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Steel Corrosion Mechanisms

The Growth and Breakdown of Protective Films in High-Temperature Aqueous Systems

Studies with 15% NaOH at 316°C

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ABSTRACT

This report summarizes what is known regarding the reaction of steel with high-temperature water as affected by sodium hydroxide additions and also presents results of a detailed study, using the hydrogen effusion method, of the reaction of steel with 15-percent sodium hydroxide solution at 316°C. The corrosion rates are correlated with a microscopic study of the growth and breakdown of the protective magnetite (Fe_3O_4) film. There are two different corrosion-rate-governing mechanisms involved prior to the onset of pitting: a large decrease of the initial corrosion controlled by the build up of a protective film on the metal surface, and a subsequent smaller decrease in corrosion rate possibly controlled by penetration of the magnetite film by the corrosive solution. The pitting is apparently due to the genesis of cracks in the magnetite film after it reaches a critical thickness.

PROBLEM STATUS

This is an interim report on one phase of the problem; work on other phases is continuing.

AUTHORIZATION

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INTRODUCTION

The effect of alkali upon the corrosion rate of steel in high-temperature water, originally studied by Berl and Van Taack (1) in 1930, has recently been the subject of a number of investigations (2-8). Berl and Van Taack heated small samples of steel powder in a static autoclave for 7.5 hours at 310°C and obtained data indicating a minimum in the total corrosion at an alkali concentration of 0.7 gram per liter, which corresponds to a pH of 12.24. Some measurements made at 316°C by the present authors, using a more precise static technique (the hydrogen effusion method (9)), showed a drop in total corrosion in the region of pH = 12.24, and more recent measurements (Table 1) confirm the actual minimum in total corrosion at this pH, as reported by Berl and Van Taack. Both of these recent studies, however, show that the phenomenon is transitory, and after 25 days the corrosion rate increases monotonically with pH (10). It is of interest to note that in dynamic systems an improvement in corrosion resistance seems to be obtained by alkalization to a pH of 9 to 12 (4,11). This is probably due to the fact that the crystallite size of the magnetite film developed in neutral solutions is in the colloidal range (< about 1000A)* and is subject to erosion in flowing streams. Increasing the alkalinity produces an increase in crystallite size (Figs. 1 and 2) and avoids erosion of the protective film in flowing streams (11).

More recently, attention has been given to more concentrated solutions. Potter and Mann (5) reported results on the corrosion of mild-steel block specimens exposed in mild-steel autoclaves containing 5 to 20 percent by weight of sodium hydroxide at 250 to 355°C, and Fraser and Bloom (6) published a hydrogen effusion study of the reaction of 40-percent sodium hydroxide solution with mild steel at 316°C. Most recently, in two papers (7,8) presented at the 2nd International Conference on Metallic Corrosion, March 11-15, 1963, Potter and Mann extended their studies with block specimens to 500°C, and Field, Stanley, Adams, and Holmes, using similar specimens, studied the reactions of mild steel with 15-percent sodium hydroxide at 315°C. In the study (6) of 40-percent sodium hydroxide solutions at 316°C using the hydrogen effusion technique, it was shown that mild-steel tubing in contact with this concentrated alkali is subject to a drastic pitting attack. The pits appeared to grow underneath substantial masses of oxide. Each pit gave the appearance of having been initiated at a single point and of having grown in all directions from this point as a nucleus. Crack formation in the oxide film, allowing access of the solution to the metallic surface at the apex of the crack, seemed a plausible mechanism. But while cracks in the oxide film were discovered on polished sections under the microscope, none was found which clearly penetrated to the metallic surface and was associated with pit generation. In order to obtain possible additional light on the corrosion mechanisms involved, a series of experiments was undertaken in which the hydrogen effusion technique was used to study the reaction of mild steel with 15-percent sodium hydroxide at 316°C.

*As determined by x-ray line broadening.

