at a concentration of around 100 ppb. Using a more sensitive test, sulfide was found to be present at low levels in loosely adherent scales in pitted locations of the piping. Monitoring of the very low sulfide content of the shipyard water was conducted under contract by the Navy to the Virginia Institute of Marine Sciences and average levels of around 10 ppb were found. There was some thought that the corrosion problem was triggered by sulfide excursions and in 1975, transients as high as 270 ppb were recorded. However, no transients were observed in 1976 and the attack continued unabated.

A second hypothesis was checked -- namely, that high sulfide levels might be generated by sulfate-reducing bacteria in a closed system where dissolved oxygen had become depleted. This was checked out but found not to be a viable hypothesis since build-up of sulfide did not occur when the solution became deaerated in 90/10 copper-nickel containers. Accordingly, the prime conclusion of the Navy was that the lower resistance to erosion-corrosion was due to sulfide at an average level of about 10 ppb obviously coexisting with the presence of dissolved oxygen in the seawater. Less work has been done by the Navy to assess the role, if any, of the ammonium ion in reducing erosion-corrosion.

The Navy has investigated two basic approaches designed to improve the corrosion performance of the copper-nickel piping. The first involved pre-filming of the seawater intake system, etc., in clean seawater. Test results showed that some four months of exposure to clean seawater was necessary to build up a protective cuprous oxide film. This time was considered impractical for use by the Navy.

Second, an attempt was made to produce protective films by the injection of ferrous sulfate into the cooling system. The greatest success with ferrous sulfate treatment in the past has been on aluminum brasses while generally more erratic results have been experienced with the copper-nickels. Early batch exposures in stagnant water over limited periods of time did not yield sufficient data to determine how effective the inhibitor really was. Later tests in flowing water with the injection of ferrous sulfate itself indicated some positive effects when the ferrous sulfate was used simultaneously with sulfide exposure. Some additional experience reported verbally to the committee showed that the production of ferrous ions by anodic corrosion of iron anodes had a significant and valuable protective effect.

B. PROCEDURE

In 1976, the Navy negotiated a contract with the National Academy of Sciences to marshall a qualified ad hoc committee to study this matter further. In March 1977, the committee, composed of individuals listed in the roster in the front of the report, was assembled. The Navy's past record on these failures together with their preliminary conclusions were provided by Messrs. Hack and Danek to the committee, which met on May 19, 1977 in Washington, D.C.--Dr. Cocks being unable to attend. In essence, the May 19 meeting was informational as well as procedural for the nine members of the committee.

The overall plan of attack outlined by the Academy to the committee chairman consisted of the organization of a workshop, which was held in Washington on July 12 and 13. Qualified individuals were selected by the committee and invited to participate in the workshop. The workshop was divided into three parallel sessions having individual objectives as listed below. The individual task groups operated within the framework of their charter and by the end of the second day, July 13, produced a draft report on their findings. The committee--F. G. Hammit being unable to attend--then reassembled on July 14 and produced a draft of a final report presenting the overall conclusions and findings of the committee.

Much of the data involved in this problem are sensitive; some is classified. Therefore, the Navy individuals were circumspect in their presentations to the committee, and as a consequence this report contains few data and no information relating, even indirectly, to ship performance. The alternative would have been the preparation of a classified report, with the resultant very limited distribution. Navy documents bearing on this problem are not cited since they generally bear the notation "For Official Use Only."

Chapter 2

TASK GROUP REPORTS

A. TASK GROUP I - DEFINITION OF THE NATURE OF THE ATTACK

This task group reviewed in detail the work done by the Navy in order to assess its technical content, reasonableness of conclusions, etc. It also was responsible for suggesting any additional work, short and long range, that should be considered by the Navy. The concerns of this group were basic corrosion studies, solid state aspects of oxide films, and metallurgy of the substrate. This task group, chaired by Dr. Lloyd A. Heldt of Michigan Technological University, included the following theoretical corrosion workers in the field:

Dr. Ugo Bertocci, Corrosion and Electrodeposition Section, National Bureau of Standards

Dr. B. Floyd Brown, Chemistry Department, American University

Dr. James E. Castle, Metallurgy Section, Department of Materials Science, Pennsylvania State University

Prof. Kenneth R. Lawless, Materials Science Department, University of Virginia

Dr. Florian B. Mansfeld, Rockwell International Science Center

Professor E. Neville Pugh, Department of Metallurgy and Mining Engineering, University of Illinois

Dr. James M. Popplewell, Olin Corporation, Metals Research Laboratories

1. Nature of the Attack

The location of attacked regions in the piping system and the appearance strongly suggest that turbulence is a major cause contributing to this very aggressive attack. Turbulent flow of sea water containing air bubbles, sand or both can mechanically remove protective corrosion product films at areas of highest local solution velocity. The resulting combination of limited areas of bare copper-nickel surrounded by large conductive cathodic areas (undamaged reactor product film) will produce aggressive pitting. If the turbulence continues to maintain the anodic areas free from reaction product film, rapid perforation will occur. This is known as "erosion-corrosion." Cavitation, i.e., collapse of gas bubbles can cause similar corrosion but usually only at substantially higher average solution velocities than were experienced in this case. The weak galvanic effect of coupling M bronze fittings to the 706 piping was dismissed as being inadequate to explain the severe attack. Pitting--not observed upstream of the M bronze fittings--would have been anticipated to some degree if the M bronze-alloy 706 galvanic couple dominated.

