

AD 710370

NRL Report 7189

**Long-Term Measurements
of the Corrosion
of Mild Steel
in 580°F NaOH Solutions**

ROBERT L. JONES

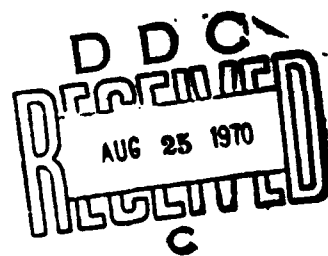
*Inorganic Chemistry Branch
Chemistry Division*

July 13, 1970



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ABSTRACT

Extended measurements have been made, using the hydrogen effusion technique, of the corrosion of low-carbon steel in static waters containing up to 40% NaOH at 580°F. Minimum corrosion was found at 1 to 2% NaOH, the corrosion mode being distinctly different on either side of the minimum. The low-concentration corrosion rates fell smoothly and rapidly from 1000 to 10,000 mg Fe/dm²mo to less than 100 mg Fe/dm²mo, whereas, with 10 to 40% NaOH, the rate curves followed a "peak/plateau/sudden-drop" course wherein the rates ranged from 300,000 mg Fe/dm²mo at the highest peak to about 100 mg Fe/dm²mo after the final drop.

These behaviors were explained as resulting from a passive to active corrosion state transition which occurs at the corrosion minimum, i.e., at 1 to 2% NaOH, with the high-concentration active-state specimens subsequently passivating spontaneously after some certain degree of corrosion has transpired. It was shown that there is some reason to believe that these two mechanisms may be involved in the pitting and stress corrosion cracking of mild steel exposed to high-temperature, high-alkalinity environments.

PROBLEM STATUS

This is a final report on this phase of the problem; work on the general problem of corrosion mechanisms continues.

AUTHORIZATION

NRL Problem M04-01
Project SF 51-542-601

Manuscript submitted April 17, 1970.

LONG-TERM MEASUREMENTS OF THE CORROSION OF MILD STEEL IN 600°F NaOH SOLUTIONS

INTRODUCTION

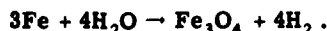
The corrosion of low-alloy steels in high-temperature water becomes a problem of major magnitude when highly alkaline solutions are involved. This is a situation of necessity in many commercial process vessels where, as for example in kraft digesters and caustic stripping columns, solutions of 10 to 50% concentration and temperatures as high as 300°F are employed (1). It also occurs in steam-generating boilers when the slightly alkaline (pH 8 to pH 10) water used in these units becomes locally concentrated in crevices, under porous deposits, or at hot spots where the heat transfer rate is disproportionately high (2). Many authors (3-6) consider the locally high concentrations induced in this way to be a primary factor in boiler-tube failure. This idea received considerable impetus when Fraser and Bloom (7) at NRL were able to produce a pitting-type attack on mild steel in 600°F, 40% NaOH in laboratory tests which yielded pits having essentially the same topography as boiler pits produced under actual service conditions.

Motivated by this finding and the obvious scientific interest and economic importance of this class of reactions, Bloom subsequently, in association with L. Goldenberg, began a systematic long-term study of the corrosion of mild steel circa 600°F in solutions ranging from water only to 40% NaOH. Unfortunately, this research could not be completed and brought into final report form before both men came to retirement. The data presented here represent a part of the experimental results which they achieved, and the present report is being written primarily to insure that these comprehensive data (some of which were obtained in tests of more than a year's duration) are appropriately recorded. The interpretations accorded them are the author's own and should not be taken as necessarily reflecting the opinions of either of the previous investigators.

EXPERIMENTAL PROCEDURE

The hydrogen effusion method of corrosion-rate measurement, which has been extensively developed by Bloom (8), was used since it allows simple, efficient monitoring of the corrosion rate over long periods while leaving the corrosion system essentially undisturbed. In this technique, the solution being tested is encapsulated in thin-walled mild-steel tubing by drawing the solution into the tubing, which is subsequently squeezed into partially flattened (to allow for thermal expansion of the electrolyte) capsule segments. The individual capsules are then cut off with a metal shear and pressure sealed by spot welding the ends. Precautions are taken to exclude air from the capsule during these operations.