Table 1

pH Value	Total Corrosion After 7.5 Hours		Corrosion Rate (mg/dm^2-mo)*	
	Data by Berl and Van Taack (1) (mg-O/g)	NRL Data (mg-Fe/dm^2)	After 7.5 Hours	After 25 Days
7.00	17	7	330	16
10.6	-	10	580	22
11.5	-	11	680	37
11.70	16	-		
12.00	16	23	970	52
12.18	11	-		
12.24	-	5	220	55
12.32	11	-		
12.40	18	12	810	81

*Milligrams of iron reacted per square decimeter of surface area per month.

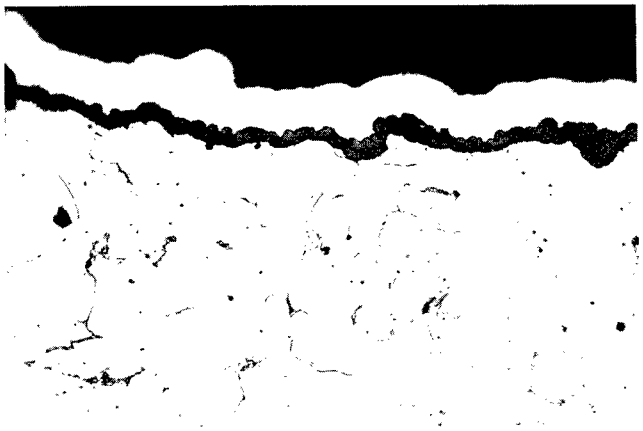

Fig. 1 – Section perpendicular to inside surface of mild-steel capsule that was filled with water and treated at 316°C for 789 days. Nital etch; original magnification 1000X. (Reduction in printing approximately 50%.) The white layer at the top is silver plating and the darker layer underneath is the oxide.

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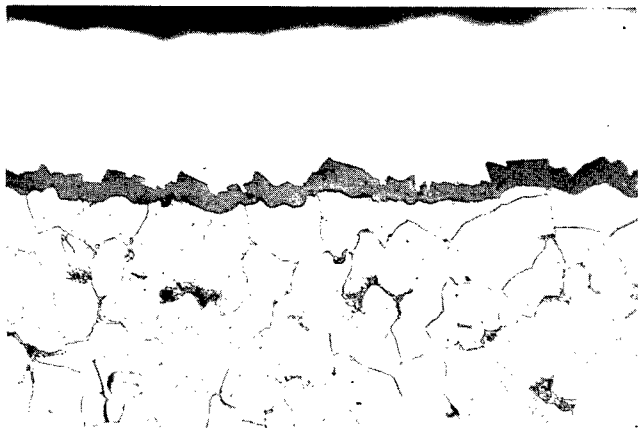


Fig. 2 – Section perpendicular to inside surface of mild-steel capsule that was filled with pH 11.5 sodium hydroxide solution and treated at 316°C for 283 days. Nital etch; original magnification 1000X. (Reduction in printing approximately 50%.) The white layer at the top is silver plating and the darker layer underneath is the oxide.

EXPERIMENTAL PROCEDURE

The hydrogen effusion technique employed has been previously described (6,9). It uses as a specimen a small metal capsule filled with the corrosive medium. The capsule is heated in an evacuated chamber and the hydrogen formed during corrosion effuses through the capsule wall into the chamber, where the hydrogen pressure is measured continuously as a function of time. The rate of pressure change (hydrogen effusion rate) is used as a measure of corrosion rate. From the rate of hydrogen effusion the rate of iron consumption is calculated, using stoichiometry based on the equation