Apparent satisfactory performance of this piping system in open sea water indicates that turbulence alone is not a sufficient condition for this form of attack. Instead, the attack is the result of a conjoint action by the turbulence and a specific corrodent. It seems probable that particular chemicals in the shipyard water serve to reduce the resistance of a normally protective cuprous oxide thereby providing a thicker and more fragile corrosion product film which is more easily removed mechanically under erosion conditions. These particular chemicals are as yet unidentified. That sulfide is necessary is being given consideration but is not established. The task group questions the claim that service failures have been reproduced with the strip specimens exposed to sulfide-bearing water during the laboratory tests; there is no evidence that the same mechanism is operative. The hydrodynamic conditions in this test are different from those in service. A realistic simulation test must reproduce the service observations: severe attack at higher velocities (more than 8 ft/sec) but not at lower velocities (6 ft/sec). Moreover, it is recognized that these test results are contradictory to established data and commercial experience for cupro-nickel alloys in sulfide environments. For example, the resistance of alloy 706 to sulfide attack is generally quite good when compared with many other copper alloys; the rapid failure of 706 is unexpected if sulfide is the only critical chemical. In view of these uncertainties, ammonia and other agents, perhaps acting synergistically, should be considered.

The task group also considered the effect of the state of iron in the alloy--i.e., whether this element is primarily in solid solution or in an iron-rich precipitate. The former state is known to enhance resistance to erosion-corrosion. A black magnetic corrosion product was observed to be coincident with severe attack on the piping systems. This corrosion product is indicative of precipitated iron in the alloy.* Thus, it appears that the alloy is not in the optimum condition to resist attack. This effect is considered not to have primary responsibility for susceptibility but it may contribute to a reduction in erosion-corrosion resistance. A procedure to evaluate this possibility is outlined below.

2. Means of Analyzing the Problem

As mentioned above, it would be valuable to dismiss cavitation as actually occurring in the operating system--i.e., whether there is a bubble formation and collapse. A model system of transparent piping may be useful in this respect.

Further corrosion tests should employ the shipyard water. During testing, crevice corrosion must be minimized to avoid cathodic protection of the exposed surface. Velocity, cavitation, ammonia concentration, sulfide concentration, and the state of iron should be taken into account separately and in combination.

Material characterization should be improved for attacked materials and this characterization should be extended to materials that have performed well in other ships of the same class (outfitted at other yards) and to material from fire lines that have seen intermittent flow.

Magnetic permeability measurements are recommended to evaluate the role of the state of iron in the alloy. Specifically, measurements should be made at various points along pipe samples removed after operation in the shipyard water to determine whether correlation exists between permeability values and severe attack at high velocity.

Characterization of the surface films to date has been extremely limited. Future work, particularly that involving Auger and electron spectroscopy for chemical analysis (ESCA), should have very specific objectives; for example, determination of the local composition of the path along which the film breaks away from the metal.

The chemistry of the water in various shipyards including sulfide, ammonia, other nitrogen compounds, and iron should be monitored as affected by time, disturbance of bottom sludge, and location.

---

* See, for example, W. C. Stewart and F. LaQue, Corrosion, 8, 259 (1952).

B. TASK GROUP II - CORROSION CONTROL FOR PRESENT SYSTEM

This task group was responsible for examining the cooling systems as they currently exist and reviewing the Navy's work on protection for the 706 alloy piping, and suggesting practical means of corrosion control not previously investigated by the Navy. Dr. Ellis D. Verink of the University of Florida chaired this task group composed of the following authorities in the field of corrosion control:

Mr. T. S. Lee III, Francis L. LaQue Corrosion Laboratories

Mr. Oliver Osborne, Lake Jackson, Texas

Mr. Donald W. White, United Engineers and Constructors, Inc.

Dr. Ronald M. Latanision, Department of Materials Science and Engineering, Massachusetts Institute of Technology

Dr. Dana R. Kester, Graduate School of Oceanography, University of Rhode Island - (absent)

The following comments are made on the assumption that corrective measures proposed should mitigate damage in the system without requiring a change of materials or design. This does not imply that certain design changes, for example, would not be beneficial. While no detailed analysis of costs was possible, the proposed measures were scrutinized with at least some concern for the costs they might involve. Some of the measures suggested can be incorporated immediately based on existing knowledge; others will require some research effort to establish operating parameters.

