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A Study of Hydrogen Evolution During Aqueous Oxidation of Mild Steel

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CONTENTS

ABSTRACT

Steel is useful as a construction material for boilers only because the product of the easy reaction between steel and water is an insoluble oxide, which forms as a thin adherent film. As boiler operating temperatures are increased, however, the endurance and integrity of this protective film are pushed past their limits. The chemical reaction by which the film is generated is

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2,$$

but in reality it is an electrochemical process. The substrate iron serves as the anode and the growing oxide film serves as the cathode; the circuit is completed by water, which serves as the electrolyte, and by direct contact between the iron and its oxide. It was envisioned that if the specific places in this system where hydrogen was evolved could be determined, more would be known about the mechanism.

An apparatus was devised to measure against time the flow of hydrogen toward the metal side of the system and toward the solution side of the system under various controlled conditions. Permeation of hydrogen from one side of the system to the other under a known pressure differential was also measured.

It was found that in the presence of strongly alkaline solutions (15%), hydrogen was evolved more toward the electrolyte, whereas with weakly alkaline (pH 11) solutions, the hydrogen went almost entirely toward the metal. It was also shown that hydrogen very readily permeates the oxide film grown from strong caustic solution as compared with a film grown from a pH 11 solution. These facts substantiate the premise of a porous film and indicate that oxidation is taking place both within the pores themselves and at places where the solution in these pores is contacting metal.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

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A STUDY OF HYDROGEN EVOLUTION DURING AQUEOUS OXIDATION OF MILD STEEL

INTRODUCTION

It is possible to fabricate steam boilers out of mild steel only by virtue of the fact that, although iron is thermodynamically unstable in contact with water, a protective film of the insoluble iron oxide, magnetite, is quickly formed at the interface, and the reaction is thus reduced to an insignificant level. Nevertheless, problems do remain, since the conditions of formation and maintenance of this film are not always ideal, and boilers continue to fail by pitting, erosion, hydrogen embrittlement, local overheating, and a number of other phenomena all too familiar to those who operate boilers. Attempts are being made to alleviate these problems by careful preparation of feed water, use of chemical additives, and improvement in boiler design. But more importantly for this discussion, attempts are being made to learn in greater detail just what happens when a boiler is corroding. What are the mechanisms of the reactions taking place? What is the morphology of the crystalline film being formed? What is the effect of foreign ions in the solution on the crystalline (spinel) aggregate being grown in the film? What does the degree of electrical conductivity of the film have to do with the continuing corrosion? Are the films porous? Where is the hydrogen, which is formed as a result of corrosion, released, and what does this tell us about the corrosion mechanism?

DISCUSSION OF MECHANISM

The latter question brings us to the subject at hand. Where is hydrogen generated during the oxidation of a mild steel surface by hot water under the conditions of usual boiler operation, and how does this hydrogen leave the scene of its genesis? Two different laboratory techniques have recently been used to obtain corrosion data. Researchers for the Central Electricity Generating Board in England (1-4) have run many corrosion tests by placing a small block of metal in a high-pressure cylindrical container. In an experiment of this type, any hydrogen generated must eventually migrate as a gas into the solution in the space beyond the specimen and its oxide film. Investigators at NRL (5-8) have made corrosion tests in small weld-sealed capsules of the test metal containing test solution and suspended in a hot evacuated space. In this type of experiment, the hydrogen formed may permeate the corroding metal in the atomic form, as it may in a boiler tube, and leave the scene without necessarily entering the solution as a gas or interfering with the growth of the oxide film. These two experimental techniques generate significantly different types of oxide film, the latter type being more dense and uniform in structure.

As is usually the case in corrosion problems, one has an electrolytic system in boiler corrosion. The water and its contained ionic species are the electrolyte, the iron is the anode, and the oxide film assumes the role of cathode as it forms. To simplify the situation under discussion, the assumption is made that one has an anaerobic system and a pH in the alkaline region. Two suggested alternative mechanisms are diagrammed in Fig. 1. In mechanism a, with no pores in the oxide film, all the hydrogen is liberated on the solution side of the growing oxide film, but in mechanism b, hydrogen is formed on each side by virtue of corrosion at the bottoms of pores. It seemed that an experiment

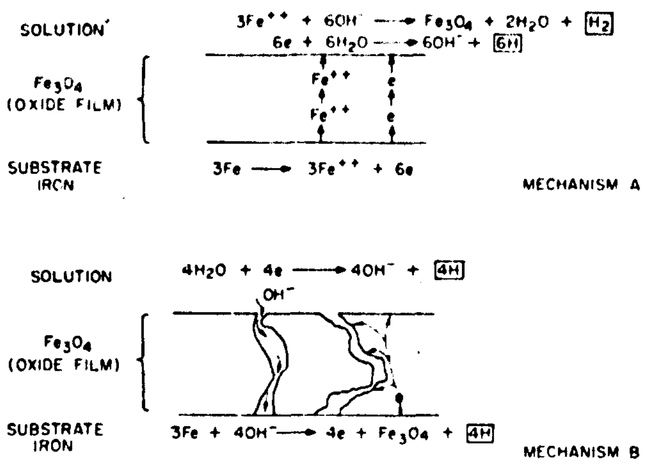

Fig. 1 - Suggested boiler corrosion mechanisms

designed to detect and measure any partitioning effect such as this would contribute to an understanding of the mechanism of the overall corrosion process.

