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SUBJECT: Carbon Steel in High Temperature Water

TO: E. G. Bohlmann

FROM: G. E. Moore

SUMMARY

Resistance of carbon steel to corrosion in oxygenated high temperature (250°C) water was unexpectedly good at high oxygen concentration. Pertinent literature, critically examined, and toroid experiments reported here, indicated that at low oxygen concentration, attack did increase with concentration, but as oxygen concentration was sufficiently increased, more protective films were formed on the metal. Some corrosion factors in the application of carbon steel to nuclear reactor systems are discussed.

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CARBON STEEL IN HIGH-TEMPERATURE WATER

The behavior of carbon steel in high-temperature water has been well investigated and has resulted in its wide use as a material of construction in some systems. (29, 53, 54, 59) Much of this work has been aimed at the proper treatment of the water in order to inhibit corrosion and scale formation. (19, 29, 53, 55) Best results were obtained when the water was very low in oxygen content, mildly alkaline and softened.

Because data were obtained in the study of circulating aqueous thorium oxide slurries in loops (47, 48) and later in toroids (37, 39, 40) that implied that carbon steel might be fairly resistant to high-temperature, highly-oxygenated, neutral water, a review of the most obvious features concerned with the behavior of carbon steel in high-temperature water as a function of oxygen content seemed indicated.

This memorandum constitutes both a cursory review of published information and a summary of some heretofore unpublished data.

It is often implied and accepted as fact that the corrosion rate of iron or steel in water is roughly proportional to the dissolved oxygen content. (53, 54) Recently, however, experiments were reported by Reed and Compere (47, 48) that indicated that a circulating aqueous thorium oxide slurry containing very large amounts of oxygen produced only mild attack of carbon steel. An apparent discrepancy existed, therefore, between these results and the much-quoted statement that "with respect to water, the rate of attack is accelerated as the dissolved oxygen, carbonic acid, temperature and acidity are increased and is retarded by the reverse of these conditions." (54)

However, further statements tend to resolve the discrepancy to a limited extent; for example, Speller (54) continues, "The rate of motion generally accelerates corrosion up to a certain point mainly by bringing more dissolved oxygen to the metal surface. Above a certain velocity, in the case of iron, however, there is a retarding effect due to the more rapid formation of protective layers of corrosion products on the metal." What is not considered

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in these comments is the effect of oxygen pressurization upon attack of steel by high-temperature water. Uhlig⁽⁵⁹⁾ does, however, consider the effect of high oxygen concentrations and states that "although increasing oxygen concentration at first accentuates corrosion of iron in water . . . it is found that beyond a critical concentration the corrosion rate may drop again to a low value This is clearly an example of iron passivated by oxygen as shown by potential (changes)."

Since these statements were based on tests at 30°C, a limited investigation seemed indicated in order to determine the effect of high oxygen concentrations in high-temperature water on the attack of iron or steel. The results of a very preliminary investigation along these lines are summarized in this memorandum. Other considerations prevent a more complete appraisal of the subject, yet it seems reasonable to record a few comments, even though of very limited scope, on this general subject.

The problem was attacked along three courses:

1. A study of the attack of carbon steel by circulating aqueous thorium oxide slurries at elevated temperatures, based on the loop results, was undertaken in the small-scale dynamic corrosion apparatus (toroids).^(38, 39)
2. A limited search of the literature was undertaken to reveal the theoretical background and experimental evidence of the behavior of steel in high-temperature oxygenated water.
3. A study of the attack of carbon steel by circulating water at 250°C as the oxygen content was varied was undertaken in toroids.

Each of these three approaches will be summarized in turn.