1. Prefilming (Altering the Surface of the Existing Materials)

The corrosion resistance of copper-nickel alloys is imparted by the presence of protective corrosion product films which form naturally on the alloy surfaces. Cu_2O is among the more protective of such reaction product films in saline environments. This is the predominant film observed on 706 in uncontaminated seawater at a pH of about 8.2. The domain of stability of Cu_2O in terms of electrode potential and pH is predictable on the basis of applicable Pourbaix diagrams. If there are excursions of pH (e.g., acidification) as in occluded cells (pits, crevices, etc.), intensification of attack can occur. It has been shown that pretreatment under conditions that will enhance formation of Cu_2O will provide a barrier which has significant resistance even when the prefilmed alloy is exposed to conditions of lower pH (where the film is not considered to be protective). The time required to penetrate the metastable film under lower pH conditions would depend on the film thickness and integrity as well as the acidity and temperature of the environment.

The practice of pretreating the material to impart corrosion resistance by forming a better passivating layer has been demonstrated in the case of aluminum alloys where use of steam treatments permit the alloy to resist certain chemical exposures. Navy tests show that 706 cupro-nickel piping preexposed 120 days to uncontaminated seawater developed a sufficiently protective film to avoid attack of the type being investigated in this study. Unfortunately, the kinetics are too slow for consideration. However, it is possible to adjust the chemical character of the electrolyte to form Cu_2O more rapidly. Probably the least expensive method would be to adjust continuously the pH of the circulating water (normally about 8.2) by 0.5 to 1.0 pH units in the alkaline direction. This would offer the additional possibility that protective calcareous films will also form if lime is used for pH control. The kinetics of film formation should be studied as a function of pH (and perhaps temperature) to provide an operating basis.

There are other ways in which pretreatments could be applied to installed piping.* For example, a passivating solution could be circulated through the piping <u>periodically</u> with retreatment based on monitoring of instantaneous corrosion rates in the system. One such treatment involves a solution of chromates and phosphates and was used successfully in tests of a desalination plant. A periodic treatment system has the disadvantage of requiring a special storage and recirculating system. The persistence of the passivating film, environmental questions, and costs all require determination before a decision could be reached on applying this prefilming process. It also is possible to apply metallic coatings to pipe interiors; however, such coatings are likely to be more costly than other

---

* The piping system is put together by welding. Therefore, factory-applied protective treatments cannot provide a viable approach. Any protective measures that are realistic must be of a field-applied "in situ" nature.

alternatives and pose significant environmental questions, hence will not be considered further.

2. Treatment of Environment

It would be highly desirable to learn what elements or compounds may now be lacking in the shipyard water but which may have been present prior to 1974. Such substances may have acted either as inhibitors via corrosion product incorporation or as chelating agents for removal of aggressive species. Of particular interest are inhibiting species such as ferrous ion, organics, etc. Comparable data also should be assembled from other shipyard locations for comparison.

Table 1 lists several possibilities for modification of the shipyard water environment to make it more compatible with Cu-Ni piping.

Research by the U.S. Navy has established the beneficial effects of ferrous additions to seawater containing low levels of sulfide. Mitigation of sulfide-accelerated corrosion has been obtained with ferrous ion introduced either as ferrous sulfate or via electrolytic stimulation of iron anodes. Ferrous ion reduces corrosion of cupro-nickels both by improving the protectiveness of the corrosion product films and by removing sulfide ion from the water through precipitation as FeS. Which mechanism is the more important depends on the circumstances and whether ferrous sulfate is added intermittently or continuously.

Stimulated iron anodes may be operated with any of a variety of auxiliary electrodes (iron, platinum, or cupro-nickel pipe). The reactions at the cathode are particularly important where cupro-nickel pipe is used as the cathode. In this case, sulfide ion removed from polluted seawater may deposit as FeS on the pipe. The consequences of such deposits should be evaluated carefully to determine whether special corrosion problems may result. By contrast, in clean seawater there is electrophoretic transfer of colloidal γFeOOH to the cathode surface, which is generally accepted as being beneficial.

While ferrous ion is known to scavenge sulfide ions from seawater, the influence of ferrous ions on ammonia compounds is not known. Information also is lacking on combinations of sulfides and ammoniacal contaminants in seawater. Research should be initiated to establish the influence of such combinations in cupro-nickels in seawater.

