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**STEEL CORROSION MECHANISMS
UNDER CONDITIONS PERTINENT TO
STEAM POWER GENERATION**

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Table C2, page 47. The $C1^-$ content of α -FeOOH
should read 0.01.

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Washington, D. C.

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ABSTRACT

A basic research program concerning the corrosion of steel at temperature and pressure conditions encountered in boiler operation is underway. One phase of this program, which has been devoted to a clearer understanding of pit formation mechanisms, has included studies of the following:

- (1) Corrosion-product formation and pitting phenomena in sealed mild steel capsules containing pure water at room and at boiler temperatures at several oxygen levels.
- (2) Transformation and stability phenomena of the corrosion products.
- (3) Effects in commercial piping at low flow rates.
- (4) Effects of water treatment chemicals.

The character of the corrosive attack was followed by microscopic observations which were correlated with determinations of the nature of the corrosion products by means of x-ray diffraction, electron diffraction, and chemical techniques.

The studies revealed that the protective film on steel under conditions pertinent to boiler operation has the spinel structure and that the major concern is the genesis and preservation of this film. Films of this kind may be produced at room temperature by reaction of steel in the absence of oxygen. In the presence of air-saturated water, however, the initial product generated is γ -FeOOH, a loosely adherent material some of which appears as islands on the steel surface, each island being the nucleus of an incipient pit. As the corrosion proceeds and the oxygen is consumed, the pH rises with gradual elimination of γ -FeOOH and its replacement by a spinel film on the metal surface.

Most of the γ -FeOOH remains as a suspension in the solution or as settled agglomerated masses. Should appreciable quantities of this material be generated during boiler shutdown periods and not be removed prior to resumption of boiler operations, it would be converted to red α -Fe₂O₃, a nonadherent insulating powder which could gather at low-velocity areas and produce hot spots or interfere with protective film formation.

Should γ -FeOOH be generated in the presence of chlorides, it may be especially destructive when heated to boiler operating temperatures and can produce cracking phenomena. The generation of this material during boiler shutdown can be eliminated by proper water treatment which can be achieved with presently used chemicals but requires revision of specifications with careful attention to phosphate:chloride ratios of pH. The prevention of this room-temperature attack under access of air may be a very important function of water treatment chemicals.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem M04-01
Projects NS 140-001, NS 200-023, and NR 513-000,
Task NR 513-001

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STEEL CORROSION MECHANISMS UNDER CONDITIONS PERTINENT TO STEAM POWER GENERATION

1. INTRODUCTION

Although the literature dealing with aqueous corrosion in ferrous systems is discouragingly voluminous to anyone attempting to analyze the available data, the amount of material dealing specifically with corrosion mechanisms has until recent years been rather meager. The need for knowledge of corrosion mechanisms has been clear to the power industry for many years but attempts to get an adequate program under way for obtaining the needed knowledge have not yet been successful. A program designed to fill this need with special attention to naval requirements was started at NRL in 1953.

In pursuance of this program the hydrogen effusion method of corrosion-rate determination was developed (1), and with its aid it was shown that while steel in contact with pure water at boiler operating temperatures reacts rapidly at first, it soon develops an adherent protective layer of magnetite which subsequently reduces the corrosion rate to very low values (1-3). It is clear that knowledge of the conditions for the development, preservation, and breakdown of such protective films is a necessary prerequisite to the understanding of corrosion mechanisms. This research program, therefore, had as one of its major goals the development of this prerequisite. A literature survey (4) made in 1955 of the corrosion products formed by iron and steel indicated that the available information on the genesis, nature, and conditions of stability of corrosion-product films was far short of that needed for analysis of corrosion mechanisms of interest in connection with naval steam generation problems, and therefore a long-range program for obtaining this information was organized.

In the fall of 1956, in response to a request from the Bureau of Ships for aid in the solution of the problem of serious water-side pitting in the generating and superheater tubes of naval propulsion boilers, one aspect of the corrosion-mechanisms program was oriented toward studying the mechanisms of pit formation in these systems. This report is a progress report in this connection.

It had been indicated, during the course of corrosion-rate studies by the hydrogen effusion method, that the introduction of hydrogen peroxide as a source of oxygen in mild-steel capsules results in the formation of pits at room temperature as well as at 316°C (600°F). The extent of pitting at 316°C, however, appeared to depend in large part on the time of exposure at room temperature, and the corrosion product $\alpha\text{-Fe}_2\text{O}_3$ seemed always to be associated with pitting at 316°C.

In an attempt to confirm these indications in mild steel piping under flow conditions, the following experiments were performed with loops manufactured from SAE 1010, half-inch, schedule-80 pipe in which a thermal convection flow velocity of approximately one foot per second was obtained by heating one leg and cooling the other leg of the loop. A surge tank connected to the loop was maintained at a temperature in excess of the temperature in the loop, thus creating a pressure which prevented boiling within the loop.

In loops of this kind, it was found that filling with distilled air-saturated water at room temperature and running for several weeks or more at 316°C produced a uniform film of magnetite with no evidence of pitting. In order to determine the effect of highly oxygenated

water upon this type of piping, both with and without such films of magnetite, portions of the piping from the above experiment were removed and replaced with fresh piping prior to refilling the loop with oxygenated water. After pressurizing the loop with oxygen to 300 psi at room temperature, the loop was reheated to 316°C and run at this temperature for 21 days. Shutdown and disassembly at this time revealed a continuous blue-gray film of spinel structure overlaid with a very thin film of α -Fe₂O₃. No pitting was observed in the area previously covered with a magnetite film, but in the sections of the piping which were bare prior to filling with oxygenated water at room temperature, the blue-gray film, in addition to being overlaid with a thin film of α -Fe₂O₃, contained a liberal distribution of circular red patches of α -Fe₂O₃, each of which overlaid a pit (Figs. 1 and 2).

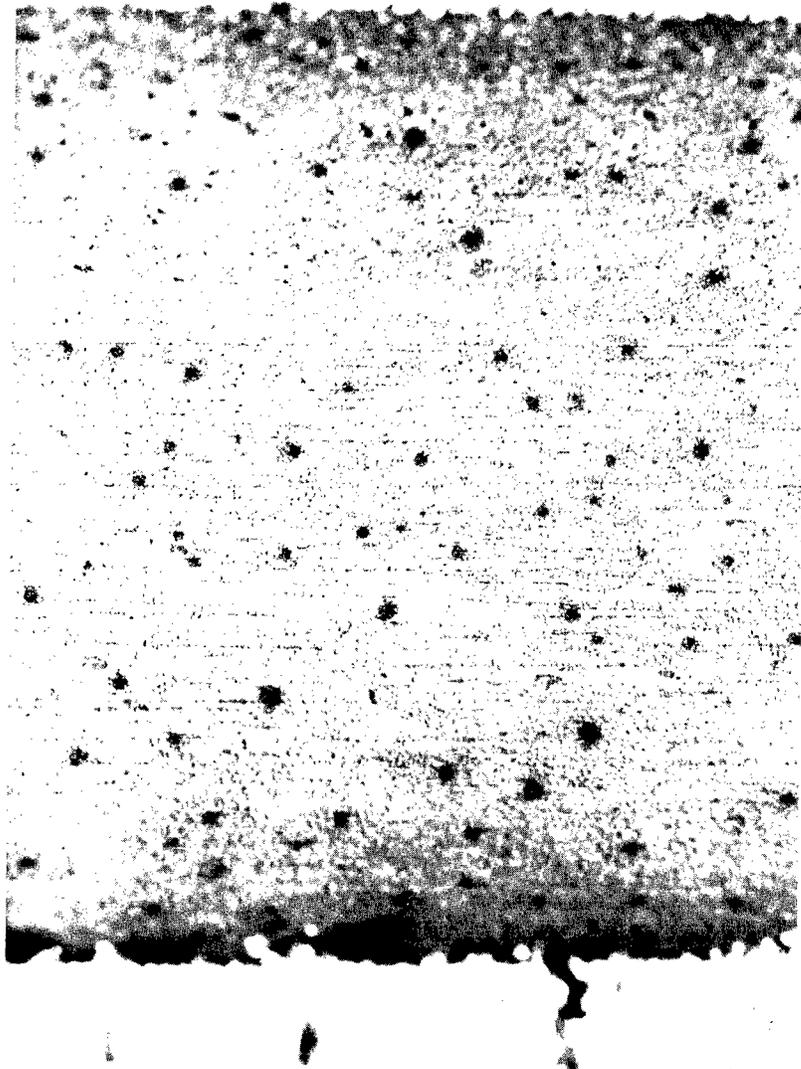


Fig. 1 - Photomicrograph of mild steel piping showing pits formed during treatment with oxygenated water at 316°C. Magnification 10X.

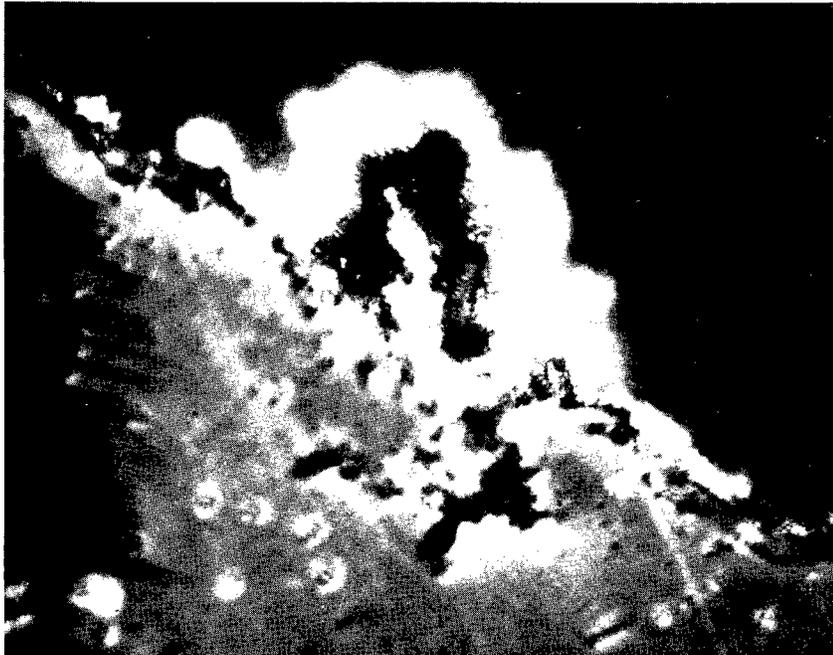


Fig. 2 - Photomicrograph through a pit formed in mild steel during treatment with oxygenated water at 316°C. The white area in the photograph is produced by red-colored α -Fe₂O₃. Underneath the cap of α -Fe₂O₃ is black-colored Fe₃O₄ extending into the pit. Magnification 800X.

In a second experiment, fresh loop piping was filled with degassed distilled water and heated as rapidly as feasible to 316 °C. After operation at this temperature for ten to fifteen minutes, the loop was pressurized with oxygen at about 300 psi and run for 21 days at this temperature. Examination of the piping from this loop after shutdown revealed a continuous blue-gray oxide film similar to the continuous films noted in the first experiment. No signs of pitting were evident.

These experiments re-emphasized the need for understanding film formation and breakdown both at room temperature and at elevated temperatures in the presence and in the absence of oxygen, and therefore the work outlined herein was initiated. Table 1 is a compilation of some of the properties of the seven different corrosion products which may be generated under boiler operating conditions.

Three different series of studies were undertaken in the work reported here:

1. An exploratory study was made to characterize the products generated by corrosion of mild steel in water containing oxygen at room temperature and at 316 °C.
2. A study was made of the influence of the presence of water and of corroding mild steel on the transformation characteristics of the various corrosion products at 25 °C and at 316 °C.
3. The effect of pH control and of the constituents of the accepted Navy boiler water treatment on the corrosion of steel at room temperature and at 296 °C* was examined.

*The temperature of 316 °C (600 °F) chosen for the original tests was somewhat in excess of the steam generation temperature of Navy high pressure boilers (1200 psi 298 °C).

Table 1
Corrosion Products of Iron

Composition (Mineral Name)	Color	Structural Type (3)*	Magnetic Character	Electrical Resistivity	Density	Thermal Behavior
Fe ₉₅₀ O to Fe ₈₃₃ O (Wustite) (5)	Black	NaCl	Paramagnetic (7)	Semiconductor (6)	5.4-5.73 (5,14)	Melts at 1371°-1424°C. Below 570° C decomposes to Fe and Fe ₃ O ₄ (5)
Fe(OH) ₂	White	Mg(OH) ₂ (Brucite)	Paramagnetic (8)	Insulator †	3.40 (15)	Decomposes at about 100° C to Fe ₃ O ₄ and H ₂ ‡ (17)
Fe ₃ O ₄ (Magnetite)	Black	Spinel	Ferromagnetic (7)	Electronic Conductor (11)	5.20 (7)	Melts at 1597° C (5)
γ-FeOOH (Lepidocrocite)	Orange	γ-FeOOH (Lepidocrocite)	Paramagnetic (9)	Insulator †	3.97 (16)	Dehydrates ¶ to γ-Fe ₂ O ₃ at about 200° C (19, a & b)
α-FeOOH (Goethite)	Yellow	α-FeOOH (Goethite)	Paramagnetic (9,10)	Insulator (12)	4.20 (16)	Dehydrates ¶ to α-Fe ₂ O ₃ at about 200° C (19, a & b)
γ-Fe ₂ O ₃ (Maghemite)	Brown	Spinel (with vacancies)	Ferromagnetic (7)	Semiconductor to Insulator (13)	4.88 (7)	Transforms ¶ to α-Fe ₂ O ₃ above 250° C (19, a & b)
α-Fe ₂ O ₃ (Hematite)	Brick Red to Black	Al ₂ O ₃ (Corundum)	Paramagnetic (7)	Insulator (13)	5.25 (7)	Decomposes to magnetite at 1457° C and 1 atm. (5)

*Figures in parens designate literature references (Page 27).

†Color indicates that these are insulators.

‡In contact with traces of oxygen, Fe(OH)₂ is unstable at room temperature and transforms to γ-FeOOH, α-FeOOH, or Fe₃O₄ depending on the conditions of the system (18).

¶Presence of water causes conversion to α-Fe₂O₃ at lower temperature.

2. CORROSION STUDIES IN CAPSULES AT ROOM TEMPERATURE AND AT 316°C

A. Experimental techniques for Studying Corrosion in Capsules

In order to examine the nature of the compounds generated by corrosion in oxygenated systems, mild steel test specimens in the form of capsules were filled with air-saturated water or hydrogen peroxide solutions and sealed. In the presence of ferrous and/or ferric ions generated by the corrosion process, the hydrogen peroxide decomposes readily (20) to form oxygen and water and these solutions thus provide a simple means for introducing oxygen into sealed test capsules. These capsules were prepared from 0.25-inch O.D. cold drawn mild steel tubing with a wall thickness of 0.020 inch; the steel composition appears in Table 2. Before fabrication into capsules the steel tubing was hydrogen annealed for 1 hour at 875°C, cooled in the hydrogen atmosphere to 60°C and then removed from the furnace. Subsequently, the tubing was annealed for 1 hour at 875°C in a vacuum furnace maintained at a pressure of less than 10⁻⁵ mm Hg and cooled to room temperature in the furnace. Dilute hydrogen peroxide solutions were prepared by adding Baker's Analyzed Reagent Grade 30% Hydrogen Peroxide to distilled water. The resistivity of the air-saturated water was greater than 400,000 ohm-cm in every case. No attempt was made to remove carbon dioxide; hence the pH of the water and of the peroxide solutions was in the region 5.4 to 6.0. The solutions were prepared and analyzed chemically immediately before the test specimens were filled.

Table 2
Analysis of Steel

Constituent	Weight Percent
C	0.09
P	0.017
S	0.032
N	0.007
Mn	0.57
Si	0.07
Cr	0.10
Ni	0.07
Fe (by difference)	99.05

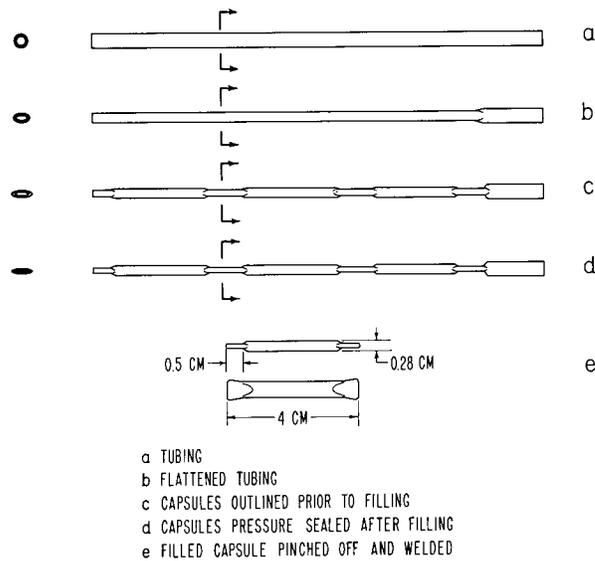


Fig. 3 - Schematic diagram showing capsule preparation procedure

The procedure for making the test specimens is described in detail elsewhere (1) but the general procedure is outlined in Fig. 3. After step c in Fig. 3, solution was drawn into the tubing by suction and sealed into the individual capsules by exerting pressure with a hydraulic press on the tube area between the capsules to give the structure shown in step d. Finally the individual capsules were cut apart and the ends sealed by spot welding as shown in step e.