APPARATUS

In accordance with the above reasoning, the apparatus in Fig. 2 was constructed. The test capsule of 0.030-in. wall tubing, with the same composition as used routinely in this laboratory for hydrogen-effusion-type corrosion rate measurements,* had an internal volume of 1 cc and was filled with enough solution to expand to slightly less than 1 cc at the test temperature (300°C). An attempt was made to provide insulation between the palladium-silver alloy diaphragm† and the metal of the coupling to prevent a galvanic effect, but this was unsuccessful. Comparison of experimental data with previous effusion experiments made by the NRL technique (8) indicated some augmentation of corrosion rate attributable to this effect.

The apparatus of Fig. 2 was immersed in an evacuated container of known volume and heated to 304°C. The tube leading from the palladium diaphragm also connected to an evacuated container of known volume. The pressure in the vacuum spaces was monitored by Pirani gages with recorders, the Pirani units having previously been calibrated with hydrogen using a McLeod gage as a primary standard.

It was determined that the palladium diaphragm would function like a window to hydrogen by imposing a hydrogen pressure differential of 1 atm on it and measuring the rate of permeation at 304°C. A flow of 3.84 cc/hr, equivalent to a corrosion rate of ca. 60,000 mg iron/dm^2-mo, was found. This is more than 30 times the amount of hydrogen which would permeate the bare capsule wall at this pressure and was considered ample for the range of rates expected in the experiments.

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*Analysis of the tubing gives a composition of carbon (0.09%), phosphorus (0.017%), sulfur (0.032%), nitrogen (0.007%), manganese (0.57%), silicon (0.07%), chromium (0.10%), and nickel (0.07%).

†This was a palladium-25% silver alloy and will be the indicated material whenever palladium is mentioned.

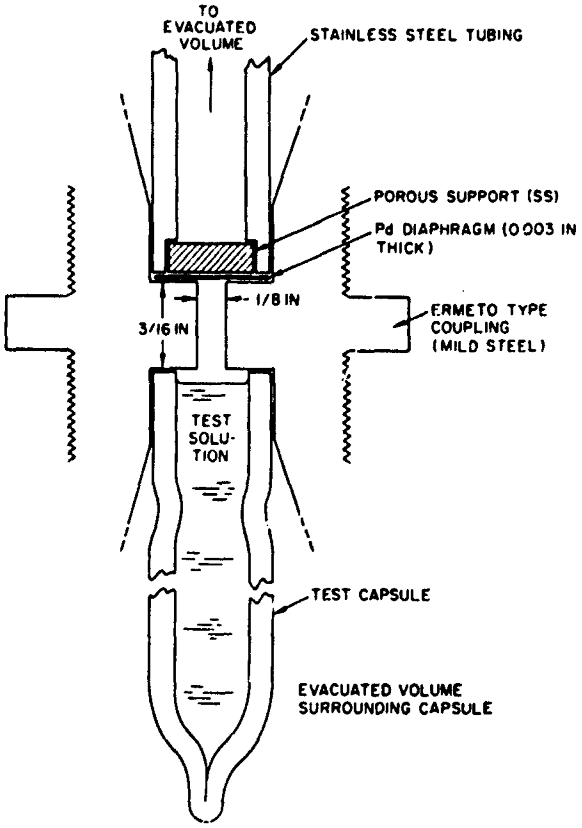


Fig. 2 - Palladium-alloy "window" apparatus

Since all experiments were conducted at one temperature, it was permissible to use a simplified form of the equation relating various parameters of a hydrogen permeation system: this form lumps the activation energy term with the permeation constant S_t:

$$dQ/dt = S_t \frac{A}{D} p^{1/2}$$

where dQ/dt is the hydrogen flow in cubic centimeters per hour, d is the thickness of the permeated medium in millimeters, A is the area in square centimeters, and p is the pressure differential of hydrogen in atmospheres. Using the flow value already mentioned, the S_t for the palladium-silver alloy was 23.8. This datum was found to agree with information from J. Bishop and Company (9) for this same alloy used in a commercial hydrogen purifier. With this value, it was an easy matter to set up a formula by which one could calculate the hydrogen pressure inside the apparatus any time a measure of hydrogen passing through the palladium window was available. This formula in terms of iron corrosion rate (for a capsule area of 0.087 dm²) was

$$P_{H_2} = 21.4 \times 10^{-6} R^2 ,$$

where P is given in torr and R = mg Fe/dm²-mo.