3. Structure and Composition of Surface Films

The degradation of otherwise protective surface films by environmental interaction is likely to play a major role

TABLE 1 Potential Environmental Treatments*

Process	Purpose
Introduction of Ferrous Iron	
Ferrous Sulfate Injection	Scavenge sulfide Form γ FeOOH
Stimulated Iron Anodes	Scavenge sulfide Form γ FeOOH
pH Control	Stabilize Cu_2O Reduce H_2S
Addition of Oxidizing Agents	
Chlorine or Hypochlorite Injections	Oxidize sulfide
Oxygen Catalyst Additions	Oxidize sulfide

* Note: In each case, research should be conducted to establish operating limits.

in the present problem. The damage to the seawater system during fitup in the shipyard was considerably more than expected from chemical corrosion alone. It seems clear, therefore, that some synergism must occur between the mechanical damage induced by flow conditions--which might occur in any case since elbow designs are suspect--and the chemistry of the shipyard water (i.e., the presence and/or absence of Fe^{+2}, HS^- content, NH_3, etc., previous to and subsequent to 1974).

In an attempt to separate these effects, a chemical and structural characterization should be made of the films formed on Cu-Ni pipes during fitup in the shipyards. Investigations which should be made include positive identification of the film (Cu_2O); determination of the C, S, and Fe content in the film from each shipyard.

Reference has been made to the possibility of utilizing the copper-nickel pipe as a cathode when adding ferrous ions through action of stimulated Fe anodes. In the event that deposition of FeS does not pose special difficulties, special advantages could result. There is evidence that some degree of cathodic protection will be provided for the piping (this would have to be controlled to avoid compromising the otherwise antifouling character of the Cu-Ni pipes) and that making the Cu-Ni pipe a cathode may lead to the beneficial attraction of collodial material to the pipe surfaces. In addition, it has been observed that enrichment of nickel occurs in the oxide film on cathodically polarized copper-nickel piping [e.g., at about -0.25 volts, standard hydrogen electrode (SHE)]; the nickel content in the film on 706 (90 Cu-10 Ni) approaches 30 percent [i.e., close to that present in 715 (70 Cu-30 Ni) alloy but not as high as the nickel content in the oxide on 715]. Similar nickel enrichment also has been observed at the corrosion potential in INCO seawater exposure tests: after four months preexposure to salt water, the nickel content in the film on 706 containing iron was about 30 percent.

4. Environmental Monitoring

Extensive previous work has demonstrated the reliability of electrochemical corrosion probes for detecting changes in corrosion rate. These devices operate on the principle that when a low potential (±10 mv) is applied to a corroding metal surface, the current required to maintain this potential is directly proportional to the corrosion rate. It is therefore possible to install these probes in operating systems and obtain continuous records of the corrosivity of the media to the metal composition of the probe.

It is suggested that probes be fabricated from CA 715, CA 706, and CA 722 (15-18% Ni) and that they be installed at locations in the system where corrosion is known to be aggressive. Furthermore, these probes should be designed to be subjected to the identical velocity conditions of the pipe wall itself. Suitable valving should be installed to permit installation or removal of the probe without having to shut down the water flow systems. Correlation between probe performance and other corresponding observations should provide a basis for setting operating parameters.

C. TASK GROUP III - CONSTRUCTION (MATERIALS AND DESIGN)

This task group was charged with reviewing changes in mechanical and hydraulic design of the piping systems consistent with good naval practice that might alleviate this erosion-corrosion problem and with suggesting alternate materials of construction for the 706 piping systems. There were two factors that limited the choice of alternate materials. One was obviously improved erosion-corrosion resistance of the piping material itself so that the perforation problem could be eliminated. The second was a biofouling restriction since alloy 706 has basically good biofouling resistance combined with normally acceptable level of corrosion resistance. In discussions at the May 19 meeting, a target for the biofouling resistance was provided in that the biofouling resistance could not be poorer than that of 715 copper-nickel. This task group was chaired by Mr. Walter K. Boyd of Battelle Memorial Institute and was composed of the following authorities in materials usage from the corrosion standpoint:

Dr. Frederic W. Pement, Materials Science Division, Nuclear Materials Department, Research and Development Center, Westinghouse Electric Corporation

Mr. Donald M. McCue, TIMET, Division of Titanium Metals Corp. of America

Mr. Louis Caruso, Phelps Dodge Brass Company

Dr. Franklin H. Cocks, School of Engineering, Duke University

Mr. Walter B. Lawrence, Bechtel Power Corporation

1. <u>Discussion of the Problem</u>

Since 1974, the Navy has experienced severe corrosion problems with the 706 cupro-nickel piping on two types (designated Type 1 and Type 2 in this report) of ships built at an East Coast Shipyard. Three other Type 1 ships have been built at two other shipyards and have experienced no corrosion problems with the piping system.