1. Slurry Experiments.

Most of the thorium oxide slurries so far considered have been suspensions of the oxides in pure water and have yielded unadjusted pH's of 5 to 9. Under these conditions, it is not illogical to consider the use of carbon steel, since it is often used in water systems of mild alkalinity. In common with other materials, however, its successful utilization in a slurry system depends first of all on the elimination of erosion (and the conjoint action of corrosion) as a factor in the circulation; this may possibly be accomplished

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by the use of a thorium of small particle size distribution.⁽⁴⁰⁾

However, the experiments reported by Reed and Compere^(47, 48) were not entirely expected in view of the very high oxygen concentrations employed. The first run (CS-27) circulated Batch LO-2 thorium oxide at an average slurry concentration of 348 g of thorium per kilogram of water, pH about 7, 300°C for 301 hr with oxygen pressurization, the oxygen concentration in the aqueous part of the slurry being about 1000 ppm; reasonably low attack rates for A-212 Grade B carbon steel were observed (11, 13 and 24 mpy at flow velocities of 10, 22, and 41 fps respectively).⁽⁴⁷⁾ A second run (CS-28-29) used a precirculated slurry of Batch LO-2 in order to observe the effect of particle size degradation on the attack; the slurry, at an average concentration of 346 g of thorium per kilogram of water and a pH of 7, was circulated at 300°C for 266 hr with oxygen pressurization (approximately 1000 ppm oxygen in solution). The mild steel specimens were attacked at a rate of approximately 21 mpy and independent of flow velocity over the range 13 to 43 fps.⁽⁴⁸⁾

These rates for steel were considerably greater than those found for the austenitic stainless steels, titanium, Zircaloy-2, etc. under comparable conditions. However, their reasonably low magnitude appeared to warrant further investigation.

As a result, A-212 Grade B steel was used in several toroid tests circulating aqueous thorium oxide slurries at 1000 g of thorium per kilogram of water, 250°C and 26 fps relative velocity for 330 hr.⁽³⁷⁾ A precirculated slurry was used to reduce the effects caused by the circulation of large particles of thorium oxide. The generalized (uniform) attack rate for the steel was indistinguishable from that for either type 347 stainless steel or titanium 75A (8 to 14 mpy)* when an oxygen overpressure was used. The distinguishing feature of the attack, however, was that carbon steel showed some localized pitting that was not found with the other alloys. Carbon steel continued to give virtually identical weight losses as the stainless steel in the presence of oxygen and either phosphate or metasilicate additions, although the carbon steel remained

* Corrected for "slug-flow", i.e., calculated on basis of continuous immersion in the fluid and, therefore, on basis believed to be more consistent with loop data.⁽³⁹⁾

characterized by a mild pitting attack. Long-term static exposures⁽³⁷⁾ showed very similar attack between type 347 stainless steel, titanium and SAE 1030 (less than 0.3 mpy) when exposed to oxygenated water containing 0.02 *m* phosphate at 250°C; there was no pitting of the carbon steel in these cases.

2. Literature Survey.

The role of oxygen in the aqueous (neutral or alkaline) corrosion of metals (especially the structural and stainless steels) has been discussed by many investigators; a review of all phases of this complex subject is impossible at the present time. However, several widely accepted volumes or discussions by recognized authorities in the field of corrosion are readily available,^(19, 20, 59, 60) and these have been used profusely to guide this survey of the behavior of carbon steel in oxygenated high-temperature water.

It is probably not inappropriate at the present time to state very briefly and naively that part of the theory of electrochemical attack and passivity of particular interest to this discussion. Iron placed in neutral or slightly alkaline distilled water containing oxygen will be attacked. Cations pass into the liquid as hydrated ions, thus:

Since an excess negative charge is thereby produced on the metal by the accumulation of electrons during the formation of the metal ion, electrical neutrality is preserved by their removal through the cathodic reduction of oxygen at the surrounding area:

This is the familiar electrochemical mechanism of corrosion. If the metal hydroxide is insoluble, it appears where M^{n+} (hydrated) and OH^{-} meet (e.g., rust for iron corrosion).

Many theories of passivity have been proposed; the so-called Generalized Film Theory is not only the one most widely held at the present time but, in much less elegant and general form, was one of the earliest to be proposed. This theory attributes passivity either directly or indirectly to a protective film which includes films of oxygen as well as metal oxide films. The Generalized Film Theory seems to work satisfactorily well for all cases of passivity.