EXPERIMENTAL DATA

Seven experiments have been run, as shown in Table 1. Plots of corrosion rate vs time for each side of the system for six experiments are shown in Figs. 3. The details of the first 3 hr of heating of the specimen in experiment 1 and varying times at the start

Table 1
Experiments Performed

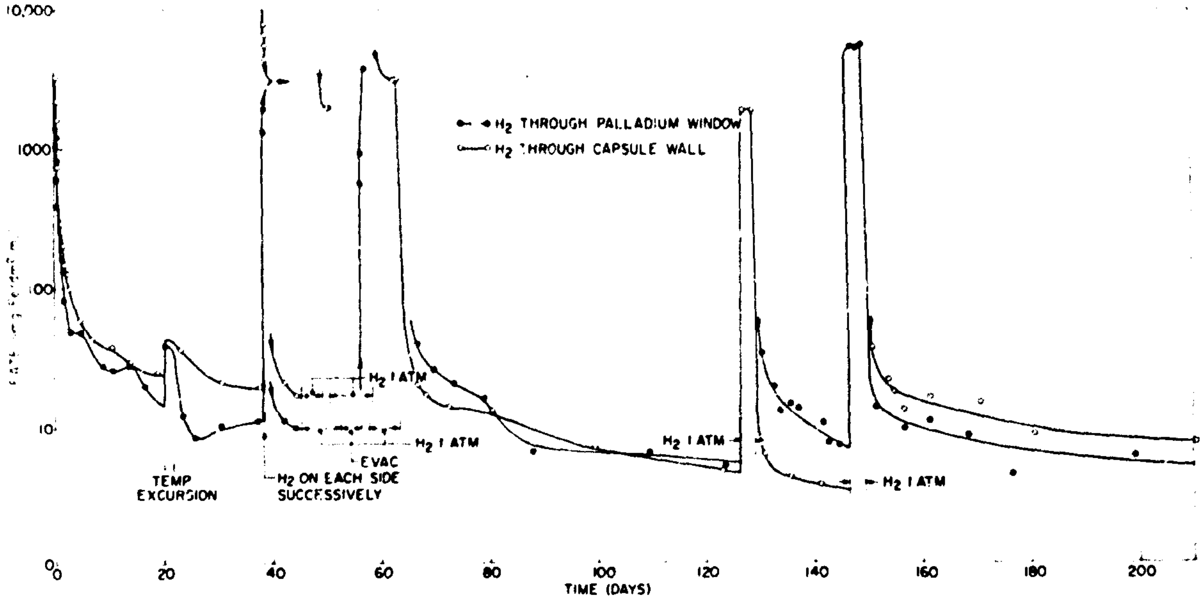
Exp. Number	Electrolyte		Duration (days)	Remarks
	Start	Finish		
1	15% NaOH	-	245	Started H_2 permeation measurement at 38 days
2	40% NaOH	Consumed	80	To detect pitting onset
3	pH 11 LiOH	pH 7.4	58	"Normal" corrosion
4	pH 11 NaOH	pH 11.2	16	Solution possibly contaminated with carbonate
5	No electrolyte		9	Capsule started with 1 atm H_2
6	pH 11 LiOH	pH 8.0	15	Apparatus leaked
7	pH 11 LiOH	pH 7.0	22	Measured early H_2 permeation

of the next three experiments were missed because of several false starts. The system leaked when the assembly was complete and had to be dismantled again. Since the heated zone was already hot before assembly (it was part of an equipment for running 15 hydrogen effusion experiments simultaneously and thus had to be maintained at temperature), the specimen was heated each time a start was attempted.

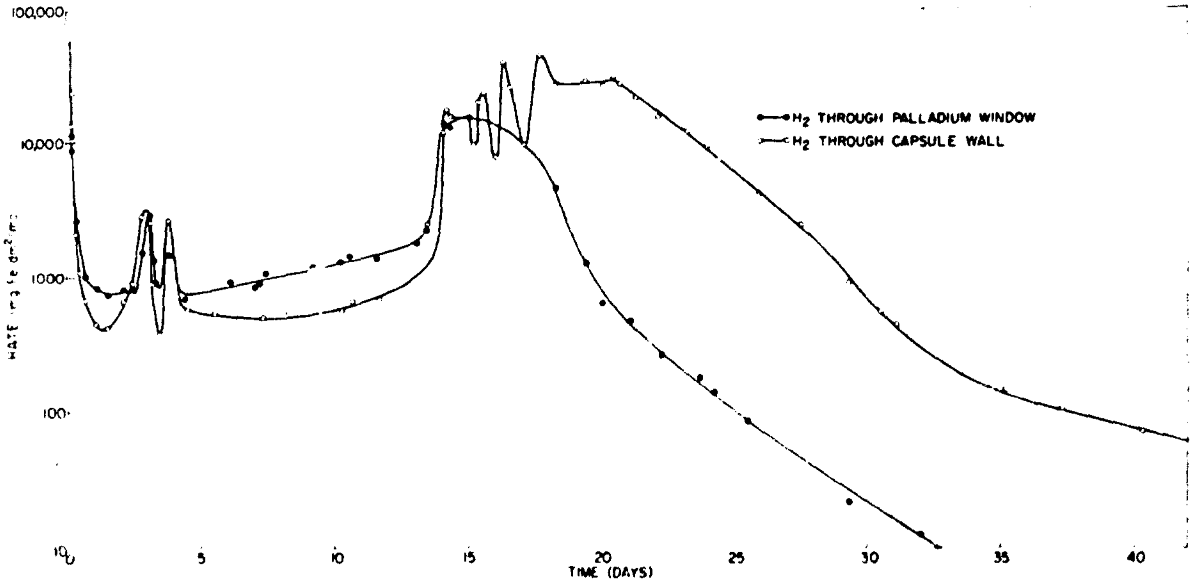
It was realized after experiment 1 had been underway for 38 days that information of potential value could be obtained by measuring the rate of hydrogen permeation from one side of the system to the other with a known pressure differential. This was done by using 1 atm of hydrogen pressure at selected times in each experiment, except experiments 2, 5, and 6, and the resulting hydrogen flows in terms of mg Fe/dm^2-mo are included in Figs. 3. These measurements (summarized in Table 2) necessitated interruption of corrosion data collection for periods of 4 or more hr to allow equilibration. (It can be seen in Fig. 3a that the data from 38 to 58 days were taken too hurriedly to reach equilibrium.)