In addition to the environmental differences, the three Type 1 ships built by the other shipyards were operated in a somewhat different manner--i.e., the seawater system was operated throttled. For the Type 1 ships built at this East Coast shipyard where corrosion damage occurrred, the modus operandi was to run the seawater system at full flow and control internal temperatures by throttling the (fresh) cooling water flow. The task group was unable to establish differences, if any, in the operations of the air-conditioning systems.

In making its recommendations, the task group also considered that:

a. There has been no corrosion on the suction side of the pumps.

b. The areas of corrosion are on the discharge side of the pumps, particularly at areas downstream of sharp bends or constrictions.

c. There has been less corrosion of the systems on Type 2 ships than on the Type 1 ships, the primary differences being that the Type 2 ships utilize large radius elbows.

d. In a high flow-rate seawater system, the corrosion is entirely limited to the piping sections leading to the heat exchanger. For the air conditioning systems, some slight corrosion has also been observed after the heat exchanger.

e. There has been no corrosion reported for the 70/30 tubes in the heat exchanger. However, it is noted that the heat exchanger tube sheets are 706 which can offer some galvanic protection to the 715 tubes at the inlet ends where turbulence-related corrosion would otherwise be maximized.

In light of the data presented by the Navy, the task group reviewed in depth the design and operation of the fluid systems. Velocity calculations were made and correlated with the incidence of attack. Table 2 provides a summary of the systems.

2. Conclusions and Recommendations of Task Group III

A critical review of the data suggests that high velocity coupled with the environment of polluted seawater is the main cause of the rapid corrosion observed. In addition, the design of the system is deficient in that very sharp radius elbows are extensively utilized, particularly in Type 1 ships.

It is recommended that the following remedial measures be initiated:

a. Steps be taken to reduce the velocities within the pipe system while at dockside. The task group strongly suggests that the mode of operation be changed to incorporate throttling of the seawater system. The throttling should be done on the discharge end of the system. It is further recommended that the dockside velocities be limited to a maximum of 7 feet per second.

b. Wherever possible in all systems, long radius elbows should be used. Extending the downstream length of the M bronze elbows was considered but rejected by the Navy personnel on the basis of severe space limitation. Further, this approach would not assist the turbulence-related common problem downsteam of flanges.

c. For alternate materials considerations, the task group suggests that realistic qualification tests be conducted on 715 cupro-nickel and the CDA 722 alloy in the shipyard water.

d. For continued use of 706 cupro-nickel, it is recommended that the Navy explore with the producers the heat treatment to ensure proper retention of iron in solid solution.

e. It also is recommended that the Navy determine the history of operations of the air conditioning systems of the ships built in other shipyards, particularly with respect to the mode of throttling, if any.

The task group also favors removal of sections of the fire main piping system for examination of the films formed on the surface and to determine the condition of the pipe.

TABLE 2 Air Conditioning Systems Experience

Ship	Pipe Size (in.)	Pipe Location	Volumetric Flow Rate (gpm)	Linear Velocity (fps)	History Comments
Type 1	8	Pump Suction	1000	6.3	No reported corrosion
Type 1	6	Pump Suction	500	5.7	No reported corrosion
Type 1	5	Pump Discharge	500	8.2	Attack
Type 2	10	Pump Suction	1575	6.4	No reported corrosion
Type 2	8	Pump Discharge	1575	10.0	Some attack*

* System uses larger radius elbows.

Chapter 3

REPORT OF THE AD HOC COMMITTEE ON ACCELERATED CORROSION OF COPPER-NICKEL PIPING

The committee met on July 14 to review the task group reports and to prepare their overall recommendations and comments on the Navy's work. Certain modifications were made to the drafts submitted by the task groups. These modifications were made with the concurrence of either the chairman of the particular task group or his designated representative.

A. RECOMMENDATIONS OF THE AD HOC COMMITTEE

1. Recommendation 1

The committee recommends strongly that steps be taken on a short-range basis to reduce the seawater velocity within the seawater piping systems of the two types of ships in question during fitting out in the shipyard, where corrosion has been encountered.

a. Rationale

Three similar Type 1 ships with (according to the Navy) identical piping system, fitted out in two other locations were without the accelerated corrosion problem. It transpired after detailed inquiry by Task Group III that the affected design had not been in service before 1974 and that the conditions of operation of the seawater system was unique at the one East Coast location. Instead of the seawater system being throttled as was practiced at the other shipyards, the practice has been to run the seawater system at full flow and to control the temperature by throttling the fresh water coolant system. The committee could not quantitatively determine how much the practice of throttling the seawater system actually reduced average flow rate because the degree of throttling is not constant in practice. However, some net reduction of maximum flow rate must have been achieved by this practice and less accelerated corrosion has occurred. Task Group III, in conjunction with the Navy, was not able to pinpoint any velocity difference in the air-conditioning system.

