THE CORROSION PRODUCTS OF IRON AND THEIR RELATION TO CORROSION IN STEAM-GENERATING EQUIPMENT

CONTENTS

ABSTRACT

The possibility of avoiding serious pitting in the generating tubes of naval boilers depends on the genesis and preservation of proper corrosion product films. The spinel films (Fe_3O_4) normally produced as a result of exposure to slightly alkaline sodium hydroxide solutions are protective but porous to the solution. Reaction at the metal surface beneath these films may give rise to drastic concentration effects under some operating conditions. When films formed become too thick as a result of such concentration effects, they may fracture, allowing free access of the solution to the metallic surface at a local spot beneath the fractured film with resultant danger of deep pitting. There is evidence that the use of lithium hydroxide instead of sodium hydroxide avoids this concentration effect.

PROBLEM STATUS

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

AUTHORIZATION

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THE CORROSION PRODUCTS OF IRON AND THEIR RELATION TO CORROSION IN STEAM-GENERATING EQUIPMENT

INTRODUCTION

This report summarizes the results of a series of investigations of the reactions of mild steel with boiler water conducted as a basis for determining the possibilities of avoiding a serious pitting problem in the generating tubes of naval boilers.

The problem is basically that the metals which we use in practical operations are unstable in the environment in which we wish to use them. Nature gives us iron ore in the form of hematite (α-Fe_2O_3), which we reduce to metal. This metal on exposure to air and water is unstable and tends to go back to the oxide from which it came. If we expose it to high-temperature water, the reaction to produce oxide is rapid. We are able to use ferrous metals in boilers only because, if we fix conditions properly, the oxide formed by reaction with water forms an adherent protective film, which tends to isolate the metal from contact with the boiler water, and thus reduces the reaction rate to such low values that almost indefinite operation is feasible. Our problem is to establish the conditions under which such a protective film may be generated and maintained during the practical operation of boilers. This is what we have been studying, and the highlights of what we have learned are the following:

The reaction of iron with water and oxygen can give rise to one or more of the oxides or hydroxides shown in Table 1 (1).

The first three of these, $Fe(OH)_2$, FeO, and Fe_3O_4, may be generated by the reaction with water in the absence of oxygen. The first one, $Fe(OH)_2$, can be obtained by the reaction of water with steel at temperatures below about 50°C. The reaction is

$$Fe + 2H_2O \longrightarrow Fe(OH)_2 + H_2 \ . \qquad (1)$$

$Fe(OH)_2$ has a substantial solubility, which causes a rise in pH to 9.3, but it does not form the protective film we desire. As the temperature is elevated, however, $Fe(OH)_2$ is converted to Fe_3O_4 by the reaction

$$3Fe(OH)_2 \longrightarrow Fe_3O_4 + H_2 + 2H_2O \ , \qquad (2)$$

and above about 50 C only Fe_3O_4 is found as the corrosion product (2). This product is in fact the product generated in oxygen-free water from this temperature up to 570°C (1058 F), and its deposition and maintenance as a protective film by the reaction

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2 \qquad (3)$$

is what has made possible the use of steel in boiler operations.

At 600 F (316 C), the approximate temperature of operation of many naval boilers, the film formed in pure water is quite protective in static systems, but the crystallites which form the Fe_3O_4 deposit are of colloidal dimensions (ca. 1000 Å) and tend to be carried away in colloidal suspension in flowing systems. For this reason, as well as