It is apparent that the oxygen activity of the water may be a fundamental factor in the attack of iron. When there is any attack at all (low oxygen activity), the cathodic reaction rate (equation (3)) is proportional to the oxygen activity at the metal surface which in turn is proportional to the rate of diffusion of oxygen in the liquid to the metal surface; this diffusion rate is governed by the concentration of the dissolved oxygen and by the agitation of the aqueous medium. The probability of attack, however, is diminished as the oxygen activity is increased and, ultimately, oxygen becomes a corrosion inhibitor because the anodic reaction (equation 1) is "stifled." Thus, oxygen offers two competing influences.

Evans⁽²¹⁾ has likened the principle of wet-corrosion to the high-temperature scaling of metals in which the rate of reaction is controlled by the movement of cations through the oxide film. Hoar and Evans⁽³⁰⁾ used this principle to distinguish between the two extremes of oxygen supply: (a) in the case of ample supply of oxygen, the cations are arrested at the oxide-aqueous interface by adsorbed oxygen and a new oxide layer is formed; (b) if the supply of oxygen in the liquid is insufficiently rapid to arrest all the cations, which presumably emerge more rapidly where the oxide film contains faults, equations (1) and (2) occur and the limited oxygen supply acts as a depolarizer (equation (3)). The adequacy of oxygen in solution depends upon the rate at which the cation can pass through the film and, therefore, the rate of oxygen supply for inhibition varies for various alloys.

For a specific alloy such as iron or steel, there are at least two ways in which the rate of supply of oxygen to the surface of iron can be made sufficiently rapid to be responsible for passivity. The first of these depends on the relative velocity of the liquid past the iron to supply sufficiently rapidly the required oxygen for the production (and retention) of a protective film; this action requires that film repair keep ahead of film breakdown.^(13, 54, 59, 67)

These investigators whirled iron or steel specimens in distilled water containing oxygen; the samples remained bright and unchanged whereas under static conditions (where oxygen replenishment was poor), similar specimens rusted badly.^(13, 19C, 20, 30, 67)

Velocity is not the only method which can provide oxygen sufficiently rapidly to iron or steel to obtain passivity; a second method is merely to increase

the oxygen concentration sufficiently. Pourbaix⁽⁴³⁾ considered the passivation of iron from a thermodynamic point of view and showed that the behavior of iron depended upon the oxygen content of the solution. Vernon⁽⁶⁴⁾ suggested increased aeration, rather than deaeration, to reduce the corrosion of steel in natural waters or dilute salt solutions on the basis of "Rotor Tests".

The use of high pressures of oxygen to this end has been suggested and discussed at length by Evans^(5, 19d) and Uhlig.^(59, 61) These authors point out that oxygen in high concentration acts as an inhibitor in the corrosion of iron in contrast to its function as a depolarizer at lower concentrations; at high oxygen concentrations, iron becomes more noble and the increased nobility results in a reduced corrosion rate.

In Copson's review⁽¹³⁾ of the effects of velocity on the corrosion (erosion) of iron by water, he points out the interrelating effects of velocity and oxygen concentration. His general review of the published literature emphasizes that passivity of iron can be achieved at sufficiently great oxygen concentrations.

Although this aspect of the behavior of iron in water has been documented to a certain extent in the literature, the vast majority of published work has been concerned with the elimination of oxygen from the system, rather than its introduction. This practice stems, of course, from investigations into water boiler operation where not only are very low generalized corrosion rates and the absence of localized attack desired, but scale formation is to be avoided as well. To achieve these results the boiler feed-water is maintained mildly alkaline and free of oxygen and is usually softened. Oxygen tends to produce pitting and its complete elimination has been the subject of much of the published literature on the attack of steel by water (see, for example, references 19e, 29, 53, 54, 55).

Even a casual inspection of the literature for recent years reveals the presence of a new topic in high-temperature water systems, however. These developments are manifested in research on high-purity water corrosion^(56, 57) and arise from considerations pertaining to nuclear power systems. Much of this work has investigated the behavior of carbon steel in water of very low to undetectable oxygen concentrations.^(50, 68) However, oxygen may be a component of parts of the system due to the radiolytic decomposition of water and

may not be readily eliminated because of its continuous generation during operations;^(4, 31) stainless steel has most often been considered for these applications.⁽¹⁶⁾

From this point of view, from the necessity of pressurization by some gas or vapor in many systems and from the considerations discussed in connection with the oxygenated aqueous thorium oxide slurry system, the literature was surveyed in an attempt to determine just what was known experimentally about the behavior of carbon steel in high-temperature aqueous systems containing oxygen. Since only a limited quantity of literature was scanned, it seemed worthwhile for the purposes of this memorandum to note negative as well as positive information.