When the specimen capsules are heated, the corrosion which occurs on their interior in NaOH solutions is given by the overall reaction



If the heating is carried out in a vacuum system, the reaction rate may be followed by measuring the rate of hydrogen effusion from the capsule into the vacuum system, since hot mild steel is readily permeable to hydrogen.

In the tests discussed here, the capsules were heated at 580°F for intervals which were in some instances longer than 1 year. The actual experimental procedures were generally the same as described in Ref. 7, and tubing from the same stock was used. The tubing is cold-drawn mild steel and has an outside diameter of 0.25 inch and a wall thickness of 0.02 inch. It was degreased in trichloroethylene vapor or hot detergent solution, hydrogen annealed at 875°C for 1 hour, cooled in the hydrogen atmosphere, vacuum annealed at 875°C for 1 hour, and finally cooled in the furnace. In the earlier work, a sample of this tubing after such pretreatment gave the chemical analysis results shown in Table 1. The solutions were made from distilled H₂O (resistivity 900,000 ohm-cm) and reagent-grade NaOH pellets in platinum or alkali-resistant glass beakers and used immediately after preparation.

Table 1
Analysis of Steel after Hydrogen and Vacuum Annealing

Constituent	Weight Percent	Constituent	Weight Percent
C	0.09	Si	0.07
P	0.006	Cr	0.10
S	0.031	Ni	0.05
N	0.0025	Mo	0.01
Mn	0.53	Fe	99.11*

*By difference.

RESULTS

The corrosion rate data set forth in Figs. 1, 2, and 3 were taken, reduced, and put into graphic form by L. Goldenberg. With Bloom's hydrogen effusion apparatus, the elemental measurement is the increase in hydrogen pressure in a vacuum vessel of known volume (and at fixed temperature) per unit time. The apparatus uses Pirani gages, however, which have a limited pressure range, and the individual vessels must be reevacuated before this range is exceeded for the pressure readings to be accurate. This is not always practical, and so while the capsule corrodes continuously, rate measurements are actually taken only over a certain number of measurement cycles with varying time intervals between cycles. A plot of these rates against time, however, yields a smooth curve from which the rate for any given time can be taken and, by appropriate integration, total corrosion as a function of time can be obtained. This allows the corrosion rate to be shown versus total corrosion, a mode of presentation chosen by Goldenberg as being particularly informative in the study at hand.

The effect of NaOH concentration is treated in Fig. 1, where corrosion rates have been plotted against weight percent NaOH at the initial peak rate and after corrosion to the extent of 100, 150, and 350 mg Fe/dm² had occurred (100 mg Fe/dm² is equivalent to the formation of 2.7 microns of Fe₃O₄, assuming the Fe to be converted to a uniform oxide layer of this stoichiometry). There is a corrosion-rate minimum at approximately 1% NaOH, a result consistent with earlier descriptions of the corrosion of mild steel in high-temperature NaOH solutions in Ref. 9 (310°C, minimum at 0.7 g/l NaOH), Ref. 10 (316°C, minimum at pH 12.2), and Ref. 11 (300°C, minimum at 2 to 4 g/l NaOH). Some question exists concerning the persistence of this minimum, however, because in the last two references cited, the experiments, which lasted 25 and 14 days, respectively,

Fig. 1 - Corrosion rate of mild steel in 580°F NaOH solutions as a function of concentration at increasing degrees of corrosion

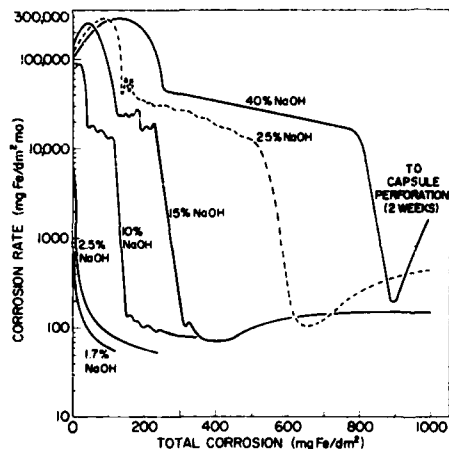
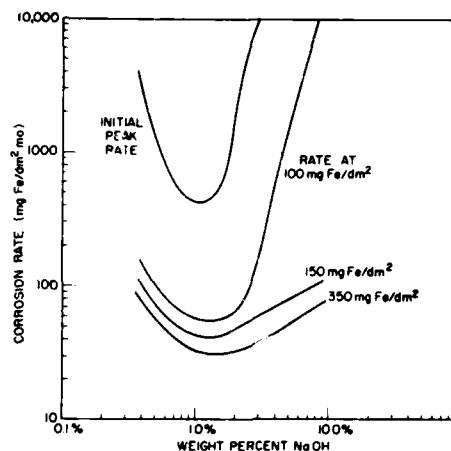