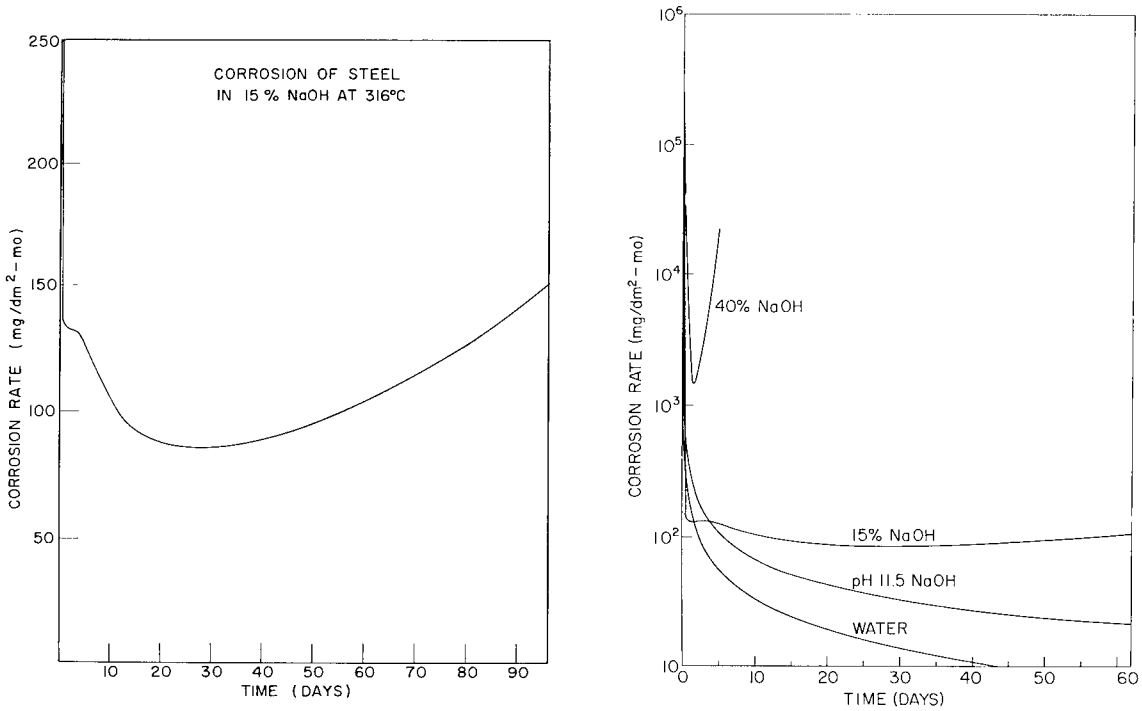
$$3\ Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2. \qquad (1)$$

The steel used for the capsules was from the same batch used for the 40-percent sodium hydroxide experiments (6), and all procedures were the same as in those experiments. The solutions were prepared either in alkali-resistant glass or in polyethylene.

RESULTS

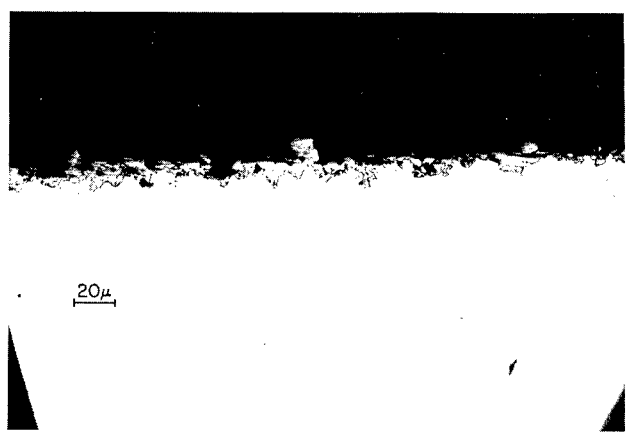
Rate data for the reaction of steel with 15-percent NaOH at 316°C was averaged for three representative capsules (Fig. 3(a)). The maximum deviation of individual measurements from this average was of the order of 15 percent. In Fig. 3(b), these averaged data are compared with similar data for other alkaline solutions.