The prepared capsule specimens were exposed in sets of 6 to 12 each. The specimens were prepared, allowed to remain at room temperature* for selected lengths of time, and then opened. Additional capsules were kept at room temperature for specific times, then placed in an oven at 316°C for one week, or twelve weeks, cooled to room temperature, and opened immediately thereafter. The capsules were opened by carefully filing one corner until the metal was sufficiently thin to be punctured by a stainless steel syringe needle. The liquid was transferred from each capsule into a glass syringe and the pH of the liquid was measured promptly, prior to reaction with atmospheric carbon dioxide. These pH measurements were made using a Beckman "one drop" glass electrode in conjunction with a Beckman Model G pH Meter. In some cases samples of the liquid were dropped onto Apiezon-wax-coated copper electrodes, evaporated to dryness under an infrared lamp, and analyzed by emission spectroscopy. When liquid was withdrawn from a capsule, a magnet was used to test suspended solids for the presence of the spinel-type oxides Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ which are the only ferromagnetic species in this corrosion product system (Table 1). Solids suspended in the capsule liquids were collected on a Millipore filter supported on a Buchner funnel and dried in a desiccator. X-ray diffraction patterns were obtained from the dry solids using the Debye-Scherrer technique. In a number of cases, to save the time of making the long exposures necessary with the Debye-Scherrer camera, diffraction data were obtained by direct exposure of the solids on the Millipore filters to cobalt K_α radiation in a Geiger counter x-ray spectrometer.

After removal of the liquid from the capsules, the walls were prepared for examination by filing away the lengthwise edges and shearing the transverse edges to expose two opposite wall surfaces. These were washed with distilled water, dried in a desiccator over $\text{Mg}(\text{ClO}_4)_2$, examined microscopically, and subjected to x-ray and electron diffraction analysis. A Geiger counter spectrometer with cobalt K_α radiation was used for the x-ray work and the diffraction attachment of an RCA EMU-2 electron microscope for the electron diffraction analyses. The x-ray patterns served to characterize the bulk of the corrosion product film when this film was thick enough to produce a diffraction pattern sufficiently intense not to be masked by the pattern of the iron substrate. The electron diffraction patterns served for characterization of very thin films on the metal surfaces and of the exterior surface layers of thicker corrosion product films. Color was sometimes helpful in characterizing corrosion products (Table 1).

The corroded capsule walls were examined microscopically to determine the character and extent of the corrosive attack and the nature of the corrosion products. The thickness of the corrosion-generated film and the depth of the pitting attack were determined by microscopic examination of cross sections of the corroded metal. For this purpose, the corrosion-product-covered capsule walls were flashed with copper and plated with 0.001 inch of silver which functioned as a backing for holding the corrosion product on the surface during metallographic preparation. Cross sections of the plated specimens were mounted in Lucite, ground, polished, and then etched with 5% nital. The specimens were placed on an American Optical Company Metallograph, Model No. 2400 A, and film thickness and pit depth measurements were made directly from the magnified image on the screen with the aid of a ruler.

B. Corrosion Products Generated in Air-Saturated Distilled Water

The data obtained in the characterization of the corrosion products generated by corrosion of sealed mild steel capsules in air-saturated distilled water at 25°C and at 316°C appear in Tables 3 and 4.

* Laboratory temperature was maintained at $25^\circ \pm 1^\circ\text{C}$.

Table 3
Corrosion Products Formed by the Action of Water*
in Mild Steel Capsules at 25°C

Solution pH before reaction**	Time metal was exposed to solution	Solution pH after reaction**	Appearance of solution	Appearance of metal	Corrosion products on metal
5.9	1 hr.	8.5	Yellow tinge	Speckled with brownish yellow islands	γ -FeOOH
5.6	6 hr.	9.4	Clear, Colorless	Same as above	γ -FeOOH and possibly spinel
6.0	24 hr.	9.5	Clear, Colorless	Same as above	γ -FeOOH and spinel
6.0	1 wk.	9.8	Clear, Colorless	Same as above	γ -FeOOH and spinel
6.0	12 wk.	9.9	Clear, Colorless	Thin gray brown film	Spinel and some γ -FeOOH
6.0	52 wk.	9.9	Few particles of spinel	Continuous black film	Spinel

*The water was initially air saturated.

**Each value represents the mean of 6 capsules.

Table 4
Corrosion Products Formed by the Action of Water in Mild Steel Capsules at 316°C

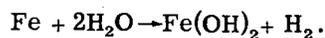
Solution pH before 316°C treatment	Time metal was treated at 316°C*	Solution pH after 316°C treatment**	Appearance of solution	Appearance of metal	Corrosion products on metal	Thickness of surface oxide
9.5	24 hr.	6.9	Clear, Colorless	Continuous gray black film	Spinel	less than 1 micron
9.5	1 wk.	7.0	Clear, Colorless	Same as above	Spinel	less than 1 micron
9.5	14 wk.	7.0	Clear, Colorless	Same as above	Spinel	1 to 3 microns
9.5	52 wk.	6.9	Clear, Colorless	Same as above	Spinel	2 to 6 microns

*The metal was exposed at room temperature for 24 hours before treatment at 316°C.

**Each value represents the mean of at least 5 capsules.

The composition of the corrosion products throughout this work was based on diffraction data. Chemical analysis is of no use in distinguishing between two polymorphs such as γ -FeOOH and α -FeOOH, or γ -Fe₂O₃ and α -Fe₂O₃. On the other hand, diffraction techniques are not always adequate for distinguishing the two spinel-type oxides γ -Fe₂O₃ and Fe₃O₄ which have very similar diffraction patterns (21) and these are reported in the data for the most part simply as "spinel." Appendix A contains typical electron diffraction data from which the corrosion products on the metal surfaces listed in Tables 3 and 4 were determined.

The following facts which were obtained in these experiments are noteworthy: The water was initially air-saturated and the small variation in pH at the outset was probably due to differences in the carbon dioxide content of the laboratory atmosphere. After six hours the pH had risen to 9.4. This is close to the pH of 9.3 which has been established (22) as the pH of a saturated solution of Fe(OH)₂, the product one would expect to be formed by the corrosion reaction



However, the rise of the pH to 9.9 where it is found even after a year's exposure is not explicable on this basis. The value of 9.9 has been obtained in a large number of similar experiments. Spectroscopic analysis of solutions withdrawn from capsules showed that in addition to iron some of the minor elements in the steel were present in the solution residues. This suggested the possibility that the high pH value might be due to the dissociation of a hydroxide generated by one of the minor constituents in the steel. Since 0.57% manganese was present in the steel (Table 2), a calculation was made to determine the pH in water containing both Fe(OH)₂ and Mn(OH)₂ at 25°C. This calculation (Appendix B-1) showed that the equilibrium pH of such a solution is 9.92, which corresponds well with the value 9.9 obtained in the experiments. The amount of manganese required to produce a saturated solution of Mn(OH)₂ within the capsule is 5.5 x 10⁻⁷ grams; 10⁻⁴ grams of steel would have to be dissolved to produce this quantity of manganese. This seems a very reasonable quantity to expect to have been dissolved in the twelve-week period during which this pH is shown to have been developed. An independent series of experiments was made to verify that the calculated equilibrium pH of 9.92 could be achieved by letting mixtures of high-purity iron and manganese stand with water in sealed platinum-lined capsules at room temperature. A more detailed description of these experiments appears in Appendix B-2. The equilibrium pH obtained in these experiments was 9.95, a value within the limits of experimental error of the calculated value, 9.92.

When the solutions withdrawn from the capsules containing water at room temperature were exposed to the atmosphere, the pH dropped over a period of one to two hours to about 6, the normal pH of air-saturated water, and a dark-colored, partially ferromagnetic solid precipitated from the colorless solution. X-ray diffraction indicated that this material was at least partially amorphous and that there was some spinel present. This precipitate is apparently a product of the atmospheric oxidation of the saturated solution of Fe(OH)₂ and Mn(OH)₂ which exists inside the sealed capsules.

It may be noted that the initial corrosion product generated on the steel surface at room temperature is γ -FeOOH. As pointed out in Appendix A, electron diffraction patterns obtained from freshly annealed tubing sometimes contain a faint line at 2.53 Å, which corresponds to the strongest line of the spinel pattern. Within an hour of room-temperature treatment, sufficient γ -FeOOH was generated to obliterate this trace. The approximately 8 ppm of oxygen introduced with the air-saturated water apparently produced the ferric ions necessary for the formation of the γ -FeOOH. This phase develops as islands on otherwise unattacked metal. After six hours, there is evidence that some spinel may be generated as indicated by the appearance in the diffraction pattern of a line whose "d" value corresponds to the strongest line of the spinel pattern. After 24 hours the generation of spinel along with the γ -FeOOH is certain. Eventually the spinel phase spreads over the entire surface of the specimen.

Table 4 shows that the films generated during treatment at 316°C consist of spinel. The drop in pH to final values of 7 and the disappearance of γ -FeOOH indicate that any $\text{Fe}(\text{OH})_2$ or γ -FeOOH initially present are converted to magnetite within 24 hours at the elevated temperature. The absence of particulate matter in the solutions removed from capsules after this treatment shows that the films are adherent. When solutions removed from these capsules were permitted to stand in air no precipitate was formed as in the case of solutions removed from capsules which received only room-temperature treatment. Spectroscopic analysis of the residues from these solutions subjected to the elevated temperature indicated that none of the minor constituents in the steel had been preferentially dissolved during treatment at 316°C. The electron diffraction patterns obtained from the oxide films show that the metal surface is covered with sizeable crystallites of spinel; the diffraction rings consist of a few scattered spots rather than of a large number of closely spaced spots characteristic of finely divided materials.

C. Corrosion Products Generated in Oxygenated Water

Tables 5 to 9 show the data obtained in the characterization of the corrosion products generated in capsules by reaction with oxygenated solutions. Some typical electron diffraction patterns used in identification of the corrosion products on the steel surfaces appear in Appendix A. Before discussing these data, it should be pointed out that when the capsules were opened, fluid spurted out whenever the residual oxygen pressure was in excess of atmospheric pressure, and the presence or absence of this residual pressure was used to give a qualitative indication of oxygen exhaustion inside the capsules. The column marked residual oxygen pressure is based on this observation.

The initial pH of 5.4 - 6.0 exhibited by the solutions before reaction is attributed to absorption of carbon dioxide from the atmosphere.

Table 5
Corrosion Products Formed by the Action of 0.2% H_2O_2 in Mild Steel Capsules at 25°C

Solution pH Before Reaction	Time Metal Exposed to Solution	Solution pH After Reaction†	Solid Corrosion Products Filtered from Solution	Appearance of Metal	Corrosion Products on Metal	Residual Oxygen Pressure
5.9	1 hour	7.1	*	Yellow islands on shiny metal	γ -FeOOH	Yes
5.9	24 hours	6.8	Spinel and some γ -FeOOH	Same as above	γ -FeOOH and spinel	No
5.8	1 week	7.4	Spinel	Yellow islands on black film	Spinel and some γ -FeOOH	No
5.8	4 weeks	8.6	Spinel	Few yellow islands on black film	Spinel and some γ -FeOOH	No
5.7	52 weeks	10.0	Spinel	Nearly covered with brownish-black film	Spinel	No

* Insufficient material for analysis

† Each value represents the mean of 8 to 12 capsules

Table 5 contains the data obtained from reaction with 0.2% H_2O_2 solution at room temperature. Although the pH increased during the first hour, it dropped somewhat during the next 23 hours, and then increased again. The only apparent explanation for this drop in pH is experimental error. No residual oxygen pressure was observed after 24 hours and thereafter the solution pH began to rise as it did previously in the case where no peroxide was added. Attention is directed to the fact that γ -FeOOH is the initial reaction product which gives way to spinel as the oxygen content decreases the pH increases to about 9.9, the value associated with oxygen-free solutions.

Table 6 exhibits analogous data obtained with a 1% H_2O_2 solution. The last column of this table shows that a residual oxygen pressure in excess of atmospheric was present in all cases. The pH again rises with time of exposure but now the corrosion product α -FeOOH appears when the pH reached 8. Data obtained using a 4% solution of H_2O_2 are shown in Table 7. Again the appearance of α -FeOOH when the pH rises above 8 may be noted and it may be observed that the pH seems to reach a plateau in the neighborhood of 8.0 to 8.5 which it maintains even after a year of exposure.

Table 6
Corrosion Products Formed by the Action of 1% H_2O_2 in Mild Steel Capsules at 25°C

Solution pH Before Reaction	Time Metal Exposed to Solution	Solution pH After Reaction†	Solid Corrosion Products Filtered from Solution	Appearance of Metal	Corrosion Products on Metal	Residual Oxygen Pressure
5.8	1 hour	6.9	None	Yellow islands on shiny metal	γ -FeOOH	Yes
5.9	24 hours	7.3	γ -FeOOH	Same as above	γ -FeOOH	Yes
5.7	1 week	8.0	α -FeOOH	Yellow film covers metal	γ -FeOOH and α -FeOOH	Yes
5.9	4 weeks	8.2	α -FeOOH	Same as above	γ -FeOOH and α -FeOOH	Yes

† Each value represents the mean of 8 to 12 capsules

All the data obtained at 25°C (Tables 3 and 8) from experiments in mild steel capsules may be summarized as follows:

(1) The reaction of steel with air-saturated water at 25°C produces γ -FeOOH within an hour. This γ -FeOOH appears as islands on the metallic surface. The pH rises within 24 hours from an initial value of about 6.0 to the value 9.5, somewhat above the equilibrium value in contact with $Fe(OH)_2$, and continues to rise to 9.9 where it apparently remains indefinitely. This 9.9 is the equilibrium pH of a solution in contact with both $Fe(OH)_2$ and $Mn(OH)_2$. This rise in pH is accompanied by the gradual elimination of γ -FeOOH and its replacement with a spinel which eventually covers the entire specimen as the oxygen is used up and the pH rises.

(2) The reaction of steel with hydrogen peroxide solutions at 25°C also produces γ -FeOOH which appears as islands on the metal within an hour. The rise in pH in this case, however, is much more gradual. With sufficient oxygen present ($\geq 1\% H_2O_2$), γ -FeOOH is at first produced, and then as the pH rises with time to a value of 8.0 or above, α -FeOOH appears.

Table 7
Corrosion Products Formed by the Action of 4% H₂O₂ in Mild Steel Capsules at 25°C

Solution pH Before Reaction	Time Metal Exposed to Solution	Solution pH After Reaction†	Solid Corrosion Products Filtered from Solution	Appearance of Metal	Corrosion Products on Metal	Residual Oxygen Pressure
5.8	1 hour	7.1	None	Shiny metal	γ-FeOOH	Yes
6.0	24 hours	7.3	γ-FeOOH	Nearly covered with yellow film	γ-FeOOH	Yes
5.9	1 week	8.2	α-FeOOH	Same as above	γ-FeOOH and α-FeOOH	Yes
5.9	4 weeks	8.6	α-FeOOH	Same as above	γ-FeOOH and α-FeOOH	Yes
Not measured	61 weeks	8.5	α-FeOOH	Same as above	α-FeOOH and trace of γ-FeOOH	Yes (?)

† Each value represents the mean of 8 to 12 capsules

Table 8
Summary of Corrosion Products Formed by the Action of Water and H₂O₂ Solutions in Mild Steel Capsules at 25°C

Time of Exposure	H ₂ O		0.2% H ₂ O ₂		1% H ₂ O ₂		2% H ₂ O ₂		4% H ₂ O ₂	
	pH	Product	pH	Product	pH	Product	pH	Product	pH	Product
1 hour	8.5	γ-FeOOH	7.1	γ-FeOOH	6.9	γ-FeOOH	7.3	γ-FeOOH	7.1	γ-FeOOH
24 hours	9.5	γ-FeOOH and Spinel	6.8	Spinel and some γ-FeOOH	7.3	γ-FeOOH	7.3	γ-FeOOH	7.3	γ-FeOOH
1 week	9.8	γ-FeOOH and Spinel	7.4	Spinel	8.0	α-FeOOH	8.3	α-FeOOH	8.2	α-FeOOH
4 weeks	--	--	8.6	Spinel	8.2	α-FeOOH	8.1	α-FeOOH	8.6	α-FeOOH
1 year	9.9	Spinel	10.0	Spinel	--	--	--	--	8.5	α-FeOOH

(3) As the solutions stand for a sufficient time in the sealed capsules the spinel phase appears when the oxygen is consumed and the pH rises to the vicinity of 9.9, the equilibrium value for a solution in contact with $\text{Fe}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$.