The second experiment was with a 40% sodium hydroxide solution, and approximately 4 hr of heating preceded a successful start. This strong solution was used because it was known to cause pitting fairly quickly. A possible reason that pitting progresses without healing might be that a great enough quantity of hydrogen is evolved in such a small area that gas bubbles form and blow back out of the pit to be dissipated by permeation through the ample available metal wall area elsewhere. This hydrogen should be seen coming through the palladium window in a disproportionate quantity.

The experiment was not successful in answering the pitting question due to a series of complications. Perturbations appearing in the third to fifth days were attributed to invasion of metal-to-metal seals by the electrolyte, evidence of which was provided by sectioning and examining by microscope. The reason for the sudden rate increase at 14 days remains unknown. The wide difference between flows after 17 days was caused by the development of a solid plug of magnetite in the neck of the apparatus. Another complication was that all the water was chemically consumed some time before the experiment ended.

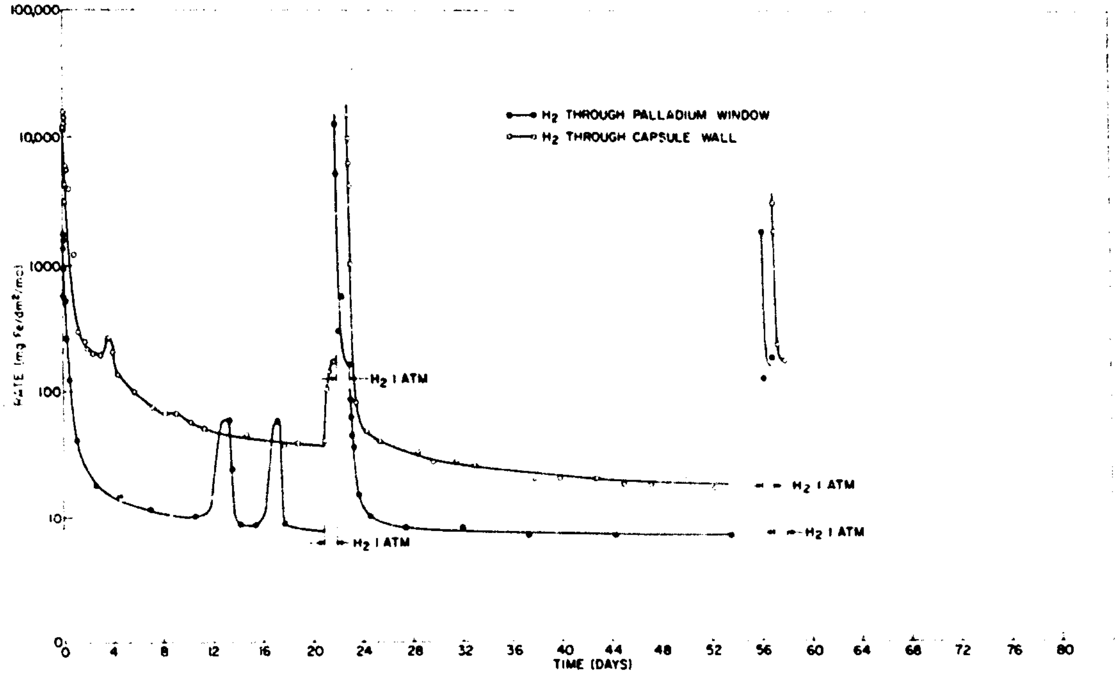


(a) 15% sodium hydroxide solution (experiment 1)