About half of the NACE corrosion abstract punch cards were consulted for information on carbon steel in oxygenated water but all references that were discovered in this fashion were to low-oxygen systems related to water-boiler corrosion. It is entirely possible that the search of subdivisions other than the one chosen may be more fruitful. Rather than pursuing this line of approach further, some of the older open literature and some of the newer project literature were reviewed.

It appears that investigations undertaken about 1930 were the beginning of a series which studied the effect of oxygen concentration on the corrosion of steel by water at room temperature. The first of these papers^(14, 22) studied the effect of oxygen concentration on the corrosion-velocity of steel. For dissolved oxygen concentrations in water up to about 7 ml/l*, the corrosion rate appeared proportional to the oxygen concentration; at higher oxygen concentrations (from 7 to 18 ml/l) the rate appeared to level off. A difference in corrosion products was noted for low-oxygen concentrations compared with higher-oxygen concentrations.

One of the first papers to report the effect of truly high oxygen concentrations (by using oxygen pressures greater than atmospheric) was that of Lee.⁽³⁴⁾ He studied the effect of oxygen pressures up to 25 atm on the corrosion of steel and concluded that up to 20 atm, the corrosion rate increased with increasing oxygen pressure: about 20 atm, the corrosion rate appeared

* The approximate solubility of oxygen-saturated water at 20°C is about 30 ml STP/liter of water; for air-saturated water at 20°C, the oxygen concentration is approximately 6.5 ml/liter of water.⁽³³⁾

to diminish with time. The change in the corrosion behavior was accompanied by a change in the nature of the corrosion product which at 25 atm was hard, granular and adhered strongly to the test specimens.

However, in 1936, Bengough and Wormwell⁽⁵⁾ attributed the results of Lee to certain experimental methods and showed that at high pressures, oxygen could act as an inhibitor, greatly reducing corrosion and making the iron passive by virtue of a surface film of oxide.

In 1938, Frese⁽²⁴⁾ published a paper in substantial agreement with the unpublished results of Bengough and Wormwell. Frese's investigation originated in a study of the corrosion of stainless steel by sea water with an attempt to accelerate the attack by increasing the oxygen pressure. When it was found that high oxygen pressures did not increase the rate, the study was enlarged to include the effect of oxygen pressure on the corrosion of mild steel and stainless steel in distilled water and sodium chloride solutions. In distilled water, at 22 - 25°C, mild steel showed a definite maximum in the corrosion rate which occurred at an oxygen pressure below 1 atm; at higher pressures, the corrosion rate decreased. At oxygen pressures below that corresponding to the maximum corrosion rate, the corrosion products were loose and fluffy; at pressures above that corresponding to the maximum corrosion rate, the products were very hard and adherent. This change in the character of the corrosion products and the decrease in corrosion rate at high oxygen pressures suggested the formation of a more protective film at higher oxygen pressures. The data of Frese for the corrosion rate of mild steel in distilled water at 22 - 25°C as a function of the oxygen pressure are plotted in Figure I for reference.

All the investigations cited above concerned the effect of oxygen on the attack of iron or steel in water at room temperature. Information on the effect of high-temperature water on carbon steel in the presence of large concentrations of oxygen is singularly scarce, although results similar in kind, but not in degree, to those at room temperature would be expected.