The results obtained from the examination of the corrosion products generated by reaction of peroxide solutions in steel capsules at 316°C are shown in Table 9. Upon heating steel capsules with peroxide, the pH decreases to the region of 6-7, just as in the case with air-saturated water, but with the difference that $\alpha\text{-Fe}_2\text{O}_3$ appears on the metal as the conversion product of $\gamma\text{-}$ and $\alpha\text{-FeOOH}$. With time, oxygen is consumed by the corrosion reaction and $\alpha\text{-Fe}_2\text{O}_3$ is reduced to Fe_3O_4 . This is clearly indicated by a comparison of the samples exposed for 1 week and 12 weeks. The data show that the compound $\alpha\text{-Fe}_2\text{O}_3$ was never formed at room temperature in these systems, and only at 316°C when $\gamma\text{-FeOOH}$ and/or $\alpha\text{-FeOOH}$ were generated during the room temperature pretreatment. If the surface of a specimen pretreated at room temperature contained splotches of $\gamma\text{-}$ or $\alpha\text{-FeOOH}$ in a background film of spinel, then following elevated temperature treatment the surface contained splotches of $\alpha\text{-Fe}_2\text{O}_3$ in a background of spinel. Furthermore, microscopic examination of cross sections of capsule tubing which had been exposed to oxygenated solutions at room temperature revealed pits under areas covered by $\gamma\text{-FeOOH}$. Similarly, pits were formed beneath areas covered by $\alpha\text{-Fe}_2\text{O}_3$, the conversion product of $\gamma\text{-FeOOH}$ produced during heating at 316°C . These observations indicate the importance of oxygen at room temperature as a promoter of pitting attack in mild steel and indicate that pitting occurs under conditions favorable to the generation of $\gamma\text{-FeOOH}$.

Table 9
Summary of the Corrosion Products Formed by the Action of H_2O_2 Solutions
in Mild Steel Capsules at 316°C

Solution and Initial pH	Exposure at 25°C	Products on Metal	Solution pH After 25°C Treatment	Exposure at 316°C	Products on Metal	Solution pH After 316°C Treatment
0.2% H_2O_2	24 hours	$\gamma\text{-FeOOH}$ and Spinel	6.8	1 week	Spinel and trace $\alpha\text{-Fe}_2\text{O}_3$	6.8
5.8 - 5.9	1 week	Spinel and some $\gamma\text{-FeOOH}$	7.4	1 week	Spinel	7.2
				12 weeks	Spinel	6.7
1.0% H_2O_2	24 hours	$\gamma\text{-FeOOH}$	7.3	1 week	$\alpha\text{-Fe}_2\text{O}_3$ and some Spinel	6.4
5.7 - 5.9	1 week	$\gamma\text{-FeOOH}$ and $\alpha\text{-FeOOH}$	8.0	1 week	$\alpha\text{-Fe}_2\text{O}_3$ and some Spinel	6.4
				12 weeks	Spinel and trace $\alpha\text{-Fe}_2\text{O}_3$	6.9
2.0% H_2O_2	24 hours	$\gamma\text{-FeOOH}$	7.3	1 week	$\alpha\text{-Fe}_2\text{O}_3$ and some Spinel	6.1
5.4 - 5.7	1 week	$\gamma\text{-FeOOH}$ and $\alpha\text{-FeOOH}$	8.3	1 week	$\alpha\text{-Fe}_2\text{O}_3$ and some Spinel	6.0
				12 weeks	$\alpha\text{-Fe}_2\text{O}_3$ and Spinel	6.0
4.0% H_2O_2	24 hours	$\gamma\text{-FeOOH}$	7.3	1 week	$\alpha\text{-Fe}_2\text{O}_3$ and some Spinel	6.1
5.9 - 6.0	1 week	$\gamma\text{-FeOOH}$ and $\alpha\text{-FeOOH}$	8.2	1 week	$\alpha\text{-Fe}_2\text{O}_3$ and some Spinel	5.9
				12 weeks	$\alpha\text{-Fe}_2\text{O}_3$ and Spinel	5.8

The data in Tables 3 through 9 show that the corrosion products generated in solutions containing oxygen at room temperature are found to some extent suspended in the liquid removed from the capsules, thus indicating that these corrosion products are loosely adherent, and therefore less protective than those generated in the absence of oxygen. The particles of γ -FeOOH and α -FeOOH appear as suspensions in the liquid, and the α -Fe₂O₃ to which these particles transform on heating at 316°C is also found suspended in the liquid. Moreover, Fe₃O₄ produced by reduction of the nonadherent α -Fe₂O₃ is also non-adherent. Accordingly, the presence of oxygen, which enhances generation of γ -FeOOH and α -FeOOH at room temperature, is responsible for producing nonadherent corrosion products (crud) at elevated temperature.

3. TRANSFORMATION AND STABILITY STUDIES OF IRON OXIDES AND HYDRATED OXIDES

To elucidate further some of the observations made in studying the corrosion of mild steel capsules in oxygenated systems, an additional series of experiments was undertaken in which samples of iron oxides and hydrated oxides were treated in sealed capsules at room temperature and at 316°C. These experiments consisted of (a) treatment of the compounds γ -FeOOH, α -FeOOH, γ -Fe₂O₃, α -Fe₂O₃, and Fe₃O₄ in platinum-lined capsules at 316°C in the presence and absence of water, (b) treatment of the above compounds in mild steel capsules at 316°C in the presence and absence of water; and (c) treatment of these compounds in mild steel capsules at 25°C in the presence of water.

The platinum-lined capsules in this experiment were prepared from 0.25-inch O.D., 0.020-inch wall nickel tubing lined with 0.010-inch of platinum. The tubing was vacuum annealed one hour at 1400°C before use in making capsules. The mild steel capsules were prepared from the 0.25-inch diameter tubing previously described. In the preparation of the capsules, the tubing was partially flattened as before, but the partially flattened tubing was cut into sections 1-1/2 inches long, so that the capsules could be filled individually. One end of the 1-1/2-inch section was cold-sealed with a hydraulic press and welded, the other end being left open for introduction of the materials for study. The chemical analysis of the oxides and hydroxides used, which were procured from commercial sources, is given in Table 10. The dry solids were inserted in the capsules with a spatula; aqueous slurries of the solids were introduced with a syringe. Slurries of the compounds in air-saturated distilled water were prepared immediately before introduction into the capsules. To produce fairly uniform samples, the slurry was stirred continuously as the samples were being taken. When the required sample had been introduced into a capsule the open end was cold-sealed and then both ends were spot welded.

Table 10
Chemical Analyses of Oxides and Hydrated Oxides

Material	Ferric Iron as Fe ₂ O ₃	Ferrous Iron as Fe ₃ O ₄	Water	Al as Al ₂ O ₃	Mn as MnO	Si as SiO ₂	Ca as CaO	Sn as SnO ₂	Mg as MgO	Total
γ -FeOOH	85.24	0.14	13.09	1.07	0.09	0.08	--	--	--	99.71
α -FeOOH	86.23	0.05	12.56	1.38	0.06	0.03	--	--	--	100.31
γ -Fe ₂ O ₃	90.90	6.52	0.65	1.63	0.03	0.53	--	0.07	--	100.33
α -Fe ₂ O ₃	97.51	0.20	0.50	1.86	0.05	0.06	--	--	--	100.18
Fe ₃ O ₄	21.76	77.22	--	--	--	0.22	1.00	--	0.02	100.22

Capsules to be treated at 316°C were placed in the oven within two hours of preparation. After treatment, the capsules were removed from the oven, cooled to room temperature, and immediately opened. In cases where dry solids were heated, the products were removed from the capsules with a microspatula to sample vials for analysis. When the solids had been heated in slurry form, the products were removed with a syringe, filtered through a Millipore filter on a Buchner funnel, and dried on the filters in a vacuum desiccator. The nature of the products was determined by x-ray diffraction, chemical analysis, color, and the presence of ferromagnetism. The Debye-Scherrer diffraction-camera technique was employed for the most part, but in some cases Geiger counter spectrometer data were obtained by direct radiation of the product on the filter. The ratio of divalent to trivalent iron in the products was obtained through the use of the orthophenanthroline colorimetric technique. The chemical analyses made it possible to differentiate Fe_3O_4 which contains divalent iron from $\gamma\text{-Fe}_2\text{O}_3$, which does not.

The observations made on the products obtained in these transformation experiments appear in Tables 11, 12, and 13. The experiments in platinum-lined capsules show that the compounds $\gamma\text{-FeOOH}$ and $\alpha\text{-FeOOH}$ convert to $\alpha\text{-Fe}_2\text{O}_3$ at 316°C within 24 hours both when dry and in the presence of water. The color of the $\alpha\text{-Fe}_2\text{O}_3$ formed is different in the two cases, probably because of differences in particle size, since the x-ray patterns are identical. As was to be expected, neither $\alpha\text{-Fe}_2\text{O}_3$ nor Fe_3O_4 transformed at 316°C in platinum-lined vessels in the presence or absence of water. The transformation of $\gamma\text{-Fe}_2\text{O}_3$ to $\alpha\text{-Fe}_2\text{O}_3$ was greatly facilitated by the presence of water. In platinum-lined capsules, $\gamma\text{-Fe}_2\text{O}_3$, which is reportedly thermodynamically unstable at all temperatures under consideration with respect to its polymorph $\alpha\text{-Fe}_2\text{O}_3$ and reportedly transforms rapidly above 250°C, did not transform in the absence of moisture even at 316°C. The stability of this particular sample of $\gamma\text{-Fe}_2\text{O}_3$ may be attributed to the presence of impurities, particularly Al_2O_3 , which can stabilize $\gamma\text{-Fe}_2\text{O}_3$ (23).

Table 11
The Behavior of Iron Oxide and Hydrated Oxide Slurries
in Mild Steel Capsules at Room Temperature

Iron compound in prepared slurry	Solids present in slurry after 48 hours	Solids present in slurry after 4 weeks
Fe_3O_4	Apparently Unchanged	No Change
$\gamma\text{-FeOOH}$	Apparently Unchanged	$\gamma\text{-FeOOH}$ and spinel*
$\gamma\text{-Fe}_2\text{O}_3$	Apparently Unchanged	$\gamma\text{-Fe}_2\text{O}_3$ and traces of Fe_3O_4
$\alpha\text{-FeOOH}$	Apparently Unchanged	$\alpha\text{-FeOOH}$ and spinel*
$\alpha\text{-Fe}_2\text{O}_3$	Apparently Unchanged	Unchanged

*Chemical analysis was not used for these cases since Fe_3O_4 seems to be the only spinel species which could be developed. In both cases, prior experimentation (16) indicates complete stability to dehydration up to temperatures in the neighborhood of 100°C. Thus $\gamma\text{-Fe}_2\text{O}_3$ could not be developed by dehydration of $\gamma\text{-FeOOH}$. In the case of $\alpha\text{-FeOOH}$, even dehydration would only produce the stable $\alpha\text{-Fe}_2\text{O}_3$. Thus the only feasible way in which the spinel structure could be developed here is by reduction to Fe_3O_4 .

Table 12
Summary of Observations on Products Formed When Iron Oxides and Hydrated Oxides are Heated
in Sealed Platinum-Lined Nickel Capsules at 316°C

Substance	Treatment	Time at 316°C	Color of Product	Ferromagnetic	Result of Treatment
γ -FeOOH	Heated with H ₂ O	24 hours	Brick red	No	Converted to α -Fe ₂ O ₃
γ -FeOOH	Heated dry with air	24 hours	Brick red	No	Converted to α -Fe ₂ O ₃
α -FeOOH	Heated with H ₂ O	24 hours	Maroon	No	Converted to α -Fe ₂ O ₃
α -FeOOH	Heated dry with air	24 hours	Brick red	No	Converted to α -Fe ₂ O ₃
γ -Fe ₂ O ₃	Heated with H ₂ O	24 hours	Maroon	Partially	All but a slight amount converted to α -Fe ₂ O ₃
γ -Fe ₂ O ₃	Heated dry with air	24 hours	Brown	Yes	Unchanged
α -Fe ₂ O ₃	Heated with H ₂ O	24 hours	Brick red	No	Unchanged
α -Fe ₂ O ₃	Heated with H ₂ O	2 weeks	Brick red	No	Unchanged
α -Fe ₂ O ₃	Heated dry with air	24 hours	Brick red	No	Unchanged
Fe ₃ O ₄	Heated with H ₂ O	24 hours	Black	Yes	Unchanged
Fe ₃ O ₄	Heated dry with air	24 hours	Black	Yes	Unchanged

Table 13
Summary of Observations on Products Formed When Iron Oxides and Hydrated Oxides are Heated
in Sealed Mild Steel Capsules at 316°C

Substance	Treatment	Time at 316°C	Color of Product	Ferromagnetic	Result of Treatment
γ -FeOOH	Heated with H ₂ O	Up to 4 hours (before cracking)	Red-brown	Partially	Converted to α -Fe ₂ O ₃ and some Fe ₃ O ₄
γ -FeOOH	Heated with H ₂ O	(All capsules tested cracked and leaked within 6 hours.)			
γ -FeOOH	Heated dry with air	24 hours	Red	No	Converted to α -Fe ₂ O ₃ and trace Fe ₃ O ₄
α -FeOOH	Heated with H ₂ O	24 hours	Black red	Yes	Reduced to Fe ₃ O ₄ with trace α -Fe ₂ O ₃
α -FeOOH	Heated dry with air	24 hours	Brick red	No	Converted to α -Fe ₂ O ₃ with trace Fe ₃ O ₄
γ -Fe ₂ O ₃	Heated with H ₂ O	24 hours	Black-brown	Yes	Converted to α -Fe ₂ O ₃ and Fe ₃ O ₄
γ -Fe ₂ O ₃	Heated dry with air	24 hours	Brown (unchanged)	Yes	Slight reduction to Fe ₃ O ₄ at Fe interface
α -Fe ₂ O ₃	Heated with H ₂ O	24 hours	Brick red (unchanged)	No	Slight reduction to Fe ₃ O ₄
α -Fe ₂ O ₃	Heated with H ₂ O	7 days	Very dark red	Partially	Considerable reduction to Fe ₃ O ₄
α -Fe ₂ O ₃	Heated dry with air	24 hours	Brick red (unchanged)	No	Unchanged
Fe ₃ O ₄	Heated with H ₂ O	24 hours	Black (unchanged)	Yes	Unchanged
Fe ₃ O ₄	Heated dry with air	24 hours	Black (unchanged)	Yes	Unchanged

In mild steel capsules, as in platinum-lined capsules, Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ were the only materials which did not transform at 316°C in the absence of water. When mild steel contacts water, the steel corrodes and hydrogen which can reduce all the trivalent species to Fe_3O_4 is generated; therefore, in mild steel capsules only the slurry of Fe_3O_4 remained unchanged. The slurries of $\gamma\text{-FeOOH}$, $\alpha\text{-FeOOH}$, and $\gamma\text{-Fe}_2\text{O}_3$ were first transformed to $\alpha\text{-Fe}_2\text{O}_3$, and the $\alpha\text{-Fe}_2\text{O}_3$ was then reduced to Fe_3O_4 by the corrosion-generated hydrogen.

A point of particular interest was that whenever $\gamma\text{-FeOOH}$ slurries were heated in mild steel capsules at 316°C , the capsule walls developed cracks from which the liquid leaked. Further exploration of this cracking phenomenon was undertaken and it was found that the cracking was associated with the presence of 0.6% chloride ion as an impurity in the commercial $\gamma\text{-FeOOH}$ supply. Research on this cracking mechanism led to the discovery that stress-corrosion cracking of mild steel can be produced at 316°C by FeCl_3 solutions at concentrations as low as 0.001 molar, as well as by aqueous slurries containing $\gamma\text{-FeOOH}$ and $\alpha\text{-FeOOH}$ which have been generated in the presence of chloride ion. The details of the stress-corrosion experiments are given in Appendix C.

A final set of transformation experiments was carried out in which aqueous slurries of the various iron oxide and hydroxide samples were permitted to stand in sealed mild steel capsules at room temperature. Table 13 contains the observations from these experiments.

It is concluded from these experiments that $\gamma\text{-Fe}_2\text{O}_3$, $\gamma\text{-FeOOH}$, and $\alpha\text{-FeOOH}$ are slowly reduced to Fe_3O_4 in the presence of corroding steel at room temperature. This is consistent with the studies of Girard (24) and of Forrest, Roetheli, and Brown (25) who concluded that "ferric hydroxide" reacts in the presence of the ions of $\text{Fe}(\text{OH})_2$ to produce Fe_3O_4 .