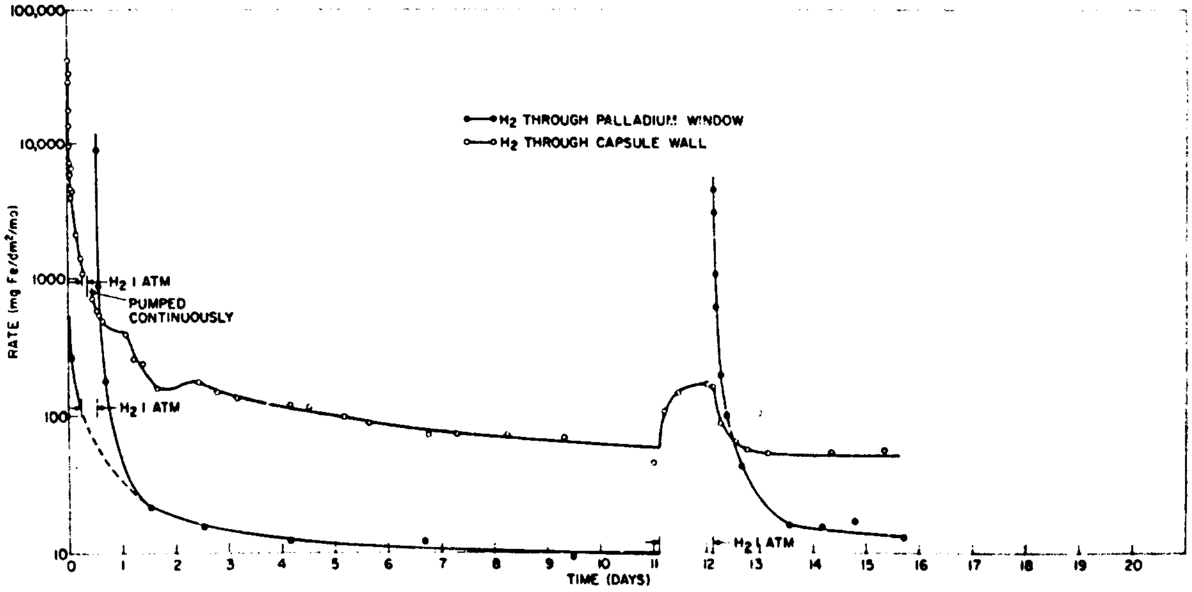


(b) 40% sodium hydroxide solution (experiment 2)

Fig. 3 - Corrosion rate-vs-time data

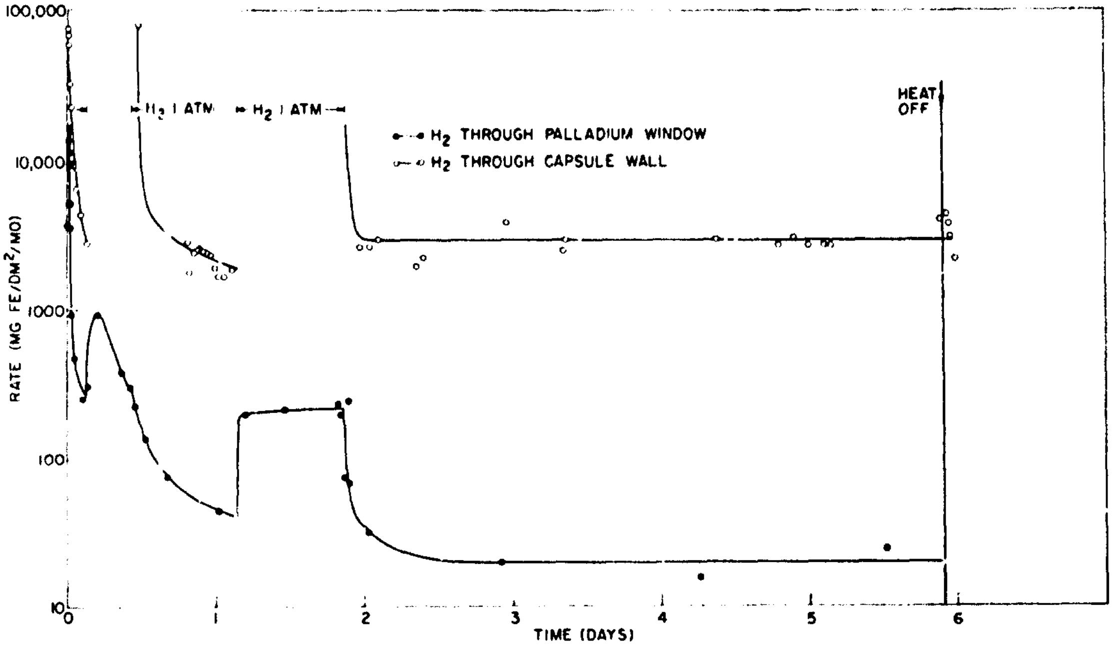


(c) pH 11 lithium hydroxide solution (experiment 3)