Table 1
Corrosion Products of Iron

Composition (Mineral Name)	Color	Structural Type	Magnetic Character	Electrical Resistivity	Density g/cm^3	Thermal Behavior
$Fe(OH)_2$	White	$Mg(OH)_2$ (Brucite)	Paramagnetic	Insulator*	3.40	Decomposes at about 100°C to Fe_3O_4 and H_2 †
$Fe_{.950}O$ to $Fe_{.833}O$ (Wustite)	Black	NaCl	Paramagnetic	Semiconductor	5.4-5.73	Melts at 1371°-1424°C; below 570°C decomposes to Fe and Fe_3O_4
Fe_3O_4 (Magnetite)	Black	Spinel	Ferromagnetic	Electronic conductor	5.20	Melts at 1597°C
α-FeOOH (Goethite)	Yellow	α-FeOOH (Goethite)	Paramagnetic	Insulator	4.20	Dehydrates‡ to α-Fe_2O_3 at about 200°C
β-FeOOH	Light brown	Not completely determined	—	—	—	Dehydrates‡ to α-Fe_2O_3 about 230°C
γ-FeOOH (Lepidocrocite)	Orange	γ-FeOOH (Lepidocrocite)	Paramagnetic	Insulator*	3.97	Dehydrates‡ to γ-Fe_2O_3 at about 200°C
γ-Fe_2O_3 (Maghemite)	Brown	Spinel	Ferromagnetic	Semiconductor to insulator	4.88	Transforms‡ to α-Fe_2O_3 above 250°C
α-Fe_2O_3 (Hematite)	Brick red to black	Al_2O_3 (Corundum)	Paramagnetic	Insulator	5.25	Decomposes to magnetite at 1457°C and 1 atm

*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 Fe_3O_4 depending on the conditions of the system.

‡Presence of water causes conversion to α-Fe_2O_3 at lower temperature.

others, mostly associated with the difficulties of obtaining absolutely pure water, it is necessary to alkalize the water fed to boilers. Thus, current Navy boiler water treatment calls for a pH of 10.4 to 11, which is generated by the addition of sodium hydroxide. We have explored quite thoroughly the action of sodium hydroxide on steel at 316°C, and a discussion of our major findings is given below.

DISCUSSION

Figure 1 shows the rate of attack of mild steel in contact with solutions of varying sodium hydroxide concentration at 316 C. It may be noted that at the end of 2 months, the corrosion rate in pure water at 316°C has been reduced to less than 10 mg/dm^2-mo, which is the equivalent of about 6 millionths of an inch per year, and that even at a pH of 11.5, the rate has been reduced to the order of about 20 mg/dm^2-mo or about 12 millionths of an inch per year. If, however, the sodium hydroxide concentration reaches 40%, the rate goes down with the buildup of a protective film for a day or two; thereafter, the rate increases rather rapidly. It may be noted that the 15% sodium hydroxide constitutes an intermediate case. If we remove a sample corroding in 40% sodium hydroxide at 316°C after passing the minimum in the corrosion rate, we find that pits have started to develop in the tubing which, starting at some sensitive spot, rapidly drill a hole in the tubing (see Figs. 2 and 3).

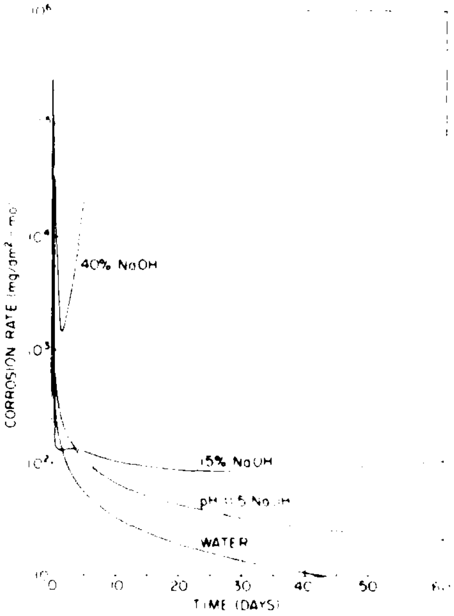

Fig. 1 - Corrosion rate as a function of time for the reaction of mild steel with water and sodium hydroxide solutions at 316 C

Thus, Fig. 3 shows perforation of a 0.030-in. wall in 52 hours. It is interesting to compare the nature of the attack revealed in Fig. 3 with that shown in Fig. 4, which is a photomicrograph published by Potter (3) of the British Central Electricity Generating Board as typical of the pitting observed in British boilers.