4. THE EFFECT OF NAVY BOILER WATER ADDITIVES ON CORROSION PHENOMENA

The Navy regularly adds NaOH and Na_2HPO_4 to the water which is used in high-pressure steel boilers. Chloride ion is always present to some extent, as sea salt is the major impurity of the water. The Navy's specifications for make-up water for a 1200-psi boiler are:

- (1) pH range - 10.4 to 11.0
(The alkalinity is obtained by addition of NaOH).
- (2) Phosphate range - 10 to 25 ppm
(The phosphate is added as Na_2HPO_4).
- (3) Chloride range - 5 to 350 ppm
(The source of chloride is sea salt, the principal impurity of the water).

In order to explore the effect of the presence of these constituents in Navy boiler water on corrosion phenomena, a series of exploratory experiments were conducted. These experiments were carried out under conditions pertinent to some phase of boiler practice including (a) boiler operation in the neighborhood of 300°C and (b) boiler shutdown at room temperature.

A. Corrosion Studies at 25 C and 296 C in Steel Capsules
Containing Navy Boiler Water Additives

In this series of exploratory experiments mild steel capsules were filled with solutions containing various combinations of the Navy boiler water additives. These capsules were treated for specified times at 25°C and at 296°C and then opened for examination of the corrosion products. The capsules were prepared and filled with solution by suction in the manner described in Section 2A. The solutions employed in the study were:

- (1) H₂O
- (2) H₂O + NaOH
- (3) H₂O + NaOH + 25 ppm phosphate as Na₂HPO₄
- (4) H₂O + NaOH + 25 ppm phosphate as Na₂HPO₄ + 350 ppm chloride as NaCl

The pH of each solution was adjusted to the region 10.5 to 10.6. J. T. Baker Analyzed Reagent Grade Chemicals and air-saturated distilled water were used in preparing the solutions.

The corrosion rates of the capsules heated at 296°C were measured by the hydrogen effusion method (1). Table 14 shows the results obtained upon exposure of mild steel capsules to water containing the above additives at 296°C for periods up to 100 days. Each value reported is the mean of five capsules. It may be observed that while there are some differences in the rate of corrosion in the first few days, there seems little difference in the rates after 10 days.

In Table 15 appear data obtained from examination of the corrosion products generated by the various treatments described above at room temperature and at 296°C. The identification of the corrosion products is based primarily on electron diffraction patterns obtained from corrosion-product films on the metal. A comparison of these data with those in Tables 3 and 4 obtained from treatment of mild steel with distilled water shows that the corrosion products generated in NaOH solution at room temperature are comparable to those formed in pure water; that is, in the early stages γ -FeOOH, as well as spinel, is present in the film and later when the oxygen from the air-saturated solution is depleted, only the spinel (almost certainly Fe₃O₄ as discussed earlier in Section 3) is formed. At pH 10.6 the addition of phosphate results in the generation of α -FeOOH in the surface film but the addition of chloride seems to enhance formation of γ -FeOOH. The data thus show that pH alone does not determine which of the hydrated oxides will form in these systems. The data indicate, as one would expect, that after the dissolved oxygen initially present in the solutions is used up in the corrosion process, only Fe₃O₄ is generated.

The corrosion produced during the first day of treatment with the various additives at room temperature is much more localized than that produced with pure water (Fig. 4). The number and size of pits appear to be very little worse after one week than after one day. This suggests that pitting ceases at room temperature when the oxygen supply is exhausted. Deeper pits were generated in presence of the additives than in presence of the water alone. Figure 4 shows how the incipient corrosive attack varied with solution composition. The addition of phosphate to the NaOH solution apparently decreased the number of pits. Each pit formed in the hydroxide-phosphate solution was surrounded by

Table 14
Effects of Navy Boiler Water Additives
on Corrosion Rates at 296°C (565°F)

Capsule Contents	Corrosion rates (mg/dm ² -mo) for Various Reaction Periods (days)								
	0.25	0.5	1	3	5	10	25	50	100
H ₂ O	261	208	168	104	78	48	24	12	6
H ₂ O + NaOH	230	187	157	110	87	50	23	14	8
H ₂ O + NaOH + PO ₄ ³⁻	526	332	202	84	60	38	19	12	8
H ₂ O + NaOH + PO ₄ ³⁻ + Cl ⁻	544	353	213	92	68	42	23	14	9

Table 15
Corrosion Products Formed by Treatment of Mild Steel With Solutions Containing Navy Boiler Water Additives

Capsule Contents	Exposure at Room Temperature	Exposure at 296°C	Solution pH Before Reaction	Solution pH After Reaction*	Appearance of Liquid†	Appearance of Metal	Corrosion Products on Metal‡
H ₂ O + NaOH	1 day	None	10.6	10.6	Clear, colorless	Scattered brown spots on shiny metal	γ-FeOOH and spinel
	1 week	None	10.6	10.6	Clear, colorless	Few additional brown spots on shiny metal	γ-FeOOH and spinel
	12 weeks	None	10.6	10.3	Clear, colorless	Thin gray film covering surface	Spinel and some γ-FeOOH
	1 day	100 days	10.6	9.5	Clear, colorless	Continuous gray-black film	Spinel
H ₂ O + NaOH + 25 ppm Phosphate	1 day	None	10.6	10.6	Yellow tinge	Few brown-yellow circles on shiny metal	Spinel and probably α-FeOOH
	1 week	None	10.6	10.7	Yellow tinge	Same as above	Spinel and α-FeOOH
	12 weeks	None	10.6	10.6	Yellow tinge	Bronze colored film containing brown circles	α-FeOOH and some spinel
	1 day	100 days	10.6	10.5	Clear, colorless	Continuous gray-black film	Spinel
H ₂ O + NaOH + 25 ppm Phosphate + 350 ppm Chloride	1 day	None	10.5	10.6	Yellow tinge	Red-brown splotches on shiny metal	Spinel and probably α-FeOOH
	1 week	None	10.5	10.7	Yellow tinge	Same as above	Spinel
	12 weeks	None	10.5	10.5	Yellow tinge	Bronze-colored film containing red-brown splotches	γ-FeOOH and some spinel
	1 day	100 days	10.5	10.5	Clear, colorless	Continuous gray-black film	Spinel

*Each value represents the mean of 5 capsules.

†The amount of solid removed from the liquid was too small for x-ray diffraction analysis.

‡Both Fe₃O₄ and γ-Fe₂O₃ have the spinel structure. The diffraction techniques employed were inadequate for distinguishing between them.

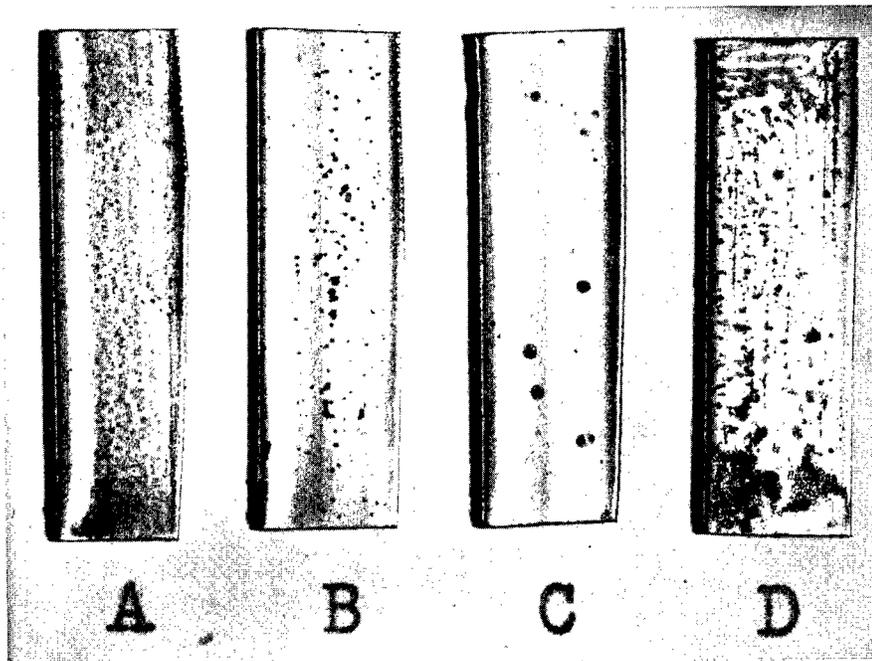


Fig. 4 - Appearance of mild steel treated at room temperature for one day with Navy boiler water additives as follows: A - pure water, B - NaOH solution (pH 10.6), C - NaOH solution with 25 ppm phosphate as Na_2HPO_4 (pH 10.6), D - NaOH solution with 25 ppm phosphate and 350 ppm chloride as NaCl (pH 10.5)

corrosion product arranged in an almost perfect circle. The most pits and the largest amount of corrosion product were generated in the solution containing chloride. However, the pitting attack appeared to cease almost completely within the first week of treatment. Apparently under room-temperature conditions the presence of 350 ppm chloride does not seriously increase corrosion in these systems unless oxygen is also present. The maximum phosphate concentration recommended by the Navy was insufficient to reduce the effect of the maximum chloride, so long as air was present at room temperature. The corrosion-product films generated by these treatments at 296°C were continuous films of Fe_3O_4 which showed no evidence that pitting initiated at room temperature had continued at the elevated temperature. The addition of phosphate to the pH 10.6 solution had the effect of maintaining the pH at 10.6 during the 296°C treatment.

B. The Corrosion at 25°C of Fe_2O_3 -Coated Mild Steel in Solutions Containing Navy Boiler Water Additives

An experiment was undertaken in which conditions approximating those encountered during boiler shutdown were produced. The mild steel test specimens employed were first coated with a film of Fe_3O_4 by heating them in water at 316°C just as the inside walls of a boiler system become coated with corrosion-generated Fe_3O_4 . These coated specimens were then placed in solutions saturated with air from the room in order to duplicate the situation of a shutdown boiler open to the air at room temperature and pressure.

More specifically, specimens for these studies were prepared by heating strips of mild steel in mild steel capsules containing distilled water. Strips approximately $1\text{-}1/4 \times 1/8$ inch were cut from annealed and flattened capsule tubing. One such strip

was inserted in a 2-inch-long capsule. Each capsule was filled with distilled water by means of a syringe and sealed by the usual procedure. Twenty-four such capsules were heated 180 days at 316°C in a tube furnace in order to coat the strips with corrosion-generated Fe_3O_4 . At the termination of the coating process the capsules were removed from the furnace, cooled to room temperature, and opened. One end was cut from each capsule with shears. The sheared end was squeezed open with pliers and the Fe_3O_4 -coated specimen allowed to fall out of the capsule into a Petrie dish containing distilled water. The specimen was immediately lifted from the dish with tweezers, rinsed with a stream of distilled water from a wash bottle, and excess water removed by lightly touching the specimen with filter paper. Great care was exercised to prevent scratching of the specimens during this treatment. Each specimen was dropped into one of the solutions containing boiler water additives within a minute after being removed from the capsule.

The following solutions were prepared from J. T. Baker Analyzed Reagent Grade chemicals and distilled water:

- (1) 350 ppm chloride as NaCl
- (2) pH 10.5 NaOH
- (3) pH 10.5 NaOH solution containing 25 ppm phosphate as Na_2HPO_4
- (4) pH 10.5 NaOH solution containing 25 ppm phosphate as Na_2HPO_4 and 350 ppm chloride as NaCl.

The addition of Na_2HPO_4 solution lowered the pH to 10.4, and subsequent addition of NaCl to the latter solution lowered the pH to 10.3. Approximately 100 ml of each solution were introduced individually into a 500-ml quartz Erlenmeyer reaction flask, and distilled water was added to an additional flask. Two specimens were dropped into each flask. Filtered, dust-free air, saturated with moisture to prevent evaporation of the test solutions was drawn by means of an aspirator through a quartz tube leading into each solution. The Fe_3O_4 -coated specimens were treated for 6 weeks in the continuously aerated solutions and in the distilled water at room temperature.

The corrosion products generated in these tests were characterized by x-ray and electron diffraction. The extent and nature of the corrosion was determined by microscopic examination. The corrosive attack generally occurred first along the edges of the specimens and spread with time over the entire surface. The data obtained from this experiment are summarized in Table 16. The pH behavior of the solutions seems difficult to interpret. No special efforts were made to purify the air, so that carbon dioxide and possibly other impurities in the air might have influenced the pH. The effect of carbon dioxide requires exploration but inasmuch as the pH is normally monitored and controlled in the course of boiler operations, carbon dioxide was eliminated in most of the subsequent experiments described in this report. For the first time in the course of this research β -FeOOH was found as a corrosion product; its generation appears to have been promoted by a combination of chloride ion and increased alkalinity. A comparison of the data obtained here with that obtained when sealed capsules were exposed to similar solutions at room temperature shows that continuous aeration (and thus oxygenation) greatly accelerates the corrosive attack.

The conclusions drawn from this experiment are that on mild steel covered with a film of Fe_3O_4 by corrosion in high-temperature water,

- (1) pits are generated during exposure to air-saturated water at room temperature.
- (2) pitting is accompanied by the generation of γ -FeOOH.

Table 16
Corrosion Products Generated on Fe_3O_4 -Coated Specimens During Six Weeks' Treatment
at Room Temperature in Solutions Containing Navy Boiler Water Additives

Solution	Initial pH	pH Behavior During Treatment	Final Appearance of Solution	Final Appearance of Specimens
Distilled water	6.3	Increased slowly to 8.6	Contained some γ -FeOOH	Pits covered and surrounded by γ -FeOOH
350 ppm Chloride	5.9	After 2 days remained constant in vicinity of 7	Contained a large amount of γ -FeOOH	Pits covered and surrounded by γ -FeOOH. More pits than with water.
NaOH	10.5	Immediately dropped to 8.3 and remained constant	Contained very little γ -FeOOH	A few pits covered and surrounded by γ -FeOOH
NaOH + 25 ppm Phosphate	10.4	Immediately dropped to 8.6 and remained constant	Clear, Colorless	Unpitted gray-black film. Electron diffraction indicates some γ -FeOOH and α -FeOOH on surface.
NaOH + 25 ppm Phosphate + 350 ppm Chloride	10.3	Dropped to 8.4 and slowly increased to 9.6	Contained some γ -FeOOH, β -FeOOH, and amorphous material	Pits surrounded and covered by γ -FeOOH, β -FeOOH, and amorphous material

(3) pitting and the generation of γ -FeOOH are increased by addition of chloride to the water and decreased by raising the initial pH to 10.5 with NaOH.

(4) pitting and the generation of γ -FeOOH are not completely eliminated by addition of 25 ppm Na_2HPO_4 to the pH 10.5 NaOH solution.

(5) pitting does not cease when the maximum allowance of chloride ion is added to a pH 10.4 solution containing the maximum phosphate specified in the Navy boiler water treatment limits.

C. The Corrosion at 25°C of Fe_3O_4 -Coated Mild Steel in Alkaline Chloride Solutions Containing Various Phosphate Concentrations

Another experiment in this series was undertaken as the result of a simple test that was carried out in this Laboratory. Fe_3O_4 -coated specimens were placed in each of two quartz Erlenmeyer flasks. One flask contained a pH 10.6 NaOH solution with the maximum concentrations of phosphate (25 ppm) and chloride (350 ppm) permitted by Navy boiler specifications. The other flask contained a solution made by adding phosphate to the first solution until the phosphate concentration was approximately 4000 ppm. The pH was lowered from 10.6 to 9.3 by the addition of this amount of phosphate. The two flasks were covered with inverted beakers to allow contact with the air and then were permitted to stand at room temperature for about 6 months. At the end of this time the specimens in the first flask were severely corroded at all surfaces. A large amount of orange-brown-colored corrosion product had been generated. The specimens in the flask containing the excess of phosphate were not attacked, as there was no visual evidence that corrosion products had been generated. This simple experiment indicated that the addition of a sufficiently high concentration of phosphate could eliminate corrosion in solutions exposed to the air and containing 350 ppm of chloride.

An experiment was then undertaken to determine more exactly the concentration ratio of phosphate to chloride which is inhibiting. Solutions for this experiment were prepared as before from J. T. Baker Analyzed Reagent Grade chemicals and distilled water. To a pH 10.4 NaOH solution, containing 350 ppm of chloride as NaCl, weighed quantities of Na_2HPO_4 were added to achieve the desired concentrations of phosphate (Table 17). These solutions were introduced into quartz flasks and then mild steel specimens, coated with Fe_3O_4 by prior treatment in 316°C water, were dropped into the flasks (the procedure for obtaining the Fe_3O_4 coating was the same as that described in Section 4B). Air, saturated with water, and free from carbon dioxide, was bubbled through the solutions continuously for 5 weeks. The pH of the solution was measured at the beginning and at the termination of the experiments. The solids filtered from the solutions at the end of the aeration process were analyzed by x-ray diffraction. Corrosion was general with some pitting, and edges of the specimens were particularly attacked. The corrosion products were nonadherent and fell off the specimen into the liquid. Results of this experiment may be summarized as follows:

- (1) The worst corrosive attack of mild steel in aerated alkaline chloride solutions containing phosphate is accompanied by the generation of $\gamma\text{-FeOOH}$.
- (2) Between 100 and 200 ppm of phosphate are necessary even to begin to retard corrosion in an alkaline solution containing 350 ppm of chloride.
- (3) Complete passivation is achieved by the addition of 4000 ppm of phosphate as Na_2HPO_4 to a pH 10.6 solution containing 350 ppm of chloride.
- (4) The corrosion product $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ is generated in the phosphate solution as the point of passivation is approached.