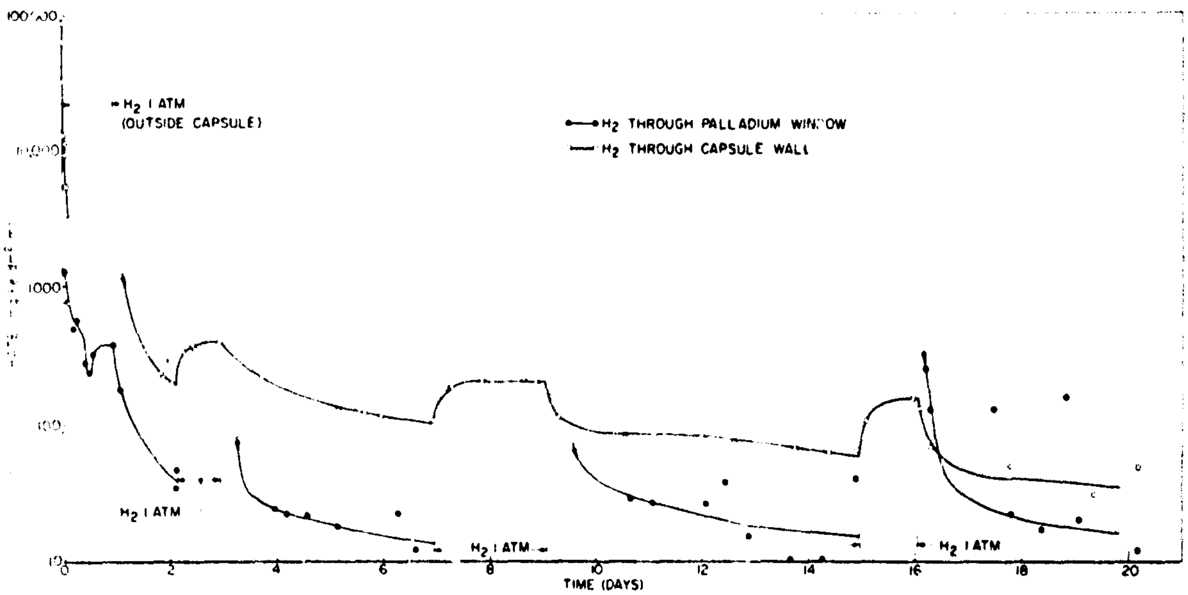


(d) pH 11 sodium hydroxide solution (experiment 4)

Fig. 3 - Corrosion rate-vs-time data (continued)



(e) pH 11 lithium hydroxide solution (experiment 6)



(f) pH 11 lithium hydroxide solution (experiment 7)

Fig. 3 - Corrosion rate-vs-time data (continued)

Table 2
Hydrogen Permeation with ΔP Across System
(One side of system was under 1 atm H_2 pressure
and the other was under a vacuum)

Electrolyte	Elapsed Time (days)	H_2 Effluent (mg Fe/dm^2-mo)	
		Pd Diaphragm	Capsule Wall
15% NaOH	40	3000	—
(Exp. 1)	40	—	3000
	50	—	1900
	57	3600	—
	129	—	1900
	149	5600	—
pH 11 LiOH	22	—	170
(Exp. 3)	23	170	—
	57	150	—
	58	—	170
pH 11 NaOH	0.5	—	650
(Exp. 4)	12	—	170
pH 11 LiOH	0.2 to 0.4	(900 down to 300)	
(Exp. 6)	1.8	220	
pH 11 LiOH	1	370	—
(Exp. 7)	3	—	390
	9	—	200
	16	—	150

Experiment 3 with a pH 11 lithium hydroxide solution was conducted without difficulty as was experiment 4 with a pH 11 sodium hydroxide solution. There was some question concerning an undue amount of contamination of the latter solution by carbonate; pH readings were ambiguous, but a reading after the experiment confirmed previous evidence that alkalinity in sodium hydroxide solutions remains constant or rises slightly because of water consumption.

Experiment 5 was a blank. No solution was placed in the capsule; instead it was simply flushed with hydrogen as closure was effected.* Rates of hydrogen permeation were measured in each direction with a 1-atm pressure differential, and S_t was found to be 8.5×10^{-4}, a figure one-tenth Norton's value for "0.1% carbon steel" (10).

Following experiment 5, a modification of the apparatus permitted complete assembly and leak testing of the apparatus before heating was started. This enabled one to get rate data starting at zero time for the two additional experiments that have been accomplished and also enabled one to measure blank leakage rates with the apparatus at room temperature. Experiments 6 and 7 were both with pH 11 lithium hydroxide. Number 6 was cut short by a crack that developed in the glassware, leaking air equivalent to an apparent corrosion rate of 3000 mg Fe/dm^2-mo.

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*This was not done rigorously in a controlled atmosphere, and some air contamination was likely.

Some work was done to determine hydrogen permeation rates through a single crystal of magnetite. The results were unsatisfactory because the available crystal had flaws that leaked hydrogen by viscous flow. It would appear from the data of Table 2, however, that magnetite is rather impermeable to molecular hydrogen.

The permeation of molecular hydrogen through this apparatus may be governed mainly by the degree of coverage of the iron surface and to a lesser extent by the size of the pores. The films from pH 11 solutions drop rapidly in their permeation rate as the surface is covered initially, and then a further slow decrease is noted as the pores lengthen (and decrease in diameter) with the thickening of the film.

The final pH measurements on experiments with lithium hydroxide (Table 1) clearly indicate that the lithium ion is incorporated in the growing spinel film. In experiment 6, 15 days were apparently not a long enough period to use all the lithium ions, but in experiments 3 and 7, the final solution was essentially neutral. However, this generation of lithiated spinel apparently had little effect on hydrogen permeation rates. The same ultimate rate was reached by either sodium hydroxide or lithium hydroxide runs in about 2 weeks.

DISCUSSION

In growing a magnetite film from dilute alkaline solution (pH 11), the hydrogen generated went through the capsule wall with ease, with only a small portion going through the palladium diaphragm even in the early part of the experiment and this decreasing to insignificant levels in 6 to 8 days with both sodium and lithium hydroxide. However, in stronger caustic solutions, the hydrogen flows were more nearly equal. In 15% sodium hydroxide, the ratio was near 1 most of the time; in 40% sodium hydroxide, the flow through the palladium was twice that through the capsule wall most of the time for 14 days.