For Type 1 vessels outfitted at the East Coast shipyard, Task Group III was able to calculate that accelerated corrosion occurred in the air-conditioning system only when the average flow velocity was somewhat in excess of 8 feet per second. This accelerated corrosion was invariably associated with turbulence created by sharp 90-degree changes in flow direction (at elbows) and by partial constrictions. It is considered to be highly significant that sections of the air-conditioning system that had earliest exposure to the incoming seawater and that operated at an average flow velocity in the regime of 6 feet per second plus did not suffer accelerated corrosion despite the fact that similar 90-degree changes in flow direction and similar partial constrictions existed. A similar correlation between accelerated corrosion and maximum average velocity was obtained in the seawater systems.

The committee recommends that the practice of throttling the seawater system be used in the shipyard to reduce seawater velocity to around the recommended level of a maximum of 7 feet per second. The committee believes that flow velocity is more influential than the water quality since the water quality conditions are believed, based on general experience, to be more aggressive at the two other shipyards than in this East Coast location but this fact is as yet unproven.

It must be pointed out that reducing seawater velocity in the piping section should aid in reducing the accelerated corrosion of 706 piping in both new and recently repiped ships. The degree of control of corrosion by reducing seawater velocity in 706 piping which is already extensively corroded is less certain. Presumably some benefit should accrue, but if extensive corrosion and near perforation had previously occurred by high velocity turbulent attack, then increase in life may be small. We see no way that reducing velocity to 7 feet per second could reduce life of previously-corroded pipe.

b. <u>Related Recommendations of the Committee</u>

(1) A survey of water quality of the same type and scope as the survey already conducted in this East Coast location which is the site of the problem should be conducted at the two other locations.

(2) Any differences in flow velocity in the air-conditioning system of the same type ships fitted out at the East Coast shipyard identified with this problem and the other two locations should be reviewed by the Navy.

(3) The Type 1 ships fitted out at the other two locations should have their 706 piping systems evaluated by nondestructive means including the determination of the magnitude of corrosion attack if any.

2. Recommendation 2

The committee recommends that long radius elbows be used wherever possible and in all systems.

a. Rationale

It was an interesting observation of Task Group III that accelerated corrosion of copper-nickel piping was less severe in the Type 2 ships fitted out in the East Coast shipyard than in the Type 1 ships. This is despite the fact that the average calculated flow velocity was some 20 percent higher in the Type 2 ships. This can be traced to the use of long radius elbows in the larger piping of the Type 2 ships. By contrast, the elbows in the Type 1 ships fitted out in the East Coast shipyard are extremely sharp and accentuate the turbulence problem at a 90-degree change in the flow direction. It is appreciated by the committee that space is always at somewhat of a premium with respect to the piping system; however, inadequate attention appears to have been paid to the hydraulic design of the elbows in the 706 Type 1 ship seawater piping system from the local turbulence standpoint. The inside bend radius needs to be expanded whenever possible.

b. Related Recommendations

The committee recommends that the Navy, if it has not already done so, conduct an experimental program using transparent models to determine the water flow patterns particularly at the downstream side of elbows of varying inner radii. The objective is to optimize and smooth the change in flow direction as much as possible consistent with space requirements. This type of study can be done by injected markers (e.g., dye or mica particles of various types) used in conjunction with high-speed photography.

B. SYSTEM CORROSION CONTROL

The two primary recommendations presented above can be implemented without the necessity of new research to justify their use. However, the task groups also have made a variety of suggestions for controlling the turbulence-related corrosion that require research and these are presented in detail below together with comments on the type of study required.

1. Alternate Materials of Construction

The committee believes that there are no feasible alternate materials of construction that are immediately available and for which satisfactory service in the East Coast shipyard under the present hydrodynamic conditions can be documented. Although much has been made of the lack of corrosion of the Alloy 715 condenser tubes in Type 1 and Type 2 vessels, this observation requires qualification. Turbulence-oriented corrosion would be anticipated primarily at the inlet end of the condenser tubes; however, the tube sheets in the condensers are made from Alloy 706, and it is well known that Alloy 706 can confer some degree of cathodic protection to Alloy 715 under these conditions.

While the committee believes that Alloys 715 and 722 are candidate materials for replacing alloy 706, it also believes that the performance of these materials is currently not fully proven for use during fitting up in the specific problem shipyard and that appropriate testing under comparable hydrodynamic conditions would have to be conducted before the candidate replacement materials could be safely used.