D. Corrosion at 25°C of Bare Mild Steel in Chloride Solutions Containing Various Phosphate Concentrations at pH of 10.6

To obtain a better picture of inhibition by phosphate in the presence of chloride at a pH in the region of normal boiler operations, a series of flasks was arranged in three rows of five flasks each (Fig. 5). From front to back the rows represented chloride concentrations of 10, 70, and 175 ppm; from left to right the rows represented phosphate concentrations of 0, 500, 1000, 2000, and 4000 ppm. The pH of each solution was adjusted to a value of 10.6, using a sodium hydroxide solution and a glass electrode.

Specimens were half-inch squares of mild steel sheared from a plate 0.105 inch thick. They were degreased in trichloroethylene, dipped in dilute hydrochloric acid, dipped in dilute ammonium hydroxide, and washed before being dropped into the solutions.

Throughout the experiments, "outside" air was bubbled into the flasks. To avoid pH change, the air was freed of carbon dioxide by being bubbled through concentrated sodium hydroxide solution, saturated barium hydroxide solution, and then water before being led into the flasks.

Within 24 hours the specimens in solutions containing 70 and 175 ppm chloride and from zero to 2000 ppm phosphate, and specimens in solutions containing 10 ppm chloride and from zero to 1000 ppm phosphate had shown signs of corrosion.

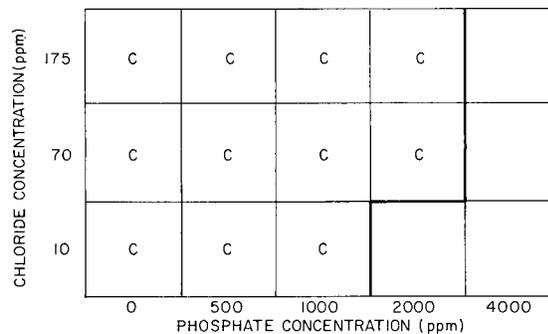
The effects at the end of 72 hours, which then changed only in degree over a period of six months, were as follows: Four flasks showed no signs of corrosion; these contained specimens in a solution of 10 ppm chloride and 2000 ppm phosphate and in solutions containing 4000 ppm phosphate and 10, 70, and 175 ppm chloride.

Table 17
The Effect of Phosphate on Corrosion of Fe₃O₄-Coated Specimens in Aerated Chloride Solutions at 25°C

PO ₄ [≡] (ppm)	Cl ⁻ (ppm)	pH Initial	pH Final	Extent of Corrosion (Approximated Visually*)	Nature of Solids Filtered from Solutions after Reaction	Composition of Corrosion Products
0	350	10.4	8.9	Very extensive	Orange-brown colored and partially ferromagnetic	γ-FeOOH with trace of spinel
50	350	10.5	9.1	Very extensive	Same as above	Same as above
100	350	10.4	9.2	Very extensive	Same as above	Same as above
200	350	10.5	9.1	Less than any above	Brown	Amorphous
500	350	10.3	9.5	Less than any above, but appreciable	Dark yellow	Amorphous
1000	350	10.1	9.0	Very little, but point of passivation not reached	Yellow-gray	Fe ₃ (PO ₄) ₂ ·8H ₂ O

*The nature of the corrosion was general with some pitting. The edges of the specimens were particularly attacked.

Fig. 5 - Corrosion results of clean mild steel held at 25°C for 72 hours to 6 months in solutions of various chloride and phosphate concentrations at pH of 10.6. Corroded samples are designated by C.



Corrosion was not severe in solutions containing 10 ppm chloride and 1000 ppm phosphate, nor in solutions containing 70 or 175 ppm chloride and 2000 ppm phosphate. In these solutions corrosion was limited to the corners and edges of the specimens, and corrosion products did not appear on the flat surfaces.

E. The Effect of pH upon the Corrosion at 25°C of Bare Mild Steel in Dilute Chloride Solutions Containing 200 ppm Phosphate

To obtain a more specific picture of effects in the region of phosphate additions that might be feasible in normal boiler operations, an experiment analogous to that described just above was set up using identical steel samples and chloride concentrations of 10, 20, and 40 ppm at pH levels of 7.0, 8.0, 9.0, 10.0, and 11.0. Corrosion was observed on all samples except those exposed to solutions with a pH of 11.0.

Since there was a sharp line of demarcation between the effects of pH 10.0 and pH 11.0, a second series of solutions was prepared with increments of pH value of 0.2 unit between the values of 10.0 and 11.0.

In this case there was a sharp line of demarcation between the effects of a pH of 10.8 and 11.0, although it should be stated that corrosion in the 10.8 solution appeared only at the edges of the specimens. No corrosion was seen on the specimens held in the solutions at a pH of 11.0.

5. SUMMARY OF MAJOR CONCLUSIONS PERTINENT TO BOILER OPERATION

Of the six corrosion products which may be generated during the corrosion of steel under normal boiler operating conditions ($\text{Fe}(\text{OH})_2$, Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-FeOOH}$, and $\alpha\text{-FeOOH}$), it appears that only those having the spinel structure (Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$) are capable of forming adherent protective films. The major problem is the determination of the conditions for maintenance of these protective films.

Mild steel exposed to air-saturated water at room temperature reacts to form $\gamma\text{-FeOOH}$, a nonadherent corrosion product which appears as islands on the metallic surface and each such island is the locus of an incipient pit. As the oxygen is used up by reaction, the material in direct contact with the steel is reduced to Fe_3O_4 which eventually forms an adherent film over the entire surface. The process is accompanied by a rise in pH from an initial value of about 6 to 9.3 and then to 9.9 as the solution becomes saturated first with $\text{Fe}(\text{OH})_2$ and then with $\text{Mn}(\text{OH})_2$. Any of the originally generated $\gamma\text{-FeOOH}$ which does not adhere to the metallic surface appears as loose particulate matter suspended in the solution or settled in aggregates.

In the absence of water treatment chemicals, if the presence of oxygen is maintained as in normal boiler shutdown with exposure of steel to water and air at room temperature, this $\gamma\text{-FeOOH}$ continues to form.

Upon heating to boiler operating temperature, such $\gamma\text{-FeOOH}$ transforms to $\alpha\text{-Fe}_2\text{O}_3$, also nonadherent and an insulator, whose presence may be a source of trouble due to its transportation and deposition on heat transfer surfaces at unfavorable locations. If the quantity of this material is not very great, it may be reduced to Fe_3O_4 by corrosion-generated hydrogen (26) when the steel is brought to boiler operating temperature, but in any event this material remains as a loose solid. Although Fe_3O_4 is a good electronic conductor and probably therefore a good thermal conductor, its presence as loose "crud" material in an operating system would also seem to be a source of trouble.

Static tests in capsules make it appear that, in the absence of oxygen, water treatment chemicals in the quantities now in use in Navy boilers do not have major effects upon corrosion rates and protective film formation at boiler operating temperatures but that they may be very important in the prevention of deterioration during shutdown periods with access of air at room temperature. No evidence of pit formation in the absence of oxygen was observed. With respect to corrosion rates, it should be noted that tests in dynamic systems (27) have indicated a beneficial effect of increase of pH.

The loop experiments described in the introduction to this report indicate that the genesis of a protective magnetite film on piping by operation at elevated temperature for some time in the absence of oxygen gives protection against the development of pits when the piping is subsequently operated for some additional time at elevated temperature in the presence of oxygen. The presence of such a magnetite film, however, does not give protection during room-temperature exposure in the presence of air and water. At room temperature the protective film breaks down at weak spots unless such breakdown is

inhibited by adequate water treatment. Such breakdown under conditions of inadequate inhibition gives rise to the formation of nonadherent γ -FeOOH or α -FeOOH both of which transform to nonadherent α -Fe₂O₃ upon heating, with the possible consequences outlined above.

This breakdown of the protective magnetite film at room temperature with access of air can be avoided by proper water treatment. One such treatment involves only presently used Navy chemicals but requires careful attention to the phosphate:chloride ratio and to pH. Preliminary experiments indicate that a ratio greater than 10:1 of phosphate:chloride is usually necessary but that the protection afforded is sensitive to pH. Thus if the pH can be maintained at 11, 40 ppm of chloride can be tolerated when 200 ppm of phosphate are present. It may be worthy of mention that the wetting of all surfaces with adequate concentrations of phosphate prior to shutdown period might preserve all the wetted surfaces against corrosion during an extended exposure with free access of air. Evaporation could only concentrate phosphate upon the wetted surfaces and thus enhance the protection. However, the minimum quantity of phosphate necessary under these conditions with free access of CO₂ requires exploration.

The experiments described in Appendix C have clearly indicated the deleterious effects which may be introduced by the genesis of substantial amounts of FeOOH in the presence of chloride or by subsequent boiler operation in the presence of chloride prior to removal of these corrosion products. This would seem to emphasize the need for avoidance of the genesis of such material or for careful corrosion-product cleanup prior to light-off when substantial amounts of such material have been generated.

6. DISCUSSION OF PROJECTED PROGRAM

In connection with further work it becomes necessary to consider three points of major importance:

- (1) Can water treatment protect the boiler steel against attack in the presence of oxygen as the temperature is raised?
- (2) Can the water treatment be so constituted that attack of the boiler steel will be avoided even when the boiler water solution is subjected locally to drastic concentration due to very high steaming rates, hot spots, or steam blanketing?
- (3) What is the effect of introducing into the system cations other than those found in the steel, such as magnesium and calcium from sea water distillate or copper from feed water systems?

A major portion of the projected program will be devoted to finding answers to these questions.

In connection with the first of these questions the few observations made in recent years (28-30) indicate only that while small amounts of oxygen may be detrimental, the presence of sufficient oxygen may be beneficial to protective film formation in both static and dynamic systems in the absence of water treatment. On the basis of available data (31,32,33,19a), one might have predicted that oxygen would tend to oxidize any Fe₃O₄ to γ -Fe₂O₃ which would in turn tend to convert to α -Fe₂O₃ under boiler operating conditions and slough off as a nonadherent red powder. However, the experiments to which reference has just been made as well as those described in the introduction to this report indicate that a spinel film on a steel surface may resist this action even in the absence of treatment chemicals. It may be recalled in connection with the loop experiments outlined in the introduction that pitting was found on a bare section of piping when it was connected to piping covered with a good magnetite film and the complete assembly subjected to heating in highly oxygenated water. The loose red α -Fe₂O₃ found in the system may have been

generated by oxidation of the outer portion of the protective magnetite film in the main loop section and transported to the bare section. This raises the question of whether some of this transported $\alpha\text{-Fe}_2\text{O}_3$ may have induced pitting in the bare section by being attached at local areas, thus preventing protective film formation in these areas and creating an oxygen concentration cell. Clearly this effect of temperature, water treatment, and the joint presence of bare and protected metal requires careful scrutiny both in static and dynamic systems.

In connection with the second question, it becomes essential to explore in a quantitative manner the attack of steel by boiler water solutions of varying concentration and their effects upon corrosion rates and the nature of the films that are generated. The fact that Potter (34) in a summary of observations on boilers operated by the British Electric Authority states "Tube embrittlement never accompanied corrosion at 350 lb/in², only rarely at 600 lb/in², but invariably at 1400 lb/in²" calls for critical examination of this phenomenon. Potter attributes this embrittlement to corrosion-generated hydrogen with accompanying decarburization and methane formation. It seems clear, however, that decarburization does not take place by reaction of mild steel with water at 316°C (600°F) over a 789-day period, since steel capsules containing water have remained at this temperature in the hydrogen effusion apparatus for this length of time without evidence of decarburization. It must therefore be concluded that the decarburization reported as always accompanying pit formation in boiler tubes at 1400 psi (590°F) must be due either to overheating at the pit sites or to accelerated attack, or both. Potter reports that "The corrosion. . . occurred preferentially in those tubes supporting the greatest rate of steaming." The fact that Adcock, in a report from The National Physical Laboratory (35), found decarburization to occur when mild steel was subjected to the action of 27% NaOH at 310°C (590°F) for 20 days indicates that concentration of NaOH with accelerated attack will produce decarburization at this temperature. The work of Purcell and Whirl (36) indicating the protective effect of phosphate in this connection and its confirmation in practice call for exploration of the effect of phosphate:hydroxide ratios and the relation of temperature, hydrogen-generation rates, and film structure upon the development of embrittlement. It might be mentioned in passing that the chemical treatment which was mentioned above as being effective in maintaining the protective film at room temperature in the presence of aerated water containing 40 ppm chloride, that is, 200 ppm phosphate at pH of 11, is within the recommended phosphate:hydroxide ratio.

Finally, in connection with the third question, it should be stated that the presence of calcium, magnesium, copper, etc., are not necessarily deleterious. It is entirely conceivable that some of these constituents may serve a useful purpose by entering the protective film and actually stabilizing it against attack by oxygen. It is noteworthy that even the presence of sodium (37) has been found capable of stabilizing $\gamma\text{-Fe}_2\text{O}_3$ against conversion to $\alpha\text{-Fe}_2\text{O}_3$ and hence of preventing the conversion of Fe_3O_4 to $\alpha\text{-Fe}_2\text{O}_3$ in the presence of oxygen. The investigation of this effect and of the effect of other substituents in the protective film is a further part of the projected program.

A subsidiary question which merits some attention is the effect of the CO_2 absorbed in exposure to air at room temperature during shutdown on the requirements for water treatment.

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APPENDIX A
TYPICAL ELECTRON DIFFRACTION PATTERNS

Table A1
 Typical Electron Diffraction Data* for Identification of Water-Formed Films on Mild Steel
 (d Values in Angstroms)

ASTM VALUES FOR COMPARISON		Exposure at 25°C							At 316°C
α-Fe	Spinel†	0 hr†	1 hr	6 hr	24 hr	1 wk	12 wk	52 wk	
	4.85VW‡					{ 4.64VW§ } { 4.74MW§ }	{ 4.74MW§ } { 4.74VW§ }	{ 4.74VW§ } { 4.81W§ }	
	4.52VW								
	4.17M		3.25W	3.20VW		3.17W	4.27VW		
	3.30VS				{ 2.96M }	{ 2.95M }	3.30VW		
	2.99M						{ 2.98S }	3.02M	
	2.97M								
	2.70VW								
	2.53VS				{ 2.51MW }	{ 2.48VS }	{ 2.51VS }	2.50VS	
	2.48VS		2.45W						
	2.44VW								
	2.36MS								
	2.27VW								
	2.19VW						2.37VW		
	2.10M								
	2.09M								
2.03VS		2.00VS	2.03VS	2.00VS	{ 2.09M }	{ 2.10M }	{ 2.10MS }	2.10M	
	1.94S				1.92MW	1.94MW	1.91W		
	1.85MS								
	1.74S								
	1.71W								
	1.61MS								
	1.57M								
	1.54MS								
	1.53S		1.51VW	1.51VW		1.55W			
	1.50M								
	1.48S								
1.43M	1.44MS	1.41M	1.43VW	{ 1.45MW }	{ 1.48VS }	{ 1.49MS }	{ 1.47S }	1.47MS	
				1.41VW				1.48MS	

Table A1 (Continued)
 Typical Electron Diffraction Data* for Identification of Water-Formed Films on Mild Steel
 (d Values in Angstroms)

ASTM VALUES FOR COMPARISON		Exposure at 25° C						At 316° C	
α -Fe	Spinel†	0 hr†	1 hr	6 hr	24 hr	1 wk	12 wk	52 wk	52 wk
	γ -FeOOH								
	1.40MS						1.42VW		
	1.38MS						1.32W	1.33VW	
	1.28MW			1.28W	1.29W	1.29W	1.27W	1.28VW	
	1.22MW			1.20W	1.21W	1.20W	1.20W		
	1.21M								
	1.20MW			1.15MW					
1.17MS		1.16MS	1.17S				1.10W	1.15VW	
	1.12VW						1.08MW	1.10M	1.09M
	1.09M			1.09M	1.09M	1.09M	1.05W	1.04VW	
	1.05W			1.00M	1.06VW	1.06VW	0.96W	0.97W	
1.01W		1.02W	1.00VW	0.90M	0.97MW	0.97W	0.87W	0.88W	
0.90M		0.90M	0.90M	0.90M	0.88W	0.85W	0.85W	0.85W	
	0.88W				0.83W	0.85W	0.81W	0.81W	
0.83W		0.83W	0.82VW						
0.76M		0.76M	0.76M	0.76W					
Compounds Represented by Above Patterns									
	α -Fe and Spinel	α -Fe and Spinel	α -Fe and γ -FeOOH	α -Fe, γ -FeOOH, and Spinel	γ -FeOOH and Spinel	γ -FeOOH and Spinel	γ -FeOOH and Spinel	Spinel	Spinel

*The lattice spacings, or "d" values, smaller than 3 Å, as obtained by electron diffraction methods, are accurate within 1%. For larger spacings inaccuracies as great as 5% are not uncommon.