It may be noted that, just as in the case of the 40-percent sodium hydroxide solutions, the corrosion rate in 15-percent sodium hydroxide reaches a minimum and then rises at an accelerating rate. Apparently, analogous phenomena are involved, except that in the case of the 15-percent NaOH it requires about thirty days to reach the minimum and the rate increase is much more gradual. The appearance of the general corrosion after various times is shown in Figs. 4(a), (b), and (c), which exhibit representative cross sections at 3.7 days, 42 days, and 68 days, respectively.



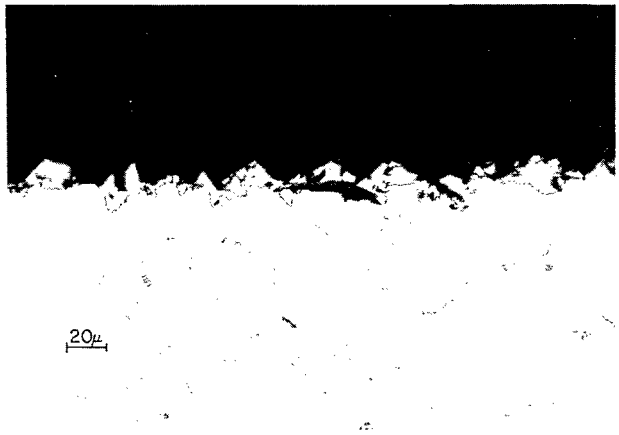
(a) (b)

Fig. 3 – Corrosion rate as a function of time for the reaction of mild steel with (a) 15-percent NaOH at 316° C, and (b) a comparison with two other alkaline solutions and water

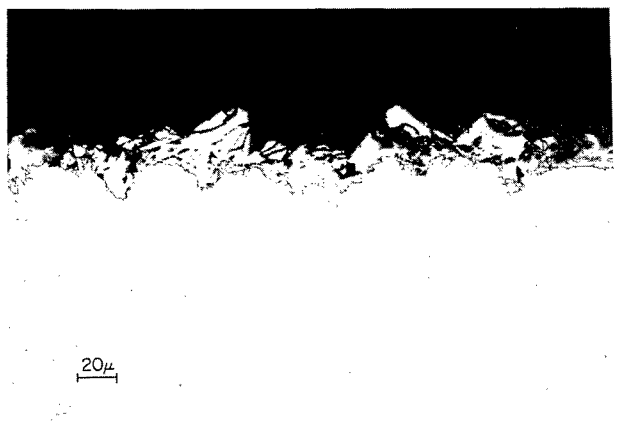


(a)

Fig. 4 – Section perpendicular to inside surface of steel capsule containing 15-percent NaOH solution after (a) 3.7 days, (b) 42 days, and (c) 68 days at 316° C. One-percent Nital etch; original magnification 500X. (Reduction in printing approximately 50%.)



(b)



(c)

Fig. 4 (Cont'd) – Section perpendicular to inside surface of steel capsule containing 15-percent NaOH solution after (a) 3.7 days, (b) 42 days, and (c) 68 days at 316°C. One-percent Nital etch; original magnification 500X. (Reduction in printing approximately 50%).

In addition to the general corrosion, pits also appeared. Quite analogous to the observations made with 40-percent sodium hydroxide, these pits were readily observable after the rate data passed the minimum. In this case, however, the attack was not so drastic, and it was possible to follow the course of pit development over considerable periods of time. Figure 5 shows typical pit cross sections after various periods of time. In Figs. 5(a), (b), (d), and (e) the specimens were silver-plated on the oxide surface prior to polishing. Figure 5(b) is an enlargement of the upper pit shown in Fig. 5(a).