Figure 5 is an expanded version of the rate data for 15% sodium hydroxide, previously shown in Fig. 1. The drop of rate to a minimum may be noticed here as in the 40% sodium hydroxide case and then the rise, but now the action is more gradual and one can study the pit development more adequately. Figure 6 shows the pit formation shortly after passing the minimum. Samples taken at subsequent times show the development of more and more pits until at the end of a year of operation, pits overlaid with fractured scabs cover the entire surface of the tube as shown in Fig. 7. If we take a section through one of these scabs and examine it at high magnification, we observe what is seen in Fig. 8.

This scab and pit formation may be compared with Figs. 9 and 10, which show typical scab and pit formation from a naval boiler.

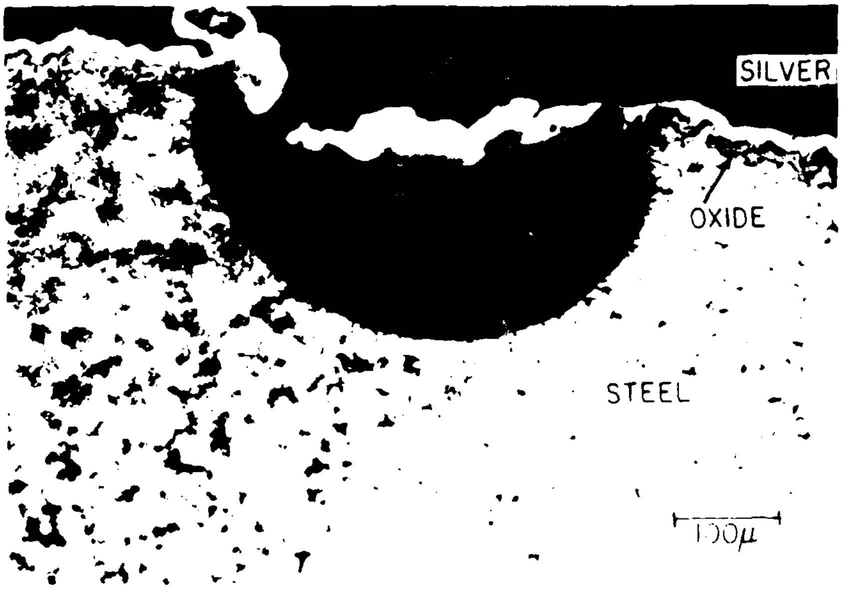

Fig. 2 - Section near the end of the capsule that contained 40% sodium hydroxide solution and was treated at 316 C for 46 hours. The specimen was silver plated before mounting to preserve the oxide during the polishing operation. A 1% nital etch was used.

Fig. 3 - Section through opposite walls near the end of the capsule that leaked after 51.6 hours at 316 C. The specimen was not silver plated before mounting, and a 1% nital etch was used. The original magnification was 50X.

Fig. 4 - Section through the pit showing metal-magnetic iron oxide interface. The original magnification was 10X. (Figure 2 of Ref. 3.)

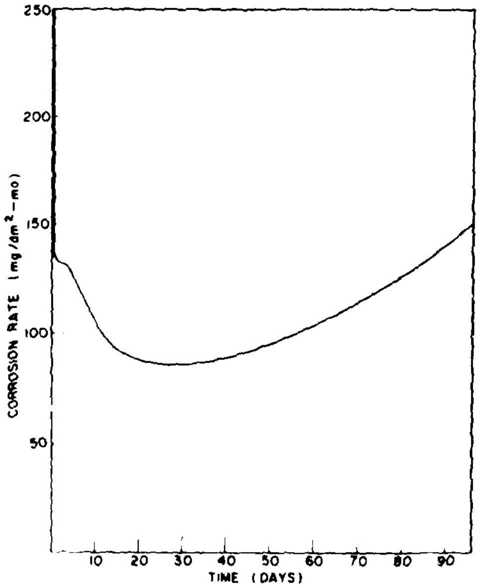

Fig. 5 - Corrosion rate as a function of time for the reaction of mild steel with 15% sodium hydroxide at 316°C