†Fe₃O₄ and γ -Fe₂O₃ each have the spinel structure. The pattern for γ -Fe₂O₃ contains a few weak lines which were never observed in these experiments; therefore, the Fe₃O₄ pattern is that given here.

‡The diffraction pattern for untreated, freshly annealed metal was that of α -Fe. Occasionally an additional line, 2.53, characteristic of the spinel oxides was present.

§Braces represent measured "d" values which may correspond to more than one spacing.

¶The intensities, estimated visually, are indicated by the following symbols: VS - Very Strong; S - Strong; MS - Moderately Strong; M - Medium; MW - Moderately Weak; W - Weak; VW - Very Weak.

Table A2
 Typical Electron Diffraction Data for Identification of Films
 Formed on Mild Steel by Treatment with 1% Hydrogen Peroxide
 (d Values in Angstroms)
 (Intensity symbols have same significance as in Table A1)

ASTM VALUES FOR COMPARISON				Exposure at 25°C				At 316°C		
α -Fe	γ -FeOOH	α -FeOOH	Fe ₃ O ₄	α -Fe ₂ O ₃	1 hr	24 hr	1 wk	4 wk	1 wk	12 wk
		4.6M	4.85VW							4.79W
	4.52VW							{ 4.45MW }		
	4.17M	4.18VS		3.68MW					3.68MW	
	3.30VS	3.36M				3.28M	3.29MS	3.29VW		
	2.99M						{ 2.94M }			3.05MS
	2.70VW	2.98MW	2.97M				{ 2.60VS }		2.69S	
		2.69S		2.69VS				2.71MS		
		2.57MW	2.53VS						{ 2.51S }	2.53S
	2.48VS	2.47MW		2.51S	2.51M	2.51VS		2.51VS		
	2.44VW	2.45S								
	2.36MS		2.42VW							
	2.27VW	2.25M		2.20MW				{ 2.26M }	2.20S	
	2.19VW									
	2.09M	2.18MS	2.10M						2.07VW	2.13M
2.03VS		2.09VW			2.00VS					

Table A2 (Continued)
 Typical Electron Diffraction Data for Identification of Films
 Formed on Mild Steel by Treatment with 1% Hydrogen Peroxide
 (d Values in Angstroms)
 (Intensity symbols have same significance as in Table A1)

ASTM VALUES FOR COMPARISON				Exposure at 25°C				At 316°C		
α -Fe	γ -FeOOH	α -FeOOH	Fe ₃ O ₄	α -Fe ₂ O ₃	1 hr	24 hr	1 wk	4 wk	1 wk	12 wk
1.94S	2.00W					1.92M	1.94M	1.94W		
1.85MS	1.91MW			1.84MS					1.82MS	
1.74S	1.80M					1.73M	{ 1.73M }	{ 1.73S }		
	1.77VW									
	1.72S		1.71W							1.72MW
	1.69M			1.69MS					1.66VS	
	1.60M		1.61MS						1.59M	1.63MS
1.57M	1.60MW			1.60MW						
1.54MS	1.56MS					{ 1.52S }	{ 1.52MS }	{ 1.52VS }		
1.53S										
1.50M	1.51M									
			1.48S						{ 1.48S }	1.51M
	1.47M			1.49MS						
	1.45MS								{ 1.47VS }	
1.43M	1.44MS			1.45MS						
	1.40MS				1.42M					
	1.39MW						{ 1.38W }			
	1.38MS									

APPENDIX B
EQUILIBRIUM pH CALCULATIONS

B1 EQUILIBRIUM CONCENTRATIONS OF FeOH^+ , Mn^{++} ,
AND OH^- IN WATER CONTACTING MILD STEEL
(CONTAINING 0.57% MANGANESE) AT ROOM
TEMPERATURE

The solubility products for $\text{Fe}(\text{OH})_2$ are*

$$[\text{FeOH}^+][\text{OH}^-] = K_{\text{sp}_1} = 4 \times 10^{-10} \quad (\text{B1})$$

$$[\text{Fe}^{++}][\text{OH}^-]^2 = K_{\text{sp}_2} = 8 \times 10^{-16} . \quad (\text{B2})$$

The solubility product for $\text{Mn}(\text{OH})_2$ is†

$$[\text{Mn}^{++}][\text{OH}^-]^2 = K_{\text{sp}_3} = 2.8 \times 10^{-13} . \quad (\text{B3})$$

In addition to the above equations a fourth relation is known.

$$[\text{FeOH}^+] + 2[\text{Fe}^{++}] + 2[\text{Mn}^{++}] = [\text{OH}^-] . \quad (\text{B4})$$

Equations (B1), (B2), (B3), and (B4) were solved simultaneously for the four variables. When the expressions for $[\text{OH}^-]$ obtained by solving (B1), (B2), and (B3) were substituted in (B4), the following relationship resulted:

$$[\text{OH}^-]^3 - [4 \times 10^{-10}][\text{OH}^-] = 5.6 \times 10^{-13} .$$

The solution of this cubic equation with the aid of Cardan's formula was found to be 8.4×10^{-5} moles/liter. The pH of a solution with this $[\text{OH}^-]$ is 9.92.

In alkaline solutions an additional reaction is possible†, namely,



The ratio of $[\text{Mn}^{++}]$ to $[\text{HMnO}_2^-]$ at pH 9.92 was calculated from K_{sp_3} , K_{sp_5} , and $[\text{OH}^-]$.

$$\frac{[\text{Mn}^{++}]}{[\text{HMnO}_2^-]} = \frac{K_{\text{sp}_3}}{K_{\text{sp}_5}[\text{OH}^-]^3} = \frac{(2.8 \times 10^{-13})}{(1 \times 10^{-5})(8.4 \times 10^{-5})^3} = 0.49 \times 10^5 .$$

This shows that at pH 9.92, the manganese is in solution substantially as Mn^{++} .

The concentrations of FeOH^+ , Fe^{++} , and Mn^{++} were calculated by substituting the $[\text{OH}^-]$ value found above in Eqs. (B1), (B2), and (B3):

* D. L. Leussing and I. M. Kolthoff, J. Am. Chem. Soc. 75:2476 (1953).

† R. K. Fox, D. F. Swinehart, and A. B. Garrett, J. Am. Chem. Soc. 63:1779 (1941).

$$[\text{FeOH}^+] = 0.48 \times 10^{-5} \text{ moles/liter}$$

$$[\text{Fe}^{++}] = 0.01 \times 10^{-5} \text{ moles/liter}$$

$$[\text{Mn}^{++}] = 4 \times 10^{-5} \text{ moles/liter .}$$

According to Leussing and Kolthoff, a saturated solution of $\text{Fe}(\text{OH})_2$ contains 1.76×10^{-5} moles FeOH^+ per liter and 0.18×10^{-5} moles Fe^{++} per liter, while a calculation based on the expression for K_{sp_3} shows that a saturated solution of $\text{Mn}(\text{OH})_2$ contains 4.1×10^{-5} moles Mn^{++} per liter. The presence of manganese in the steel has repressed the solubility of the iron.

The amount of steel containing 0.57% manganese which must corrode from a capsule having a liquid volume of 0.25 ml in order to provide 4×10^{-5} moles/liter of Mn^{++} in solution was calculated.

$$4 \times 10^{-5} \times \frac{0.25}{1000} \times 55 \times \frac{1}{0.0057} = 10^{-4} \text{ grams of steel.}$$

B2 EXPERIMENTS FOR DETERMINING THE EQUILIBRIUM pH OF WATER CONTACTING IRON-MANGANESE MIXTURES AT ROOM TEMPERATURE

Capsules 4 inches in length were prepared from nickel tubing (0.25-inch O.D. x 0.020-inch wall) lined with 0.010-inch platinum that had been vacuum annealed one hour at 1400°C . The capsules were formed individually and one end was completely flattened and then welded. Through the remaining open end of each capsule, high purity water (resistivity $>10^6$ ohm-cm) was introduced with a syringe and then samples of metal were introduced with a spatula. Finally the open ends were flattened and welded.

Capsules containing carbonyl iron powder alone, chips of electrolytic manganese alone, and mixtures (unweighed) of the iron and manganese were prepared and permitted to stand at room temperature. The pH values of the solutions removed from such capsules after 3 weeks were the same as those obtained after 2 weeks, thus showing that equilibrium was achieved within 2 weeks. The pH values are believed accurate within 3 significant figures because sufficient solution was contained in the 4-inch-long capsules to allow rinsing the pH meter electrodes as well as the making of 2 or 3 individual measurements on the solution from each capsule. Moreover, the pH in this region is not very sensitive to carbon dioxide from the atmosphere. The data from these experiments appear in the table on page 37.

These experiments show that the pH of 9.9 obtained in steel capsules containing water at room temperature can be attributed to the dissolution of manganese from the steel during the corrosion process.

The Equilibrium pH of Water Contacting
Fe, Mn, and Mixtures of Fe and Mn at 25°C

Capsule Content	Measured Equilibrium pH		Equilibrium pH Based on Literature and Calculations
	Individual Capsules	Mean Value	
Carbonyl Iron Powder	9.25	9.37	9.32*
	9.40		
	9.45		
Electrolytic Manganese Chips	10.04	9.95	9.92†
	9.92		
	9.89		
Iron Powder and Manganese Chips	9.95	9.95	9.92‡
	9.96		
	9.95		

* Calculated from K_{sp_1} and K_{sp_2} .

† Calculated from K_{sp_3} .

‡ Calculated from K_{sp_1} , K_{sp_2} , and K_{sp_3} .

* * *

APPENDIX C
THE CRACKING OF LOW CARBON STEEL
BY FERRIC CHLORIDE SOLUTIONS

A surprising phenomenon was encountered during the studies of the transformation behavior of slurries of commercially obtained iron oxides and hydroxides in mild steel capsules. Of 11 steel capsules heated with aqueous slurries of γ -FeOOH at 316°C, all 11 developed cracks in the metal and leaked within 6 hours. In some cases capsules heated with γ -FeOOH slurries burst open explosively. The capsules were made from partially flattened steel tubing sealed by welding at the ends. Figure C1 is a photograph of one capsule which burst in the welded area. The partially flattened edges of capsules are also susceptible to the cracking and Fig. C2 shows an example of a burst along the flattened edge of a capsule. This capsule also has deep cracks in the unseparated edge. About 10% of the capsules heated at 316°C with γ -FeOOH slurries burst open in the manner shown in these two figures. All others of some 90 capsules tested which contained greater than 0.3 weight percent γ -FeOOH developed cracks which penetrated the metal walls and permitted fluid to leak. Analogous capsules containing α -FeOOH, α -Fe₂O₃, γ -Fe₂O₃, or Fe₃O₄ did not develop leaks.



Fig. C1 - Capsule which burst in the welded area as a result of heating with an aqueous slurry of commercial γ -FeOOH. Magnification approximately 2.5X.



Fig. C2 - Capsule which burst in the deformed, partially flattened region as a result of heating with an aqueous slurry of commercial γ -FeOOH. Magnification approximately 2.5X.

The composition of the steel is shown in Table C1. Some of the changes undergone by a piece of steel tubing during capsule fabrication and treatment at 316°C are shown in Fig. C3. In this figure the uppermost diagram is that of longitudinal and transverse cross sections of a piece of 1/4-inch-diameter 20-mil-wall mild steel tubing. This tubing was hydrogen and vacuum annealed before use in making capsules. The middle diagram of Fig. C3 shows cross sections of a formed capsule prior to heating. In the preparation of capsules the tubing is partially flattened to allow for expansion at the elevated temperature. One end is then completely flattened and sealed by welding. The other end is left open for introduction of the slurry. The open end is next flattened completely and welded. The lower diagram is that of a capsule which has been heated to 316°C with an aqueous solution or slurry. Such a capsule has expanded as a result of hydrostatic pressure which is somewhat in excess of 1550 pounds per square inch at 316°C.

Table C1
Analysis of Steel

Constituent	Weight Percent
C	0.09
P	0.017
S	0.032
N	0.007
Mn	0.57
Si	0.07
Cr	0.10
Ni	0.07
Fe (by difference)	99.05

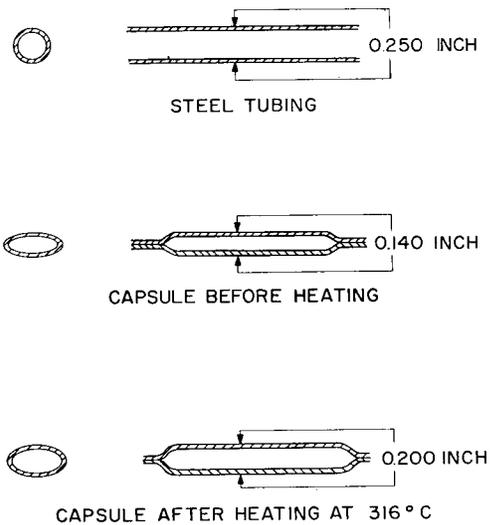


Fig. C3 - Diagram showing changes undergone by steel tubing during capsule fabrication and treatment at elevated temperature

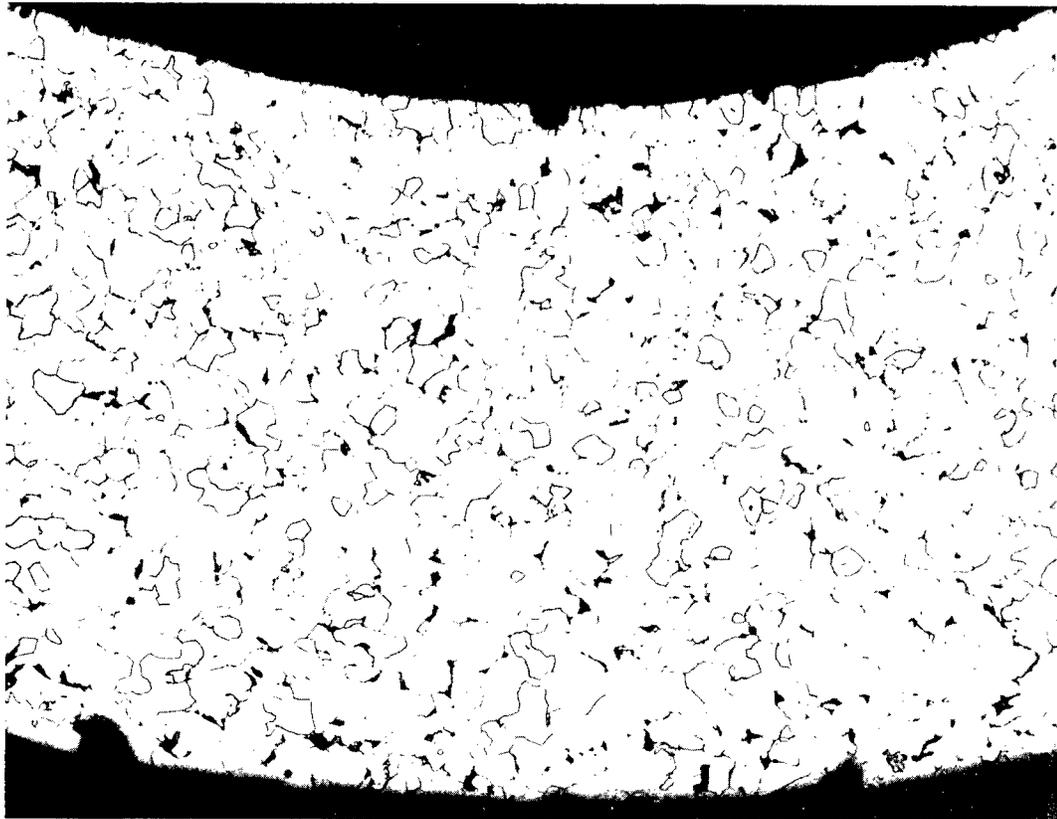


Fig. C4 - Cross section through the partially flattened edge of a capsule heated with high purity water for 4 weeks at 316 °C. Magnification 200X.

Photomicrographs were made from sections cut through the areas susceptible to cracking, that is, the plastically deformed areas at the welds and along the flattened edges. Figure C4 is a typical photomicrograph and shows a cross section through the partially flattened edge of a capsule which was heated with high purity water for 4 weeks at 316°C. Corrosion has not significantly penetrated the metal in this capsule. In a capsule heated with water for 2 years the maximum penetration was 2 mils. Figure C5 shows that the weld region of the capsule heated 4 weeks with water is unattacked. The weld metal has a martensitic structure.