2. Metallurgy of Alloy 706

Both Task Groups I and III drew attention to the fact that there is evidently rather substantial precipitation of iron in many of the 90/10 alloy cupro-nickel piping samples that they examined. Further, it is well known that extensive iron precipitation reduces the normally good erosion-corrosion resistance of Alloy 706. Earlier, Popplewell measured Severn gauge permeabilities between 1.2 to 1.5 from random piping samples . Further, during the meeting of Task Group I, it was shown that the corrosion product in extensively corroded areas of a pipe sample was strongly ferromagnetic, a normal indication that there was substantial iron precipitation in the alloy.

The committee does not recommend at this time that the Navy write a magnetic permeability specification for Alloy 706 to be used in piping systems. The source of supply is relatively narrow for the piping at the present time and should not be jeopardized without good reason. Furthermore, there is no reason to believe that the cupro-nickel piping existing in the Type 1 ships fitted out at the other locations did not show approximately equivalent iron precipitation. However, Task Group I has outlined a procedure that it recommends the Navy follow for trying to relate severe corrosion in the piping in the air-conditioning system of the Type 1 ship to magnetic permeability. Since the Navy apparently has samples from one whole corroded system, this nondestructive permeability test could be conducted easily. If there is a strong correlation between high permeability and extensively corroded pipe downstream of elbows and flanges, then the question of a specification on maximum permeability acceptable to suppliers of the piping material should be considered. The Navy claims to have made permeability tests that were nonconclusive, but the information it has presented to the committee is too vague to know whether the evaluation has been done under the conditions outlined above.

3. <u>Ferrous Additions to the System</u>

The Navy test program has shown in simulated tests that ferrous sulfate additions are somewhat helpful in reducing the corrosion of the Alloy 706. Producing ferrous ions by anodic corrosion of iron with separate cathodes has proved even more effective and exercises major leverage in reducing accelerated corrosion in laboratory tests. Task Group II has proposed that the cupro-nickel piping itself might be used as the cathode and that there are specific advantages to maintaining a potential of around -0.25 volts (SHE). The rationale is as follows:

a. It would presumably aid the electrophoretic migration of colloidal lepidocrocite to the cathode areas where it is most immediately needed.

b. The nickel content of the cuprous oxide reaction product film on Alloy 706 would be increased rapidly toward that of cuprous oxide normally formed on Alloy 715 in clean seawater.

Task Group II proposed that this be checked out experimentally on a relatively short-range basis by the Navy and the committee concurred with this. The risk is that ferrous sulfide might also be driven preferentially to the Alloy 706 surface and this might adversely affect corrosion resistance.

4. <u>Control of pH</u>

Task Group II pointed out that by control of pH of the seawater to a value of about 9.0, the stability of cuprous oxide, an important component of the protective system on cupro-nickels in seawater, is enhanced. It also suggested the achievement of pH control in the system by pre-exposure of the incoming seawater for an adequate period to lime, this having the possibility of precipitation of calcium carbonate on otherwise low-resistance cathodic areas. Obviously, some research and development would have to be done on the design of a suitable system and on the achievement of pH and calcium ion control together with the evaluation of the results obtained under realistic hydrodynamic conditions. The committee supports this proposal technically if the cost is not prohibitive.

5. Monitoring of Corrosion

Extensive work has demonstrated the reliability of electrochemical corrosion probes for detecting changes in corrosion rate. Task Group II recommended and the committee agrees that probes of Alloys 706, 715 and 722 be installed in portions of the seawater system where corrosion is aggressive so as to monitor alloy response. This study cannot definitively prove the suitability of Alloys 715 and 722 for piping service, but can provide a short-term guide as to whether properly scaled (from the hydrodynamic standpoint) pipe corrosion tests are warranted.

C. COMMENTS ON THE NAVY RESEARCH STUDIES

One of the stated objectives of the committee was to comment on the research studies carried out by the Navy on the accelerated corrosion of copper-nickel piping in the East Coast shipyard. These comments are as follows:

1. The Navy refers to the accelerated corrosion as being pitting while admitting to some accelerating effect of local high velocity. The committee and the task groups unanimously felt that the accelerated corrosion was actually erosion-corrosion due to local regions of high turbulence, with there being some chemical component of this specific shipyard seawater that was reducing breakaway velocity under turbulent flow conditions. The difference may appear perhaps semantic but becomes more important in detailed considerations given below.

2. The Navy has concentrated its efforts on sulfide as being the single component of the East Coast shipyard seawater that has reduced resistance to corrosion under turbulent flow conditions. However, by most standards, the chemistry of the shipyard water would be conceived as being

relatively benign to Alloy 706. Conventional water analysis at first failed even to detect the presence of sulfide and it was only when much more sensitive techniques were utilized that very low concentrations of sulfide, of the order of 10 ppb, were consistently detected. The committee and the Task Force I believe that the role of ammonia either singly or in combination with the sulfide has not received adequate consideration and have proposed that some be given in any future research.