Fig. 2 - Corrosion rates during the course of corrosion for mild steel in 580°F NaOH solutions of the indicated concentrations

indicated that the minimum vanished with time and the corrosive attack increased monotonically with pH, rising smoothly from pH 7 upward. The reason for this discrepancy is not known. In dynamic systems, pH 10 waters definitely have beneficial effects in boiler tests, because it is thought (12) that they induce the formation of a precipitated layer of secondary crystals which provide additional protection for the underlying metal. Whether or not the corrosion minimum ultimately disappears here may depend then on the increase in protectiveness brought by such a precipitated layer, a factor which may be affected by minute differences in solution purity or tubing composition, since precipitation from solution is strongly influenced by trace impurities.

Whatever the reason for these experimental differences, it is evident when the full course of corrosion is viewed (Fig. 2) that the corrosion mechanism is different above and below the corrosion minimum region. The concentrations 0.4% (see Fig. 3), 1.7%, and 2.5% NaOH give the "normal" decrease in corrosion rate with time, while the 10% through 40% NaOH solutions form a family whose corrosion behavior is characterized by

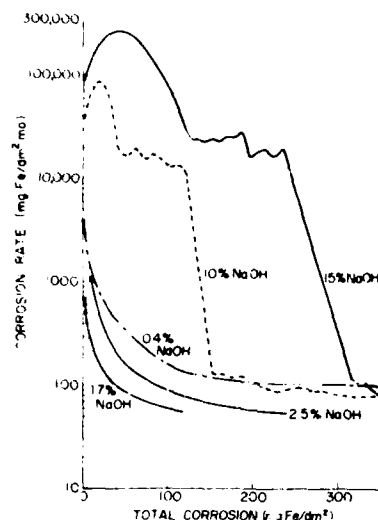


Fig. 3 - Comparison of corrosion rates for mild steel in various NaOH solutions at 580°F

the unusual features in common shown in Fig. 2. The precipitous drop in corrosion rate which occurs midcourse with these solutions is especially intriguing since it leads to a situation, as indicated in Fig. 3 (where the abscissa has been expanded for clarity), in which mild steel actually corrodes faster in 0.4% NaOH than in 15% NaOH.

DISCUSSION

Several possible explanations for the peculiar corrosion behavior revealed in Fig. 2 are discussed below. In considering these, it should be borne in mind that the proposed mechanism must rationalize not only the unique corrosion pattern of the 10% and higher solutions but also the change in corrosion mode which takes place at the corrosion rate minimum.

Change in Solution Bulk Concentration

Even though H_2O is used up in the corrosion reaction, which causes the solutions to become more concentrated, there is no time at which their concentrations all become equal. No simple relation exists between the various calculated film thicknesses and solution concentrations at the point of sudden drop in corrosion rate.

Change in Pore Structure

It is assumed in this mechanism that the pore structure (and hence protectiveness) of the Fe_3O_4 film which forms on the capsule interior changes with NaOH concentration and perhaps film thickness. There is evidence that the oxide films here, at least those formed in the more concentrated media, are in fact porous (13). However, it is difficult to set down (and more difficult to experimentally verify) a scheme by which a pore forming-blocking reaction could produce all the features shown in the corrosion curves of 10 to 40% NaOH. The problem in explaining the distinct change in corrosion mode circa 1% NaOH also remains.