Figure C6 is a photomicrograph of the partially flattened region of a capsule treated at 316°C for 4 weeks with α -FeOOH slurry. There is evidence that corrosion has started. Figure C7, a photograph of the same capsule, shows that the metal was only slightly attacked at the weld junction during 4 weeks' treatment with α -FeOOH at 316°C.

Figure C8 shows a cross section cut through the partially flattened edge of a capsule heated with γ -FeOOH slurry to the point at which fluid leaked from the capsule as a result of severe cracking. This penetration was produced in many capsules in as short a time as 2 hours.

Figure C9 shows a similar cross section of another capsule heated with γ -FeOOH which shows more clearly that the cracking is transgranular. The weld area of the same capsule appears in Fig. C10. Severe attack has occurred at this point. In those capsules which did not burst, leaks occurred in some cases through a penetration at the weld and in other cases through a penetration in a flattened edge.

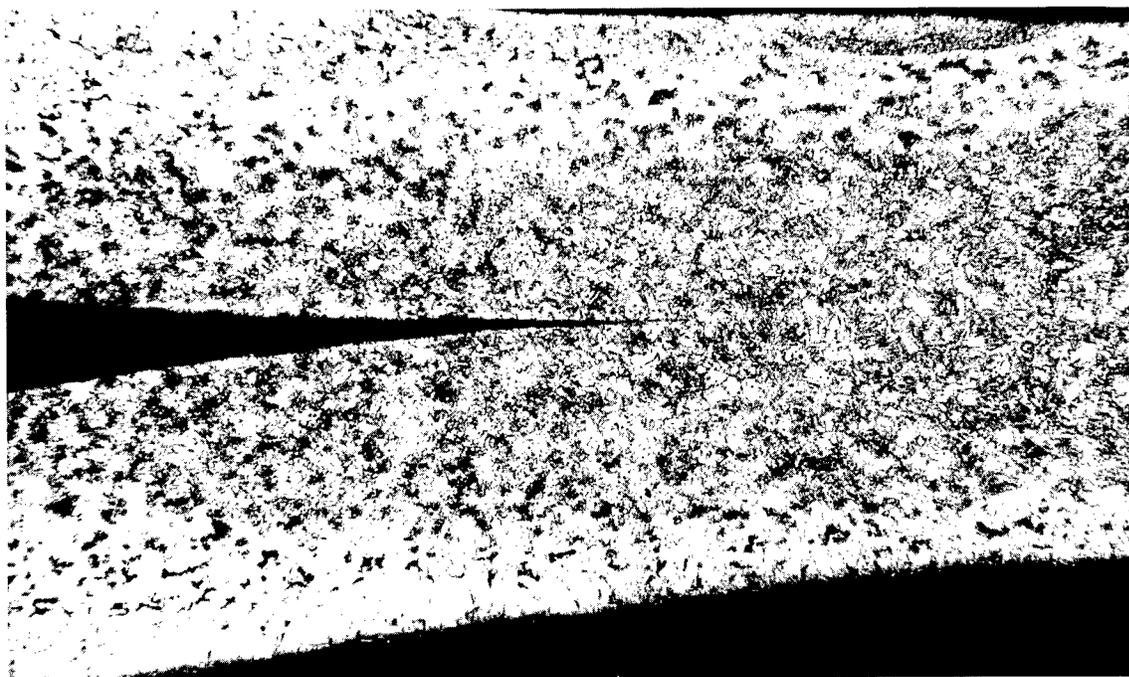


Fig. C5 - Cross section through the weld in a capsule heated with high purity water for 4 weeks at 316°C. Magnification 100X.

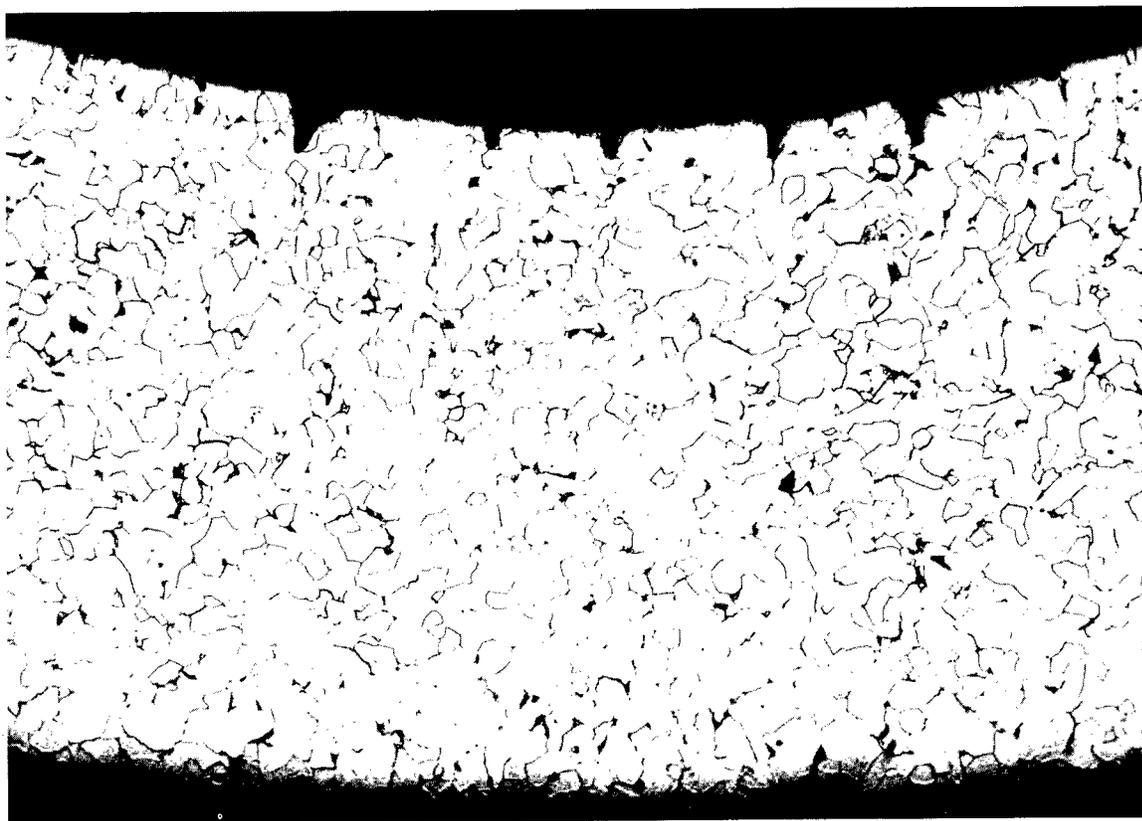


Fig. C6 - Cross section through the partially flattened edge of a capsule heated with an aqueous slurry of commercial α -FeOOH for 4 weeks at 316°C. Magnification 200X.

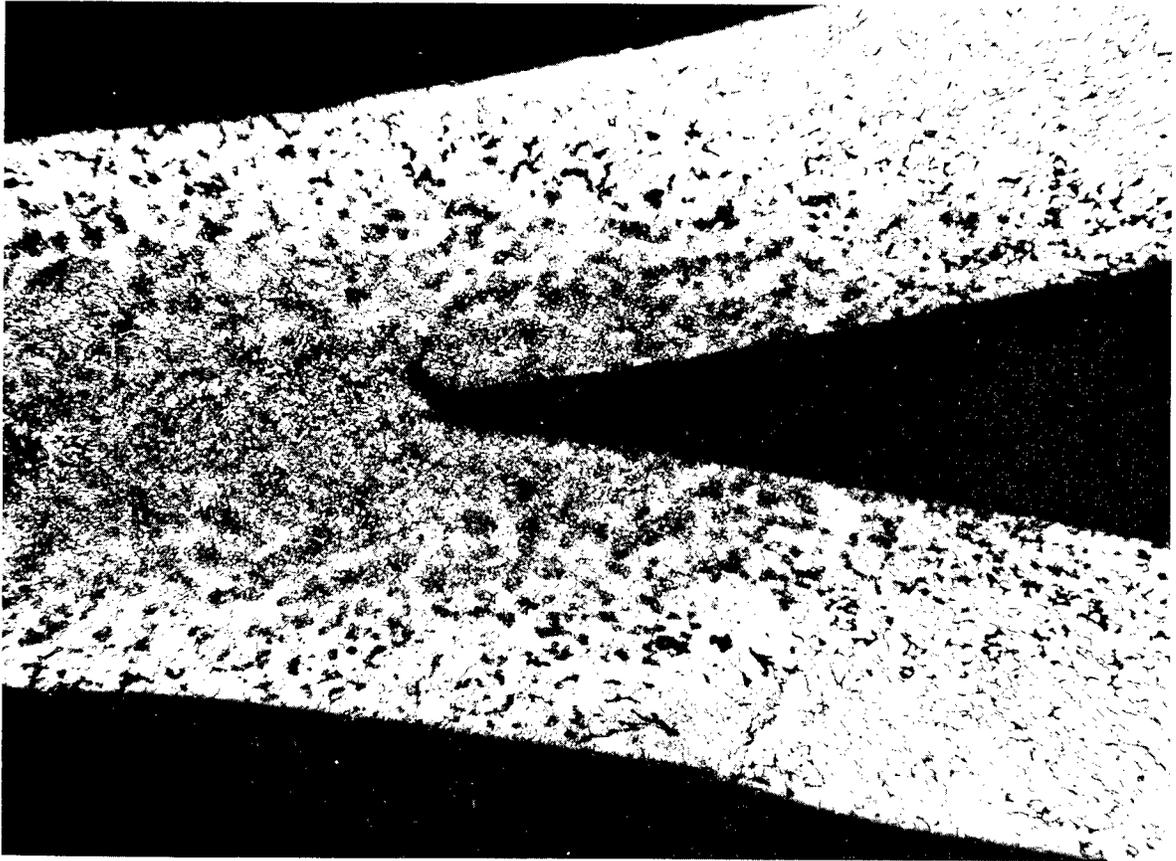


Fig. C7 - Cross section through the weld of a capsule heated with an aqueous slurry of commercial α -FeOOH for 4 weeks at 316 °C. Magnification 100X.

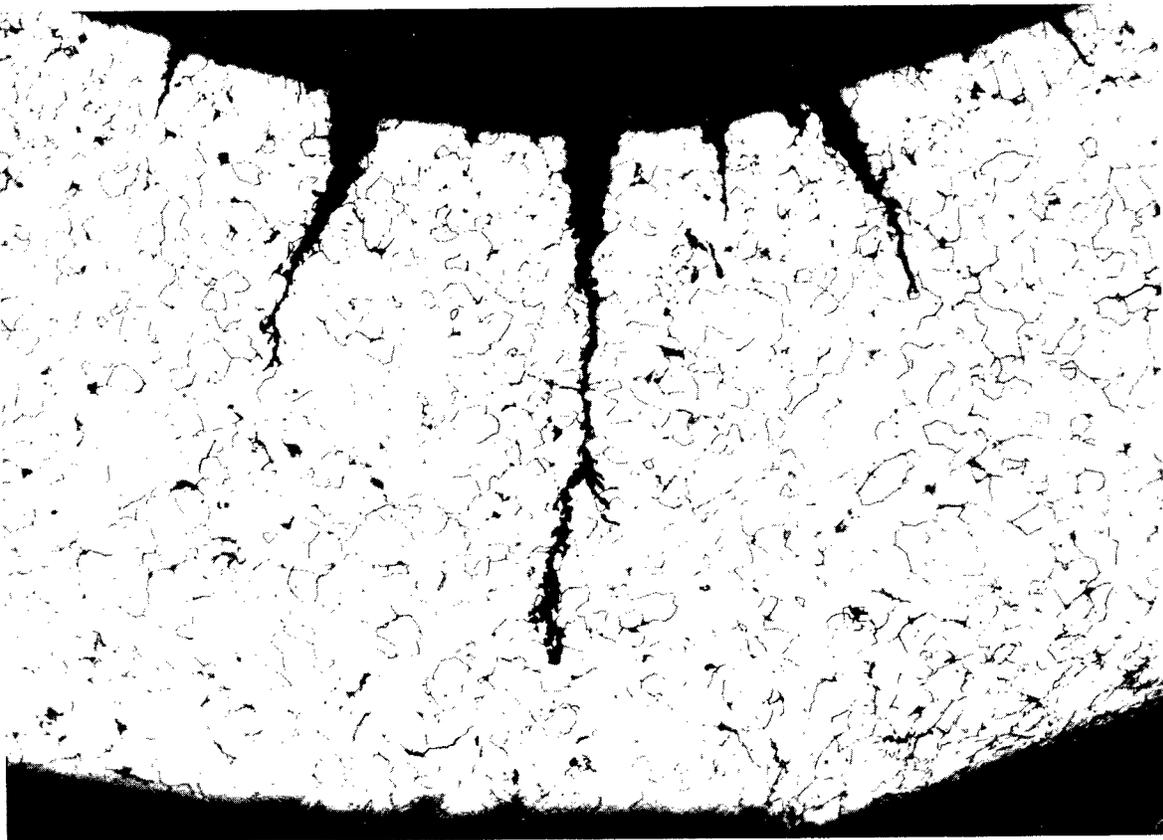


Fig. C8 - Cross section through the partially flattened edge of a capsule heated with an aqueous slurry of commercial γ -FeOOH to the point at which the capsule leaked. Magnification 200X.

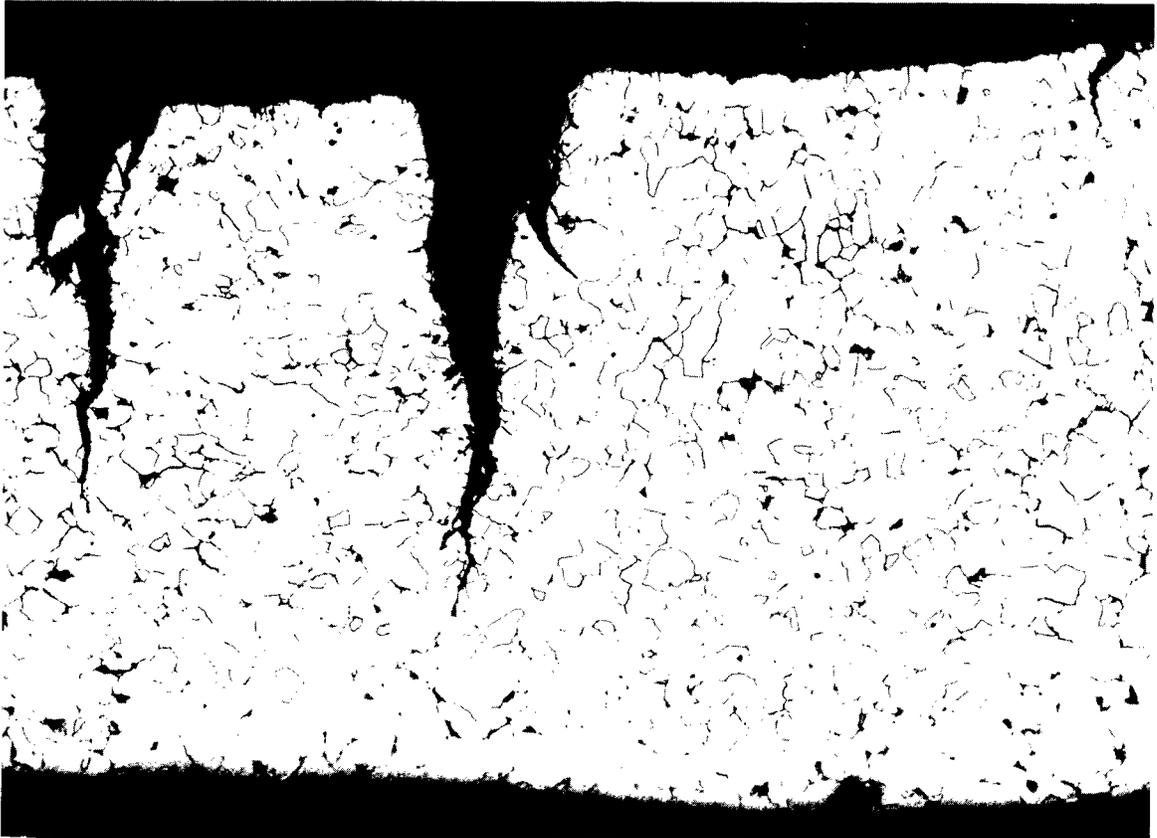


Fig. C9 - Cross section showing the transgranular nature of the cracking produced in mild steel during heating with slurries of commercial γ -FeOOH. Magnification 200X.