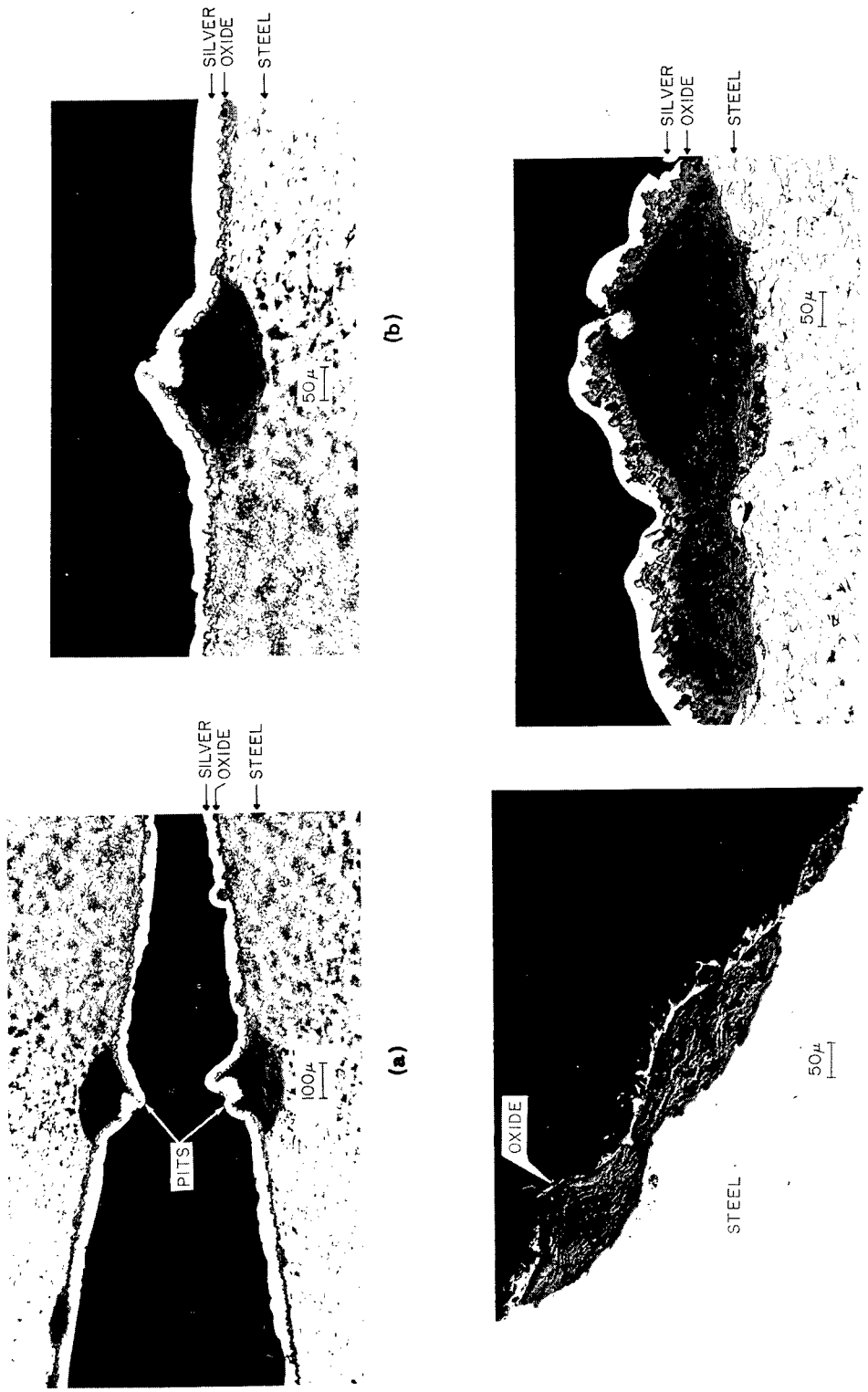


Fig. 5 – Section perpendicular to inside surface of steel capsule containing 15-percent NaOH after (a) 68 days, (b) same as (a) with enlargement of upper pit, (c) 119 days, (d) 180 days, and (e) 1 year at 316° C. One-percent Nital etch; original magnification 200X, except (a) is 100X. (Reduction in printing approximately 50%.)