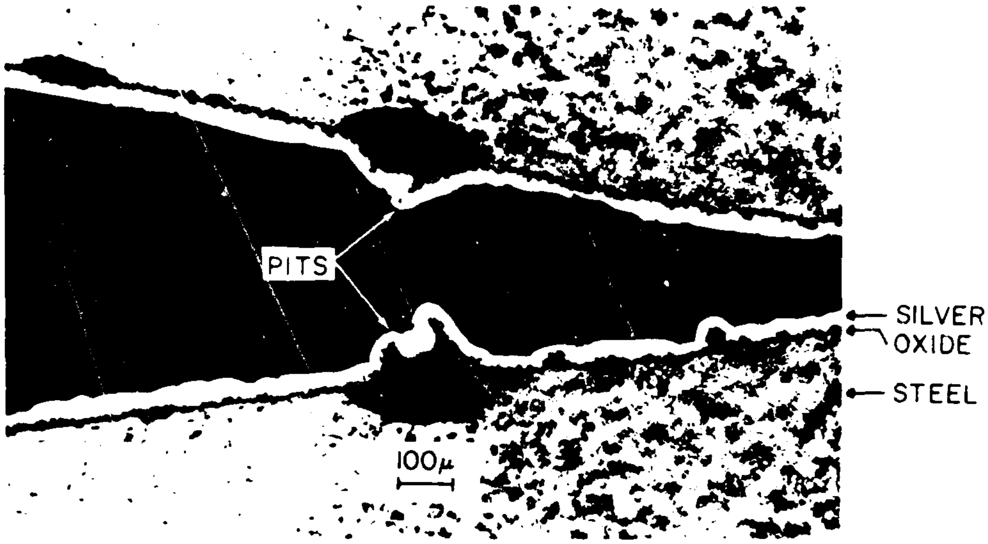

Fig. 6 - Section perpendicular to the inside surface of the steel capsule containing 15% sodium hydroxide solution after 68 days at 316°C. The original magnification was 100X. The specimen was silver plated before mounting to preserve oxide during polishing operation, and a 1% nital etch was used.

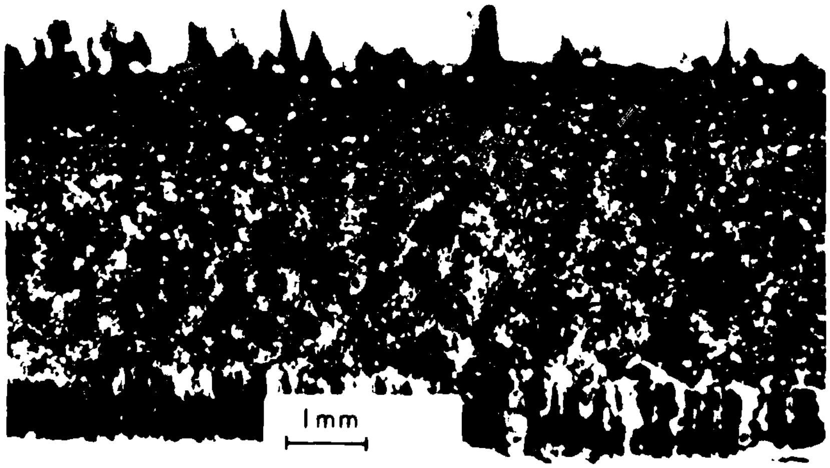

Fig. 7 - Section parallel to the axis of the steel capsule containing 15% sodium hydroxide after 1 year at 316°C. The original magnification was 16X.

Fig. 8 - Section perpendicular to the inside surface of the steel capsule containing 1% sodium hydroxide solution after 1 year at 316°C. The original magnification was 200X and a 1% nital etch was used.