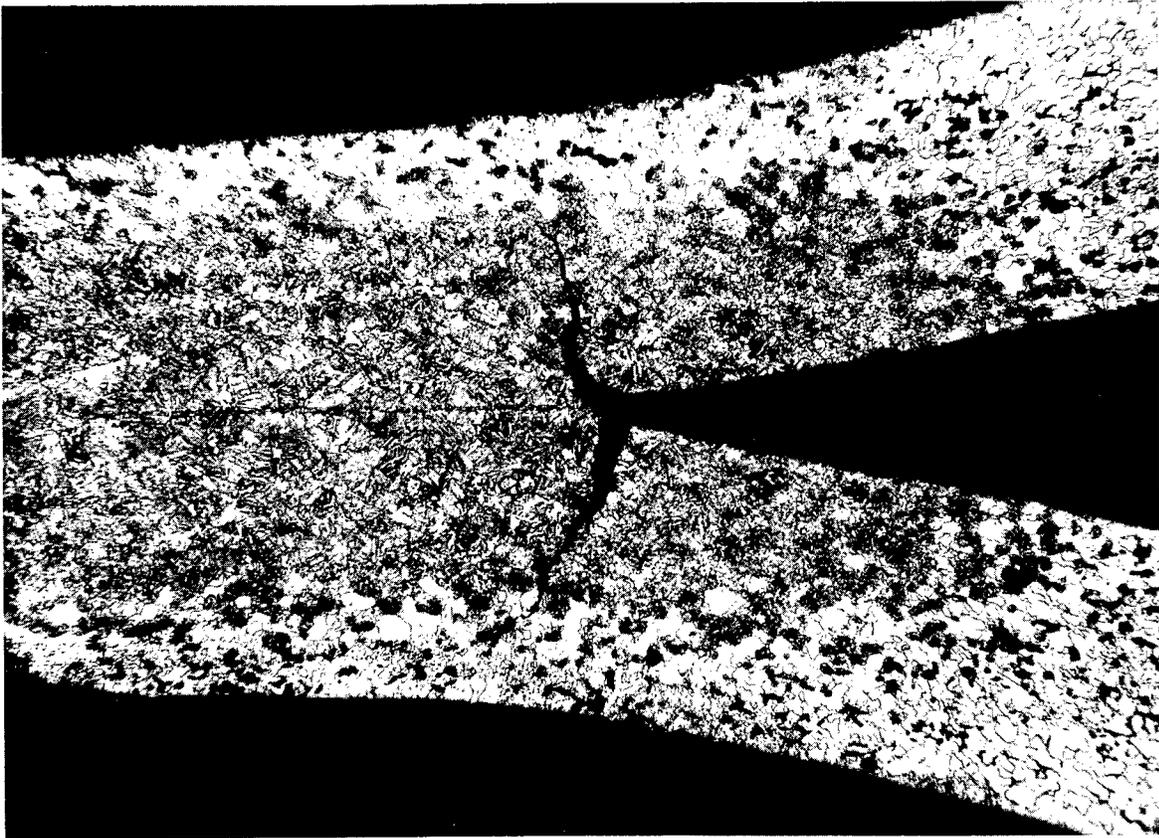


Fig. C10 - Cross section through the weld of a capsule heated with an aqueous slurry of commercial γ -FeOOH. Magnification 100X.

Capsules heated with γ -FeOOH slurries do not expand more than do capsules heated with water or other oxide slurries. Therefore, in considering mechanisms responsible for the cracking, the possibility seemed unlikely that the cracking could be produced by excessive internal pressure such as a pressure which might result from generation of some gaseous products that could not escape from the capsules. It was demonstrated by experiment that about 4000 psi of hydraulic pressure is required to burst capsules at the welds. That pressure does not produce cracks in the partially flattened edges. This indicated that the cracking process must be associated with corrosion and not with mechanical stress alone.

In order to determine if the attack produced by γ -FeOOH slurries at 316°C is associated with a stress-corrosion mechanism, pieces of capsule tubing were flattened in the manner ordinarily used in the preparation of capsules. The partially flattened edges were sliced off the tubing to form trough-like specimens each 1 inch long. When these specimens were heated at 316° in sealed capsules containing slurries of γ -FeOOH, the capsules cracked along the stressed, deformed edges, but no cracking or other accelerated attack was evident in the unstressed, deformed edges of the loose specimens inside the capsules, demonstrating that stress corrosion cracking is operative in this attack of mild steel by slurries of γ -FeOOH.

A study made to determine the effect of slurry composition on cracking time showed no relationship between the amount of solid in the slurry and the time of leaking except that slurries containing less than 0.3 weight percent γ -FeOOH did not produce leaking.

Corrosion-rate data were obtained by the hydrogen effusion technique.* In this method the amount of hydrogen effusing through the wall of a corroding steel capsule is continuously measured. In Fig. C11 appear typical rate curves for capsules heated with aqueous slurries of γ -FeOOH and α -FeOOH. Rate data for capsules heated with water are shown for comparison. It may be noted that in the case of the α -FeOOH slurries, very high initial rates are reduced to those comparable with water after about 2 hours. These data correlate well with microscopic examination which showed that capsules heated with α -FeOOH slurries undergo some attack (Fig. C6).

Figure C11 includes data from the first 30 minutes of the rate measurement. In these early minutes when the capsules are coming to temperature and the metal is outgassing, the data are not very reproducible as indicated by the two curves for water. However this figure does show that the amount of hydrogen effusing from the capsules containing γ -FeOOH and α -FeOOH is very high compared to the amount effusing from water capsules. It is a coincidence that the maxima for the capsules chosen as examples containing γ -FeOOH and α -FeOOH nearly coincide. Of the capsules studied these early maxima varied between 20,000 and 50,000 mg/dm²-mo. It was originally thought that these high hydrogen effusion rates might of themselves play the major role in the cracking phenomenon, but more recent experiments have indicated that in some caustic solutions the generation of much larger quantities of hydrogen does not produce so drastic a cracking phenomenon.

Examination of the composition of the γ - and α -FeOOH samples which were obtained from a commercial source indicated little difference (Table C2) except for the small amounts of Cl⁻ and SO₄⁼. The fact that slurries of γ -FeOOH produced cracking, while α -FeOOH slurries did not, seemed surprising. To investigate the possibility that the Cl⁻ and SO₄⁼ in the hydroxides might play a role in the cracking mechanism, due to the generation of acid the pH of γ - and α -FeOOH slurries was measured after standing at room temperature in steel capsules for 1 hour. This pH was 6.3 and was the same for slurries removed from capsules after 24 hours. The pH of slurries after being heated 2 hours at 316°C (a time shortly before many γ -FeOOH slurries cause cracking) was 6.5. After

* M. C. Bloom and M. Krulfeld, J. Electrochem. Soc. 104:264-269 (1957).

Fig. C11 - Typical corrosion-rate curves obtained by the hydrogen effusion technique during heating of slurries of γ -FeOOH and α -FeOOH in steel capsules

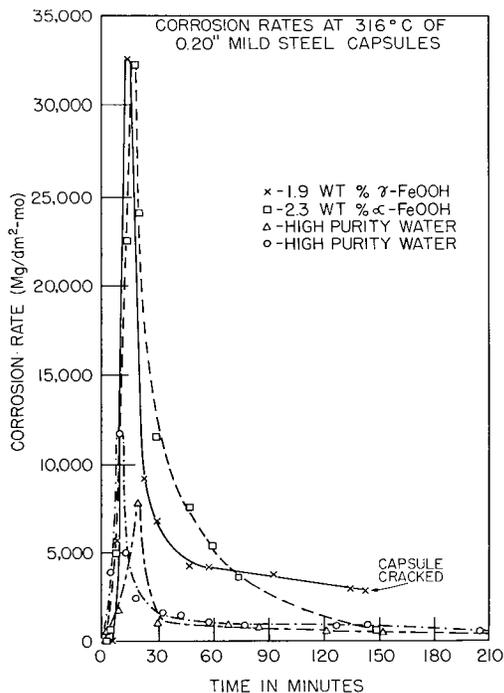


Table C2
Chemical Analyses of Oxides and Hydrated Oxides

Material	Ferric Iron as Fe ₂ O ₃	Ferrous Iron as Fe ₃ O ₄	Water	Al as Al ₂ O ₃	Mn as MnO	Si as SiO ₂	Ca as CaO	Sn as SnO ₂	Mg as MgO	Total Cations as Oxides	Cl ⁻	SO ₄ ⁼
γ -FeOOH	85.24	0.14	13.09	1.07	0.09	0.08	--	--	--	99.71	0.60	0.15
α -FeOOH	86.23	0.05	12.56	1.38	0.06	0.03	--	--	--	100.31	--	0.05
γ -Fe ₂ O ₃	90.90	6.52	0.65	1.63	0.03	0.53	--	0.07	--	100.33	< 0.01	not determined
α -Fe ₂ O ₃	97.51	0.20	0.50	1.86	0.05	0.06	--	--	--	100.18	0.02	determined
Fe ₃ O ₄	21.76	77.22	--	--	--	0.22	1.00	--	0.02	100.22	< 0.01	

heating 4 weeks at 316°, the pH of slurries removed from capsules containing α -FeOOH or containing such low concentrations of γ -FeOOH that leakage did not occur was 6.8 - 7.0. These pH values did not seem unusual or capable of explaining the high corrosion rates. In an attempt to eliminate the possible effects of such impurities, some γ -FeOOH was generated by corroding steel and also a high purity iron in 1% and 2% hydrogen peroxide solutions at room temperature. X-ray diffraction patterns obtained from these corrosion products showed that all were mixtures of γ -FeOOH with α -FeOOH and/or spinel oxide. Slurries made from the samples containing the greatest amount of γ -FeOOH produced cracks and caused leaks in capsules heated at 316°C. One of the samples which effected cracking contained very little, if any, α -FeOOH as the latter did not appear in the diffraction pattern. These experiments seemed to show that the corrosion cracking of mild steel under these conditions is characteristic of γ -FeOOH, but that some minimum concentration of γ -FeOOH must be present in order to produce the phenomenon.

The accelerated corrosion rates in capsules filled with slurries of γ -FeOOH and α -FeOOH suggested that the attack might be due to the presence of ferric ion alone. Therefore mild steel capsules were filled with 0.001 M solutions of FeCl₃, or the equivalent concentration of Fe(NO₃)₃ and Fe₂(SO₄)₃ to keep the ferric ion concentration constant. The results of this study are shown in the upper part of Table C3. Only the capsules containing

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Table C3
The Effect of Various Solutions and Slurries Containing
Ferric Ion and/or Chloride on Cracking at 316°C

Capsule Contents	Result of Treatment (3 or more capsules treated)
(1) 0.001 M FeCl ₃	Capsules cracked and leaked within 6 to 15 hours.
(2) 0.0001 M FeCl ₃	Very shallow cracks were produced within one week.
(3) 0.0005 M Fe ₂ (SO ₄) ₃	No cracking observed within one week.
(4) 0.001 M Fe(NO ₃) ₃	No cracking observed within one week.
(5) 0.003 M NaCl	No cracking observed within one week.
(6) 0.01 M NaCl	No cracking observed within one week.
(7) 0.1 M NaCl	Slight attack at weld junction during one week.
(8) 1 M NaCl	Localized corrosion in martensite penetrated welds within 20 hours.
(9) Aqueous slurry of γ -FeOOH containing 0.6% Cl ⁻	Capsules cracked and leaked within 6 hours.
(10) Aqueous slurry of γ -FeOOH generated by corrosion at room temperature in H ₂ O ₂ containing 0.0005% Cl ⁻	Capsules cracked and leaked within 12 hours.
(11) Aqueous slurry of γ -FeOOH generated by corrosion at room temperature in high purity water	No cracking observed within one week.
(12) Slurry of γ -FeOOH in line 11 and 0.0001 M FeCl ₃	Capsules cracked and leaked within 16 to 18 hours.
(13) Aqueous slurry of α -FeOOH containing 0.01% Cl	Shallow cracks were produced within one week.
(14) Supernatant liquid from γ -FeOOH slurry in line 9	No cracking observed within one week.
(15) Slurry of α -FeOOH in line 13 and liquid in line 14	Capsules cracked and leaked within 3 to 4 hours.
(16) Slurry of α -FeOOH containing 0.01% Cl ⁻ and 0.003 M NaCl	Moderately deep cracks were produced within one week.
(17) Slurry of γ -Fe ₂ O ₃ containing 0.01% Cl ⁻ and 0.003 M NaCl	Moderately deep cracks were produced within one week.
(18) Slurry of α -Fe ₂ O ₃ containing 0.02% Cl ⁻ and 0.003 M NaCl	Very deep cracks were produced within one week. One capsule cracked and leaked within 4 days.
(19) Slurry of Fe ₃ O ₄ containing < 0.01% Cl ⁻ and 0.003 M NaCl	No cracking observed within one week.

FeCl₃ solution cracked indicating that ferric ion alone was not responsible for the accelerated corrosion. This directed attention to the combined effect of ferric and chloride ions. Capsules heated with 0.0001 M FeCl₃ solution were attacked very slightly, but did not leak, while capsules heated with 0.001 M FeCl₃ cracked and leaked within 6 to 15 hours. Capsules heated with 0.003 M NaCl did not crack, and this further emphasized the deleterious effect of the combination of ferric ions with chloride ions at this low concentration. As shown in Table C3, increasing the chloride concentration to 0.1 M and 1 M produced only localized attack in the martensitic area at the welds.

Examination of the chloride content of the commercial γ - and α -FeOOH samples (0.6% and 0.01% respectively) and calculation of the FeCl₃ content generated by the slurries indicated that the difference in chloride analysis might explain the observed phenomena. Analysis of the hydrogen peroxide used in the genesis of γ -FeOOH by corrosion of mild steel indicated a chloride ion content in the peroxide of 0.0005%. If all the chloride in the

peroxide were incorporated into the corrosion products generated, sufficient chloride to cause cracking could have been introduced into capsules filled with slurries of these corrosion products.

As indicated in Table C3, chloride-free corrosion products consisting primarily of γ -FeOOH, obtained by corroding steel at room temperature in high purity water, did not produce cracking when heated with water in capsules at 316°C; however, a slurry of this material with 0.0001 M FeCl₃ solution did produce cracks which penetrated the metal within 16 to 18 hours. Cracking was also produced by a slurry made from the commercial sample of α -FeOOH and the supernatant liquid filtered from a 4% slurry of commercial γ -FeOOH. This supernatant liquid was 0.001 M with respect to chloride ion and did not produce cracking in the absence of α - or γ -FeOOH.

The transformation studies showed that aqueous slurries of α -FeOOH and γ -FeOOH transform to α -Fe₂O₃ and Fe₃O₄ during heating in steel capsules at 316°C. The compound γ -Fe₂O₃, which may be an intermediate in the transformation of γ -FeOOH, also transforms to Fe₃O₄ and α -Fe₂O₃. Accordingly some experiments were undertaken to determine if slurries of γ -Fe₂O₃, α -Fe₂O₃, and Fe₃O₄ could also produce cracking in mild steel capsules during heating with chloride solutions. Table C2 shows that the chloride content of the commercial supply of these materials is in the same order of magnitude as that of the α -FeOOH supply; for this reason analogous cracking tests were made on capsules containing slurries of α -FeOOH in chloride solution. The exact slurry compositions were not determined in this set of exploratory experiments, but were purposely made to be very concentrated with solids in order to determine whether or not the cracking could be produced under any circumstances. The slurries contained at least 2 or 3 times as much iron as did most of the γ -FeOOH slurries discussed earlier; i.e., 5 to 10 weight percent of iron. Capsules heated at 316°C with aqueous slurries of these materials for 4 weeks did not leak, although superficial cracking like that shown in Figs. C6 and C7 was produced by the chloride-bearing α -FeOOH, γ -Fe₂O₃, and α -Fe₂O₃ slurries. No cracking was observed in capsules heated with the Fe₃O₄ which contained less chloride than the other compounds. Lines 16 to 19 of Table C3 show that slurries of α -FeOOH, γ -Fe₂O₃, and α -Fe₂O₃ with 0.003 M NaCl produce more serious cracking than without the additional chloride. The fact that no cracking was observed in capsules heated with Fe₃O₄ in 0.003 M NaCl suggests that Fe₃O₄ remains unattacked under these circumstances.

This investigation has shown that mild steel can undergo stress-corrosion cracking at 316°C in FeCl₃ solutions. Chloride-bearing slurries of the ferric oxides and hydrated oxides γ -FeOOH, α -FeOOH, γ -Fe₂O₃, and α -Fe₂O₃ or slurries of these compounds in contact with chloride-bearing solutions at this temperature can also produce this cracking.

These observations may be of practical significance in connection with boiler operations where substantial amounts of chloride may be present. During lay-up periods when boilers are open to the atmosphere, corrosion is likely to occur at room temperature with generation of γ -FeOOH. With chloride present, this could give rise to corrosive attack, especially in stressed areas, if sufficient amounts of such material should be generated and not removed prior to the resumption of operation at elevated temperature. Any circumstances which result in the generation of ferric oxides in a boiler containing chloride ion could also result in analogous attack.

ACKNOWLEDGMENTS

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