Formation of a Sodium-Containing Spinel

Another explanation associates the corrosion minimum near 1% NaOH with the formation of a sodium-containing spinel analogous to LiFe_5O_8 , which is formed in 600°F LiOH solutions at concentrations below 1% (14). Support for its existence lies with Goldenberg's findings that (a) the iron oxide generated in 15% NaOH at 580°F contained 50 ± 17 ppm sodium from the very beginning of the corrosion test through 64 days' heating and (b) x-ray diffraction lines corresponding to d spacings not allowed by the Fe_3O_4 crystal structure (5.33, 3.28, 2.78, 2.31, 1.89, and 1.62 Å) are found with iron oxides produced by 88 hours or 12 weeks heating (but interestingly not with 6 or 15 months heating) in 600°F 15% NaOH solution. Other workers (15) have reported sodium incorporation in iron oxide films grown in 300°C (570°F) strong caustic, but they concluded that although the lattice was expanded, the oxide structure was still basically Fe_3O_4 . However, even given the formation of a new oxide phase commencing at 1% NaOH, which might explain the corrosion mechanism transition at this concentration, one must still show how the presence of this phase could result in a corrosion-rate curve as, for example, with 15% NaOH, especially when the phase is present (according to the sodium analysis) from the earliest times of the test onward.

Passive-Active Corrosion State Transition

There is a characteristic change in oxide morphology and reaction activation energy at the corrosion minimum point, according to Moore and Jones (11), which, they believe, reflects a change from passive to active corrosion mode as the limit of passive oxide stability (as predicted by potential-pH diagrams for the Fe- H_2O system (16)) is exceeded with increasing NaOH concentration. Under this hypothesis, the 0.4, 1.7, and 2.5% NaOH solutions would yield one family of corrosion-rate curves, and the 10 to 40% solutions would yield a second and distinctly different family because the first series, lying below the transition concentration, gives "passive-state" corrosion and the second, lying above it, "active-state" corrosion.

The particular form of the 10 to 40% NaOH curves would seem to indicate a spontaneous passivation of these active specimens as the corrosion reaction proceeds, the exact point of passivation being determined by the concentration of the individual solutions, and occurring progressively later as the solution strength increases (Fig. 2).

Examples of spontaneous passivation from an active state are noted in the literature, although few have been reported in high-temperature situations, possibly because of the experimental difficulties. The observations of Mueller (17) in studying the corrosion of carbon-steel digesters in kraft pulping of wood are perhaps the most pertinent to the present phenomenon. In this process, wood is digested in strongly alkaline pulping liquors (principally 10% NaOH plus 3.5% Na_2S), which are heated to 100 to 120°C in large mild-steel vats. Mueller found that although these vessels initially assumed an active potential (-1.0 v. SCE) and suffered high corrosion rates, their potential would subsequently rise to passive values (-0.85 v. SCE) and the corrosion rates diminish sharply; i.e., the vessels would passivate spontaneously as the "cook" continued.

Barnartt and van Rooyen (18) have reported spontaneous passivation for both 16 Cr-20 Ni and 18 Cr-8 Ni stainless-steel alloys in boiling MgCl_2 at 146°C. Passivation occurred after about 100 minutes exposure, and it was marked by an abrupt potential rise and cessation of hydrogen evolution from the metal surface, the latter point being taken as evidence of a greatly reduced corrosion rate. The effect was greatest with the 18-8 alloy (-400 to -320 mV SCE), which was susceptible to stress-corrosion cracking (the 16-20 alloy was not), and there seemed to be some relation between the potential rise and the cracking mechanism, because these investigators found with stressed 18-8

specimens that: "Potentiostatic corrosion at potentials 50 to 100 mV more noble than the initial immersion potential eliminated the crack-initiation period and increased the density of cracks by two orders of magnitude in the susceptible alloy."

However, while spontaneous passivation, as indicated by a more or less abrupt shift of the corrosion potential in the noble direction during extended corrosion, is well known, there is no commonly accepted theory to explain the phenomenon. It has been attributed in at least one instance to the buildup of a corrosion product film, however. Lee and Uhlig (19) related the noble potential shift shown by stainless steels corroding freely in boiling 130°C MgCl_2 to the formation of a surface film which they concluded was not the usual passive film because of its thickness and the absence of a Flade potential, but nonetheless slowed the rate of anodic dissolution and thereby ennobled the corrosion potential in accord with the theory of mixed potentials.

The characteristics of this film suggest that it may be a "precursor" film as sometimes found in potentiostatic passivations (20,21). These films form in the transition from active to passive state (although they are not "passive" films), and they are generally associated with the passivation peak in anodic current which occurs in these same potential regions. And there is the interesting possibility that whereas an increase in potential can induce the formation of these "precursor" films, the presence of such films can result conversely in an increased corrosion potential.