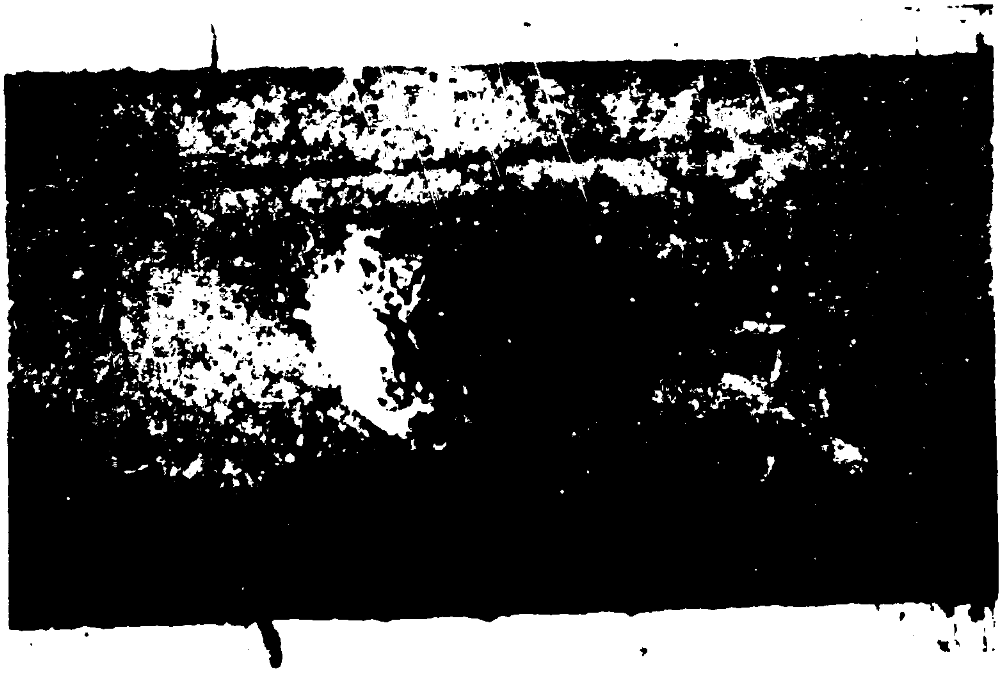

Fig. 9 - Scab found in the failed tube from a naval boiler

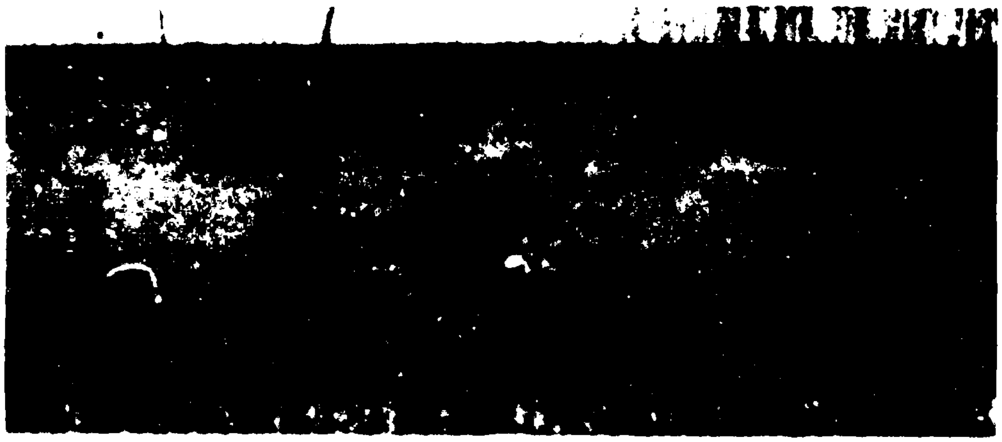

Fig. 10 - Pit found beneath the scab in failed tube from a naval boiler

CONCLUSIONS

When steel reacts with boiler water at elevated temperature in the absence of oxygen, a protective film of Fe_3O_4 is generated which increases in thickness with time and thus tends to prevent contact of the boiler water with the metal of the boiler tubing. This protective film is, however, porous on a microscopic scale, and some boiler water seeps through to continue the reaction. The amount of reaction decreases with time as the film thickens and makes access of the boiler water to the metal more and more difficult. If the pH of the water could be maintained at 11.5 or below, the life of boiler tubing would be almost indefinite. There is, however, one major difficulty. That is, when boiler water seeps through the microporous protective oxide to the metallic surface of the boiler tube, the reaction which takes place,