3. The committee and Task Group I feel that the Navy's shore-based simulation of accelerated piping corrosion is not adequate and can be misleading. The committee feels that the shore-based tests must be run on the basis of a reasonable simulation of the hydrodynamic conditions existing in the Alloy 706 piping at locations where turbulence-accelerated corrosion is occurring. To be meaningful, suitable simulated shore-based test must surely produce little or no accelerated corrosion when the net flow velocity is in the vicinity of 6.5 feet per second and where a sharp 90-degree change in flow direction or a constriction exists. It must, however, produce accelerated turbulence-related corrosion at an average flow velocity at somewhat in excess of 8 feet per second when the same sharp 90-degree change in flow direction or a constriction exists. The Navy's flat strip test showed a steady increase in corrosion (weight loss) when average flow velocities ranging from 2 to 15 feet per second were employed. This is the reason why the committee and Task Group I feel that the results from the Navy test are not easily related to the hydrodynamic conditions existing within rapidly corroding pipe where there is a sharp discontinuity in flow rates between 6.5 and a little over 8 feet per second average flow velocity.

4. The committee together with the Task Groups I and II felt that the Navy's work on characterization of reaction product film structures and compositions was relatively sparse. The feeling was that this important facet of the overall study needed greater emphasis. Specific suggestions have been made on how this may be accomplished and these are contained in the appropriate task group reports.

BIBLIOGRAPHY

John P. Gudas and Harvey P. Hack, Sulfide-Induced Corrosion of Copper-Nickel Alloys, Paper No. 93, presented at "Corrosion/77," the International Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials, March 14-18, 1977, San Francisco, California.

Harvey P. Hack, Effectiveness of Ferrous Sulfate as an Inhibitor for Sulfide-Induced Corrosion of Copper-Nickel Alloys, David W. Taylor Naval Ship Research and Development Center, Materials Department Research and Development Report 77-0072, July 1977.

D. V. Vreeland, "Review of Corrosion Experience with Copper-Nickel Alloys in Sea Water Piping Systems," Materials Performance, 15, October 1976, pp. 38-41.

THE NATIONAL ACADEMY OF SCIENCES was established in 1863 by Act of Congress as a private, non-profit, self-governing membership corporation for the furtherance of science and technology, required to advise the federal government upon request within its fields of competence. Under its corporate charter the Academy established the National Research Council in 1916, the National Academy of Engineering in 1964, and the Institute of Medicine in 1970.

THE NATIONAL ACADEMY OF ENGINEERING was founded in 1964 as a non-profit membership institution, by action of the National Academy of Sciences under the authority of its congressional charter of 1863 establishing it as a private, self-governing corporation to further science and technology and to advise the federal government. The two Academies share those purposes in their fields.

THE NATIONAL RESEARCH COUNCIL was established in 1916 by the National Academy of Sciences to associate the broad community of science and technology with the Academy's purposes of furthering knowledge and of advising the federal government. The Council operates in accordance with general policies determined by the Academy by authority of its Congressional charter of 1863 as a non-profit, self-governing membership corporation. Administered jointly by the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine (all three of which operate under the charter of the National Academy of Sciences), the Council is their principal agency for the conduct of their services to the government and the scientific and engineering communities.

THE COMMISSION ON SOCIOTECHNICAL SYSTEMS is one of the major components of the National Research Council and has general responsibility for and cognizance over those program areas concerned with physical, technological, and industrial systems that are or may be deployed in the public or private sector to serve societal needs.

THE NATIONAL MATERIALS ADVISORY BOARD is a unit of the Commission on Sociotechnical Systems of the National Research Council. Organized in 1951 as the Metallurgical Advisory Board, through a series of changes and expansion of scope, it became the Materials Advisory Board and, in January 1969, the National Materials Advisory Board. In consonance with the scope of the two Academies, the general purpose of the Board is the advancement of materials science and engineering, in the national interest. The Board fulfills its purpose by: providing advice and assistance, on request, to government agencies and to private organizations on matters of materials science and technology affecting the national interest; focusing attention on the materials aspects of national problems and opportunities, both technical and nontechnical in nature, and making appropriate recommendations as to the solution of such problems and the exploitation of these opportunities; performing studies and critical analyses on materials problems of a national scope, recommending approaches to the solution of these problems, and providing continuing guidance in the implementation of resulting activities; identifying problems in the interactions of materials disciplines with other technical functions, and defining approaches for the effective utilization of materials technologies; cooperating in the development of advanced educational concepts and approaches in the materials disciplines; communicating and disseminating information on Board activities and related national concerns; promoting cooperation with and among the materials-related professional societies; maintaining an awareness of trends and significant advances in materials technology, in order to call attention to opportunities and possible roadblocks, and their implications for other fields, and recognizing and promoting the development and application of advanced concepts in materials and materials processes.