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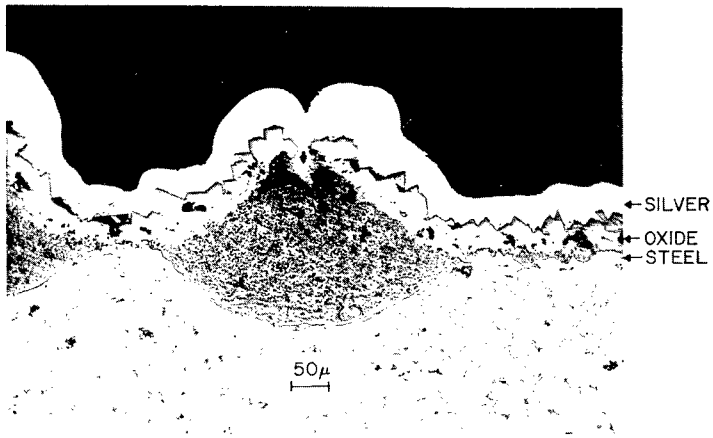

(e)

Fig. 5 (Cont'd) – Section perpendicular to inside surface of steel capsule containing 15-percent NaOH after (a) 68 days, (b) same as (a) with enlargement of upper pit, (c) 119 days, (d) 180 days, and (e) 1 year at 316°C. One-percent Nital etch; original magnification 200X, except (a) is 100X. (Reduction in printing approximately 50%.)

DISCUSSION AND CONCLUSIONS

The exposure at 316°C of mild-steel capsules containing 15-percent sodium hydroxide in the hydrogen effusion apparatus has revealed several phenomena of special interest from the standpoint of corrosion mechanisms. First, the corrosion rate vs time curve shows a rapid drop of the corrosion rate to a plateau during the first few days of operation, then a further drop to a minimum after approximately 28 days, followed by an increasingly accelerating rate of attack. Second, the increase in corrosion rate following the minimum was accompanied by the development of pits. These data would seem to indicate that at least two mechanisms of general attack are involved, even before the onset of pitting. It is interesting to note in this connection in Fig. 3(a) that in the early stages of corrosion a 15-percent sodium hydroxide solution develops a more protective film than pure water. This is undoubtedly due to the more rapid development of magnetite in the 15-percent sodium hydroxide solution within the first few days. It may be noted in Fig. 6 that at the end of one day, 240 mg/dm^2 of iron have been consumed. In pure water, approximately 10 mg/dm^2 would have been consumed in this time period. If all the corrosion went to protective film development, this would have produced a protective film of the order of 6 microns from the 15-percent NaOH solution. The fact that, subsequently, the NaOH solution produced higher corrosion rates than the water, despite the thicker magnetite films (Fig. 4), is consistent with the general effects in these alkaline systems.

In a discussion of the mechanism of general corrosion in these alkaline systems (6), it was pointed out by two of the present authors that the explanation of the effect of increased alkalinity in increasing the corrosion rate might be due to one of two alternate processes, depending upon whether the films were sufficiently porous to allow access of the solution to the metallic surface or not. In the case where they are sufficiently porous, we would expect

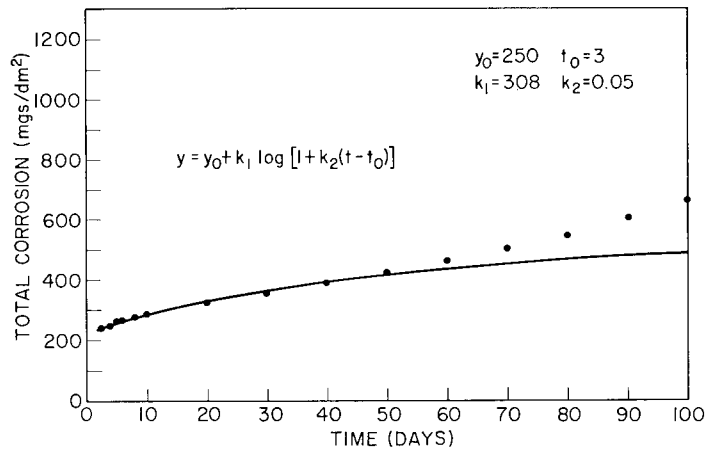

Fig. 6 – Time history of total corrosion of mild-steel capsules containing 15-percent NaOH solution at 316°C (dots) compared with pore-blocking-mechanism type equation (line)