It is also apparent that a more compact film is generated from a dilute electrolyte than from a concentrated one. This is shown in Table 2. It may be noted that after about 50 days in the 15% sodium hydroxide solution, the hydrogen permeation rate out of the palladium diaphragm began to rise. Previous data (8) indicate that pit development could account for this since pitting occurred after 1 month at 316°C with similar solutions.

Figure 1 shows two suggested variations in the corrosion process which would result in different hydrogen partitioning. Mechanism "a" depicted in Fig. 1 might be expected to result in pushing much, if not all, of the hydrogen through the palladium diaphragm. This is clearly not in accord with the observations. Mechanism "b" depicted in Fig. 1, on the other hand, would seem to call for a large amount of hydrogen to penetrate the capsule wall, either by direct permeation of atomic hydrogen generated at the base of a pore or by the development of molecular hydrogen within a pore and its subsequent migration to and through the metallic surface at the pore base. This seems consistent with the data and indicates that a porous structure is being generated. The data are also consistent with a picture of this kind of structure in which the porosity increases with increasing alkalinity. There are, however, certain considerations which indicate that mechanism "b" in Fig. 1 cannot be the full story. Thus, if the total reaction were of mechanism "b", all the magnetite would be formed at the bases of pores. The approximately two-to-one ratio of volumes of oxide to metal, however, would generate large stresses not consistent with the development of adherent films (2). A mechanism which might account for the development of Fe_3O_4 without much stress (Fig. 4) is one which calls for the occurrence of both processes in pores: mechanism "a" at the pore surfaces and mechanism "b" at the bases.

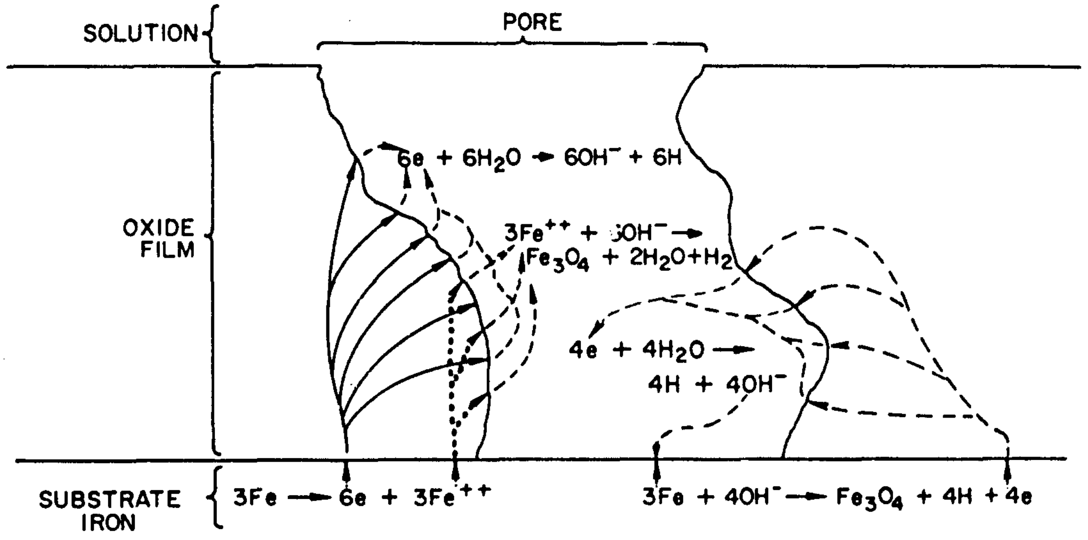

Fig. 4 - Probable boiler corrosion mechanism

The reasons dictating the partitioning between the two processes will require further analysis. It probably depends on the dimensions and frequency of pores and on the actual relationship between pore base area and total area of iron.

However, one can see another possible mechanism for relief of film stress consistent with the flow of most of the hydrogen through the metal wall. If one assumes that reaction takes place by mechanism "b" of Fig. 1, it may be noted that the solution within the pore can be saturated with respect to Fe_3O_4 at the in situ pH level. As one proceeds up the pore, the hydrogen discharge reaction will create alkalinity, hence, there will be a variable solute concentration up the pore — the alkalinity rising to a maximum and then tapering off to the bulk solution value at the solution end of the pore. This alkalinity gradient would be expected to lead to a magnetite dissolution along pore walls and reprecipitation further along the pore toward the oxide solution interface. Such a picture is in accord with the conclusions of Castle and Masterson (11) that solution transport of soluble iron is the dominant factor in the development of films in the Potter and Mann type of experiment. It also would provide a mechanism for iron transport in films developed in capsules.

It is of further interest to note that this postulated porous oxide, with reaction taking place between solution and exposed metal at the base of the pore followed by dissolution and reprecipitation of the oxide some distance away, is similar to one proposed by Moore and Jones (12) from electron microscope studies of analogous films grown in capsules from pH 11 lithium hydroxide solution.

In experiment 1 there appears to be an appreciable dependence of the hydrogen permeation rate on its direction of flow (ignoring the first two points, which were not equilibrated. This is believed to be caused by the physical requirement of dissolution in the electrolyte at a small area interface, plus convection or diffusion to the oxide film in one direction, whereas the hydrogen coming in through the capsule wall could simply bubble up through the electrolyte and leave via the palladium window. In other experiments the barrier at the oxide film was great enough to mask this effect.