In this conjunction, it may also be noted that similarities exist between the 10 to 40% rate curves in Fig. 2 and the anodic polarization curves which are obtained in potentiostatic passivation when the active corrosion state is stable (22). This similarity is not an unreasonable circumstance since the electrons in the external circuit in potentiostatic polarizations are, in the absence of competing side reactions, essentially just a measure of the instantaneous corrosion rate, the function which hydrogen evolution serves in the present work. It lends support by inference that the growth of a corrosion product film on a metal surface can in fact result in, or is equivalent to, a rise in the specimen corrosion potential.

An increase in specimen potential as the oxide surface film thickens might also be consistent with Goldenberg's observation of extra lines in x-ray diffraction patterns taken from 15% NaOH capsules heated intermediate times, because Humphries and Parkins (23) have found an oxide entity giving many of these same lines which is produced when mild steel in boiling 35% NaOH is held at a potential (-480 mV NHE) midway between those at which Fe_3O_4 (rest potential, -710 mV NHE) and $\gamma\text{-Fe}_2\text{O}_3$ (-50 mV NHE) are generated.

Supporting experiments requiring techniques (e.g., high-temperature electrochemistry) not available when these tests were run are needed before more can be said. Nothing is known, for instance, of the mechanism of the presumed spontaneous passivation with 10 to 40% NaOH. Nor, for that matter, has it been proved that a potential rise actually occurs under the conditions of these experiments. The basic hypothesis appears to offer direct insight into the two critical problem areas in high-temperature aqueous corrosion, pitting and stress corrosion cracking, however, and may therefore be worthy of further study.

Analogy with potentiostatic polarization curves would suggest from Fig. 2, for example, that pitting and capsule perforation are a result of the specimen going transpassive. This possibility has been considered by Mueller (17) and apparently observed by him with pulping vessels, because he notes: "Evidently a shift to extreme anodic potentials may be caused by some changes during long-time operation, for instance, when scale is formed on an increasing ratio of the surface." To carry through these implications and to determine whether or not pitting can in fact be caused by a transpassive transition would likely prove an interesting and valuable area of research.

The existence of a transition to active corrosion at 1 to 2% NaOH may, on the other hand, have significance in the stress corrosion cracking of mild steel in NaOH, since it is generally agreed (24) that boiling caustic does not produce stress corrosion cracking at concentrations lower than 5%, i.e., it appears that the specimen must be at least initially in the active corrosion state. There may also be involvement of a spontaneous passivation process, for it has been found in boiling concentrated NaOH (25) that cracking occurs only over a narrow potential range. This range is only .00 to 300 mV in extent and lies generally just above the active rest potential, coinciding with the potential regions in which the "passivation" current peak falls in potentiostatic anodic polarizations. That is to say, it is just the potential range into which an active nonpotentiated specimen would move if its potential were raised 100 mV or so by spontaneous passivation. This potential rise is not sufficient to bring the specimen to potentials which are ordinarily considered in the "passive" realm, i.e., those where $\gamma\text{-Fe}_2\text{O}_3$ exists; it may be enough, however, to permit the formation of a primary passivating layer of Fe_3O_4 as has been described for iron in alkaline solution by Hurlen (26).

The arguments in the preceding paragraph would suggest that in spontaneous passivation there is a step, probably associated with the development of a passivating film (which does not have to be $\gamma\text{-Fe}_2\text{O}_3$), that can lead to stress corrosion cracking (cf. Ref. 18). Moreover, if mild steel freely corroding in 580°F concentrated NaOH ultimately comes to self-passivation, as Fig. 2 would seem to indicate, there will be a time, not necessarily at the first, at which the metal in this environment will become susceptible to stress corrosion cracking.

The experimental findings of this report (due to Bloom and Goldenberg) are of sufficient range and detail to bring new insight to many aspects of high-temperature, high-alkalinity corrosion reactions and thereby represent a significant contribution to corrosion science. The explanation advanced by the author for the particular corrosion behaviors, i.e., the postulation of a transition from stable "passive" state to active corrosion at 1 to 2% NaOH, with the active specimens subsequently passivating spontaneously after a certain degree of corrosion has occurred, is a working hypothesis, which, although with important implication, requires further substantiation.