a gradual filling of the pores with magnetite as a result of an anodic reaction at the solution-metal interface, such as

$$3\ Fe + 4\ OH^- \longrightarrow Fe_3O_4 + 4H + 4e^-, \tag{2}$$

where the OH^- would be rate-controlling. In the case where they are not sufficiently porous to allow access of the solution to the metallic surface, the corrosion would have to proceed by diffusion of ionic or atomic species through the film, and the controlling effect of OH^- would have to be attributed either to its control of the diffusion of oxygen-bearing species from the solution to the metallic surface, if diffusion were rate-controlling, or to its effect upon a surface reaction at the oxide-water interface, such as

$$3Fe^{++} + 6OH^- \longrightarrow Fe_3O_4 + H_2 + 2H_2O, \tag{3}$$

if the surface reaction were rate-controlling.

It is interesting to note that Field, Stanley, Adams, and Holmes (7) in their exploration of the reaction of 15-percent sodium hydroxide on steel block specimens in autoclaves at 315°C found evidence that porosity is present; they also obtained data which they interpreted as consistent with a pore-blocking mechanism. These authors, in agreement with Potter and Mann (5), present evidence for the development of a two-layered scale over the entire surface of the specimens, an inner layer of extremely fine crystallites generated in situ from the steel and a coarsely crystalline outer layer perhaps generated by recrystallization from solution. Their evidence of a pore-blocking mechanism was based upon examination of the thickness of their inner layer as a function of time. They found that for the first 40 days this was consistent with an equation of the type $y = k_1 \ln (1 + k_2 t)$, where y is the total corrosion up to time t, and k_1 and k_2 are constants. This is a type of equation consistent with a pore-blocking mechanism (12). Beyond about 40 days, substantial deviations in the direction of increased corrosion were obtained. The period of 40 days is not far from the time that substantial rate increases and significant pit formation were observed in the hydrogen effusion experiments reported herein. An analysis of the hydrogen effusion results (total corrosion) on the basis of an equation of this type, starting after 3 days when the processes dominating the initial corrosion were apparently complete (Fig. 3(a)), yields a fair fit from 3 to 40 days (Fig. 6).

Microscopic examination (Fig. 4) of the oxide films developed in this study, however, did not reveal evidence of a two-layered scale, and the corrosion rates observed were much less than those found with the block specimens. Perhaps the two-layered scale is related to the fact that hydrogen is generated on all sides of the block specimens, and any hydrogen generated at the metal-oxide interface by such a reaction as Eq. (2) would have to penetrate the growing oxide scale to escape. Interference with crystal growth under these conditions may produce the finely divided inner layer which has been observed. In the hydrogen effusion capsules, however, hydrogen thus generated can escape through the capsule walls, and an apparently uniform compact film of oxide is formed. The appearance of this film, and the fact that it is much more protective in equivalent thickness than the double-layer films under discussion, would indicate that the films produced in the hydrogen effusion capsules are less porous. The further possibility that these films may be sufficiently less porous so as to be nonpermeable to the solution cannot yet be discarded.