A very interesting feature of this system with regard to hydrogen permeation was exposed by the first permeation datum of experiment 4 (ph 11 sodium hydroxide). The palladium window side of the apparatus was pressurized to 1 atm with hydrogen at only 1/2 day's elapsed time, and no augmentation of flow through the capsule wall was evidenced. Instead, two additional points fell right on the corrosion rate curve for the capsule side, i.e., 710 and 570 mg Fe/dm -mo. The fact that no additional flow was observed here would seem to indicate at first glance that the hydrogen dissociation equilibrium, $H_2 \rightleftharpoons 2H$, was satisfied at the oxide/metal interface with the molecular hydrogen equilibrium pressure at some value higher than 1 atm. However, the situation is a dynamic one, not conducive to the development of equilibria but rather only steady-state conditions. Therefore, it seems unwise to invoke the presence of molecular hydrogen in any specific amount.

Further consideration of this matter provides evidence that the pressure of hydrogen gas above the solution in these experiments bears little mathematical relation (or certainly an unusual one) to the flow of corrosion-generated hydrogen through the capsule wall. Thus, if one calculates the flow of hydrogen through the capsule wall per unit "back pressure" over the solution at random times during the various experiments, one obtains the values in Table 3. The final notation is calculated using Norton's S_t for low carbon steel (10), which was obtained by placing hydrogen gas on one side of a heated membrane and measuring the amount permeating into a vacuum. The corrosion values are seen to be far above the range of gaseous hydrogen; it can be observed, however, that the lowered Q/P_{H_2} values for the 15% and 40% sodium hydroxide experiments reflect the previously mentioned fact that the effectiveness of the oxide film as a barrier is diminished by growth from strongly caustic solutions. One is further led to believe that the hydrogen generated by corrosion in dilute solutions passes directly into the metal without forming molecular gas — to a much greater extent than is the case in concentrated solutions.

Attempts were made in experiments 6 and 7 to pinpoint more exactly the corrosion rate and time (in effect, a measure of film thickness) at which a flow discontinuity could be brought about by pressurizing with hydrogen at 1 atm, but this time the gas was placed outside the capsule wall. These data have not yet been fully evaluated.

It is believed that if one could obtain a continuous measure of the hydrogen permeation rate from the beginning of an experiment that it would drop very rapidly from a high starting rate, finally leveling off at 100 to 150 for a pH 11 solution of either sodium or lithium hydroxide. In a concentrated solution of sodium hydroxide, the leveling off would be appreciably higher in accord with a more open and porous structure.

CONCLUSIONS

The following features of the corrosion system involving boiler steel and alkaline water are indicated by this study:

1. The magnetite film is indeed porous.
2. Hydrogen is evolved at the metal surface at the bottoms of pores and/or close to it along pore walls.
3. There must be a hydroxide ion gradient in the pores.
4. The porosity of a film grown in the presence of an alkaline solution increases with the alkaline strength.
5. Hydrogen generated by corrosion in dilute solutions passes through the metal with very little concurrent formation of molecular hydrogen, whereas more association occurs in the presence of strong caustic solutions.

Table 3
Corrosion Hydrogen Flow Versus "Back Pressure" Above Solution

Elapsed Time (days)	Rate through Pd (mg Fe/dm^2-mo)	P_{H_2} above Solution (torr)	Corrosion Hydrogen through Wall, Q (mg Fe/dm^2-mo)	Q/P_{H_2}
40% NaOH (Exp. 2)				
1-1/2	750	12	400	33
5-1/2	800	14	500	36
10	1200	31	560	18
15% NaOH (Exp. 1)				
10	26	0.014	38	2,630
37	11	0.0026	19	7,340
100	7	0.0010	7	6,670
170	7	0.0012	12	10,000
200	5	0.0006	8	12,800
pH 11 LiOH (Exp. 3)				
2	22	0.014	200	14,800
4	15	0.0048	160	33,300
9	10	0.0021	60	28,000
pH 11 LiOH (Exp. 7)				
2	30	0.019	150	7,770
4	10	0.0021	130	60,700
6	1	21×10^{-6}	50	2,340,000
14	1	21×10^{-6}	7	327,000
pH 11 NaOH (Exp. 4)				
1/4	115	0.283	1,400	4,950
2	18	0.0069	150	21,600
4	12	0.0033	110	32,900
6	11	0.0026	86	33,200
9	10	0.0021	66	30,800
Bare capsule (no solution)				
–	–	760	1,450*	1.9

*Using Norton's S_t for mild steel.

It remains to be seen what interference the presence of a chelating agent such as EDTA might introduce into hydrogen partitioning. It also seems important at this time to set up experiments with more concentrated lithium hydroxide solutions since the lithium ion is so obviously consumed. Furthermore, some of the experiments reported need to be studied microscopically.

There is a possibility that continuous hydrogen permeation experiments can be run without interference of corrosion-generated hydrogen. A film of magnetite can be grown using lithium nitrate as the oxidizing agent instead of water — hence, no hydrogen product. (The nitrogen is reduced.) Electron micrographs of a magnetite film grown in this way indicated a strong similarity with the usual films.

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13. ABSTRACT

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Hydrogen evolution						
Mild steel						
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