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 , \qquad (3)$$

uses up water and thus concentrates the boiler water in the region near the metal surface. This concentration of boiler water increases the sodium hydroxide concentration, which, as we have seen, increases the corrosion rate, which uses up more water, and we have the elements of a runaway reaction. However, additional dilute boiler water seeping through the protective film tends to bring the alkalinity back down again, and some steady state is reached. If for any reason the temperature at the tube surface is elevated or fresh boiler water is prevented from achieving dilution at the base of the protective film, a caustic concentration and film thickening will take place. If the film thickening becomes great enough, the protective film may crack, allowing access of the boiler water to the steel at the base of the crack. This is the dangerous situation, for since the protective film of magnetite is a very good electrical conductor, the iron dissolves at the base of the crack and the released electrons can be neutralized all over the surface of the protective film, allowing large currents to flow and drill a hole at the base of the crack. Thus, the boiler tubing is in danger whenever the normal operations are disrupted. If accumulations of deposit from the preboiler cycle cause a rise in temperature at a localized spot, this tends to thicken the protective film. If this thickening is too great, fracture of the film and the development of dangerous pitting may occur.

In examining other sources of alkali, we were particularly attracted to lithium hydroxide, because the lithium ion has a size close to that of the ferric ion, and it was thought that it might enter the protective film and substitute for the ferrous ion in the manner indicated:

$$2Fe_3O_4 + Li \longrightarrow LiFe_5O_8 + Fe \; . \tag{4}$$

Our exploration of this possibility has been very fruitful. We have been unable to pit steel tubing with any concentration of lithium hydroxide up to saturation, and we have found that in the presence of lithium hydroxide, formation of $LiFe_5O_8$ is readily obtained by the reaction

$$5Fe_3O_4 + 3LiOH + H_2O \longrightarrow 3LiFe_5O_8 + 5/2H_2 \, . \tag{5}$$

Careful examination of this reaction reveals that such a reaction taking place beneath a protective oxide film does not produce the alkaline concentration associated with the reaction of sodium hydroxide because now 3 lithium hydroxide molecules are used up for each water molecule, and the solution in the immediate vicinity of the reaction decreases in alkalinity. It has been found that reaction 5 takes place when the lithium hydroxide concentration reaches about 0.5% and that the film formed by this reaction is a very protective one. Thus, nature has furnished us an automatic control of alkaline strength. All our explorations to date have confirmed the protective action of lithium hydroxide. This includes tests on an experimental boiler in the Naval Ship Research and Development Center at Annapolis.

Another difficulty with maintaining protective films comes about during shutdown periods when the boiler water is exposed to air. Under these circumstances, the protective magnetite film tends to break down at weak spots with the generation of one of the FeOOH molecules shown in Table 1. These form nonadherent powders.

$$2Fe_3O_4 + 1/2O_2 + 3H_2O \longrightarrow 6FeOOH \; . \tag{6}$$

If these powders are not removed prior to operation, they may be carried along in the flowing stream, deposited in areas of slow flow, etc., and thus act as sources of pit formation. Moreover, they may adsorb chloride, which, if not properly neutralized by alkali, can even give rise to stress corrosion cracking (4). In connection with film breakdown on exposure to air, $LiFe_5O_8$ as a protective film has the advantage that all iron is already in the +3 valence state and is therefore not subject to oxidation. The detrimental effect of loose powder carryover has recently been dramatically demonstrated in "A Research Study on Internal Corrosion of High Pressure Boilers" conducted under the sponsorship of the Research Committee for Boiler Feedwater Studies of the American Society of Mechanical Engineers and presented by C. L. Burton at the 1968 Joint Power Generation Conference of ASME-IEEE, San Francisco, September 20, 1968.

Further details of the research conducted at NRL may be found in Refs. 5 through 17.

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13 ABSTRACT

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