REFERENCES

1. Schmidt, H.W., Gegner, P.J., Heinemann, G., Pogacar, C.F., and Wyche, E.H., Corrosion 7:295 (1951)
2. Evans, U.R., "The Corrosion and Oxidation of Metals: Scientific Principles and Practical Application," London:Arnold, p. 455, 1960
3. Partridge, E.P., and Hall, R.E., Trans. ASME 61:597 (1939)
4. Rivers, H.M., Combustion 53:67 (1952)
5. Kaufman, C.E., Trautman, W.H., and Schnarrenberger, W.R., Trans. ASME 77:423 (1955)
6. Kawashima, N., and Asai, O., Hitachi Review, Special Issue (No. 5), p. 13, Dec. 1962
7. Fraser, W.A., and Bloom, M.C., Corrosion 18:163t (1962)
8. Bloom, M.C., and Krulfeld, M., J. Electrochem. Soc. 104:264 (1957)
9. Berl, E., and Van Taack, F., Forsch. Gebiete Ingenieurw. 330:1 (1930)
10. Bloom, M.C., Newport, G.N., and Fraser, W.A., J. Electrochem. Soc. 111:1343 (1964)
11. Moore, J.B., Jr., and Jones, R.L., J. Electrochem. Soc. 116:1080 (1969)
12. Warzee, M., Sonnen, C., and Berge, Ph., "Corrosion of Carbon Steels and Stainless Steels in Pressurized Water at High Temperature," EURAEC 1896, S.E.R.A.I., Brussels (1967)
13. Kovacina, T.A., "The Porosity of Protective Films on Mild Steel," NRL Report 6786, Dec. 31, 1968
14. Bloom, M.C., Krulfeld, M., and Fraser, W.A., Corrosion 19:327t (1963)
15. Asai, O., and Kawashima, N., Extended Abstracts, 4th Int. Conf. on Metallic Corrosion, Amsterdam, Sept. 7-14, 1969, NACE, Houston, p. 126, 1969
16. Townsend, H.E., Extended Abstracts, 4th Int. Conf. on Metallic Corrosion, Amsterdam, Sept. 7-14, 1969, NACE, Houston, p. 125, 1969
17. Mueller, W.A., Can. J. Chem. 38:576 (1960)
18. Barnartt, S., and van Rooyen, D., J. Electrochem. Soc. 108:222 (1961)
19. Lee, H.H., and Uhlig, H.H., J. Electrochem. Soc. 117:18 (1970)
20. Cartledge, G.H., Corrosion 24:223 (1968)

21. Pigeaud, A., and Kirkpatrick, H.B., Corrosion 25:209 (1969)
22. Reinoehl, J.E., and Beck, F.H., Corrosion 25:233 (1969)
23. Humphries, M.J., and Parkins, R.N., Proc. Conf. Fundamental Aspects of Stress Corrosion Cracking, Ohio State, Sept. 11-15, 1967, NACE, Houston, p. 384, 1969
24. Parkins, R.N., Proc. Conf. Fundamental Aspects of Stress Corrosion Cracking, Ohio State, Sept. 11-15, 1967, p. 361, 1969
25. Humphries, M.J., and Parkins, R.N., Corrosion Sci. 7:747 (1967)
26. Hurlen, T., Electrochim. Acta 8:609 (1963)

Security Classification		
DOCUMENT CONTROL DATA - R & D		
Security Classification of title, body of abstract and indexing annotation must be entered when the overall report is classified		
1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION
Naval Research Laboratory Washington, D.C. 20390		Unclassified
		2b. GROUP
3. REPORT TITLE		
LONG-TERM MEASUREMENTS OF THE CORROSION OF MILD STEEL IN 580°F NaOH		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
Final report on this phase of the problem; work on the general problem continues.		
5. AUTHOR(S) (First name, middle initial, last name)		
Robert L. Jones		
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
July 13, 1970	14	26
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)	
NRL Problem M04-01	NRL Report 7118	
b. PROJECT NO.		
SF 51-542-601		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. DISTRIBUTION STATEMENT		
This document has been approved for public release and sale; its distribution is unlimited.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY
		Department of the Navy (Naval Ship Systems Command), Washington, D.C. 20360
13. ABSTRACT		
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