With regard to pitting, the postulate of crack formation after the achievement of a critical film thickness receives some support from Figs. 5(b) to 5(e), which show pit development after 68 days, 119 days, 180 days, and 1 year of exposure, respectively. Figure 5(b), which is a photomicrograph of a cross section of capsule tubing after 68 days of exposure, shows pit formation at a stage corresponding to a time when the corrosion rate had passed the minimum and was rising at a substantial rate. The successive appearances of the pit in Figs. 5(b) to 5(e) are suggestive of film breakdown at a localized area, allowing solution access to the metal and causing a rapid build up of a mound of finely divided corrosion product which, either by itself or with the aid of corrosion-generated hydrogen, elevated the original protective film producing a volcano-like structure. The general appearance of the attack after 68 days (Fig. 5(a)) is similar to that exhibited by samples attacked by 40-percent sodium hydroxide after 46 hours (6). It may be noted that for the attack by 40-percent sodium hydroxide, 46 hours represents a position on the corrosion rate vs time curve when the rate has passed the minimum and is rising rapidly, quite analogous to the position of the 68-day samples on the corrosion rate vs time curve for the 15-percent sodium hydroxide. The attack started at the same sensitive area–the area of major plastic deformation in the welded ends. Figure 5(b) is a higher magnification of one of the pits shown in Fig. 5(a). The slower action of the 15-percent sodium hydroxide allows the progress of the attack to be more clearly seen. Figures 5(c) through 5(e) show analogous sections after 119 days, 180 days, and 1 year, respectively. It may be noted that although the initial attack was observed in the weld heat-affected zone (Figs. 5(a) and (b)), the attack subsequently spread beyond this zone (Figs. 5(c), (d), and (e)). Figure 7, which exhibits a capsule surface after a year of exposure, shows the spread of the cracking phenomenon over the entire surface of the capsule.

Fig. 7 – Section parallel to axis of mild-steel capsule containing 15-percent NaOH after 1 year at 316°C. Original magnification 16X. (Reduction in printing approximately 50%.)

If crack formation after the achievement of a critical film thickness, is the cause of these pitting phenomenon, it is of interest to ask (a) what is the magnitude of this critical thickness and (b) what causes crack formation at this thickness. Some indication of the answer to the first question is obtained by an examination of Figs. 5(b) to (e). If we assume that the thickness of the observable oxide which forms the external surface of the volcano-like structure represents the thickness of the deposit in contact with the metal at the time of crack development, we obtain from Fig. 5(b), the 68-day exposure, a value of about 20 microns; from Figs. 5(c) and (d), the 119-day and the 180-day exposures we obtain 20-50 microns; and from Fig. 5(e), the 1-year exposure, we obtain 40-60 microns. Since in the case of the 1-year exposure practically the entire surface is cracked, one might take the thickness 40-60 microns as a maximum achievable without crack development. It may be of significance in this connection that Field, Stanley, Adams, and Holmes (7) report the loss of ability to distinguish two distinct layers on their block specimens when the film thickness reaches the neighborhood of 60 microns, and they present photomicrographic evidence which seems consistent with the postulate of film cracking and recrystallization of smaller crystals to larger ones inside the film.

With regard to the second question, it is suggested that crack formation is probably due to compressive stresses developing in the magnetite as it thickens. Analogous cracking phenomena have been observed in the dry-oxidation of titanium (13), and of niobium and tantalum (14,15), and these cracking phenomena have been related to compressive stress development in oxide films growing at the metal-oxide interface. Pawel, Cathcart, and Campbell (15) found evidence of stresses in the oxide of sufficient magnitude to create deformation lines in the metal surrounding the cracked areas. Maldy (16), using x-ray techniques, has recently demonstrated that oxidation of iron in a mixture of water and hydrogen at 800-850°C gives rise to analogous stresses in the iron of considerable magnitude, but these stresses appear only after a critical thickness of oxide has been exceeded. Perhaps some phenomenon of this kind is responsible for the fact that Field, Adams, Stanley, and Holmes (7) did not observe curvature of thin foils of iron which were gold-plated on one side and treated in 15-percent sodium hydroxide at 315°C.

Another phenomenon which may deserve mention is the striated appearance of the corrosion product within the pits. This is especially notable in Fig. 5(c). It is perhaps indicative of an alternating protective film formation and breakdown. Such striated deposits within pits are found in pitted steam-generator tubes of power boilers (17).

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