Breden, Roebuck and coworkers^(8, 49, 50) have investigated the corrosion of many engineering materials and alloys in 500°F (260°C) distilled water and have made more extensive tests up to 650°F (343°C) using the more resistant materials. These reports included tests completed before June 1, 1951, and

Fig. 1. Corrosion of Mild Steel in Rocking Pressure Vessel After 8-Day Exposure To Distilled at 22-25°C. (Data of F. G. Frese, *Ind. Eng. Chem.*, 30, 83 (1938).

were intended to screen materials on the basis of their resistance to environmental factors anticipated to occur in reactor operations. Of the almost 120 metals and alloys tested, Table I summarizes the results reported for A-212 Grade B carbon steel exposed to distilled water at elevated temperatures; these results were taken from reference (8) with a slight transposition and addition of data for clarity. The results indicated that carbon steel appeared "good" in high-temperature water containing a large concentration of oxygen, whereas in water containing much less oxygen, the steel was "poor".

Unpublished data of English⁽¹⁸⁾ confirmed these results which indicated that high-oxygen concentrations were beneficial in the behavior of carbon steel in high-temperature water. Specimens of SAE 1030 carbon steel (0.37% carbon) were exposed in distilled water at 200°C in static autoclaves; two oxygen pressures were used, 25 psi (70 ppm) and 200 psi (530 ppm). The water of lower oxygen content produced an initial (70 hr) rate of 5 - 7 mpy which decreased to 0.5 mpy after 839 hr: the specimen was dull black, possessed a roughened surface and a loose oxide film which was easily scrubbed off. On the other hand, the water with the higher oxygen concentration showed a weight gain of 0.05 mg/cm² after 70 hr and then no further change in weight during the following 769 hr: after the first 70 hr, the specimen possessed a thin blue lustrous film which changed to brown with time. The film was quite adherent, thin, and not bulky.

The work by Breden, et al.⁽⁸⁾ and English⁽¹⁸⁾ comprises all of the information discovered by the author with respect to the behavior of carbon steel in high-temperature highly-oxygenated water. A recent Harwell document⁽⁶⁵⁾ has summarized some recent studies of the corrosion of mild steel in high-temperature water; it is stated that "the effect of oxygen on corrosion (of mild steel) in high-temperature water requires further study."

On the other hand, the studies of many investigators have been directed toward carbon steel in deoxygenated water at elevated temperatures, often using an hydrogen atmosphere or other additives as inhibitors. Such studies were aimed at developing environmental conditions for carbon steel that would give only very mild attack and that would limit, or at least minimize, the release of corrosion products (crud) to the circulating medium. Such investigations have tended to follow the recommendations dictated by experience

TABLE I

Corrosion Data on A-212 Grade B Structural Steel
in Distilled Water. Date of Breden, et al., Water
Corrosion of Structural Materials. October 1948-
June 1951, ANL-4519 (July 15, 1951) p 50, 111.

<u>Temperature</u> <u>°F</u> <u>°C</u>		<u>Time</u> <u>Hr</u>	<u>Atm</u>	<u>Concn.</u> <u>cc/l</u>	<u>Unfilmed</u> <u>mg/cm²/mo</u>	<u>Comments</u>
500	260	338	H ₂	18	- 3.5	Sample covered with faintly lustrous black coating. Some can be rubbed off. Poor.
500	260	338	Degas	-	± 0.00	Sample covered with faintly lustrous black coating. Some can be rubbed off. Rust spots on one face. Poor.
500	260	338	O ₂	30*	- 3.2	Sample covered with faintly lustrous black coating, of which some can be rubbed off. Poor
500	260	2899	O ₂	30*	- 0.52	Sample covered with loose rust. Poor.
500	260	340	O ₂	240**	- 0.44	Sample covered with lustrous black tarnish. Good.
600	316	330	Degas	-	+ 0.16	Black oxide film over entire surface. Good.

* Oxygen dissolved in degassed water at room temperature under partial pressure of 1 atm at start of test.

** Oxygen dissolved in degassed water at room temperature at start of test under partial pressure of 8 atm.

in operating water boilers.

Thus, the Babcock and Wilcox Company Research Center⁽¹⁵⁾ tested further the most promising materials screened in the Argonne National Laboratory tests.⁽⁸⁾ However, apparently because structural steels appeared "poor" in 260°C water containing relatively low oxygen concentrations (Table I), no further testing of carbon steel in any system was undertaken. The ANL screening tests⁽⁸⁾ and the B. and W. results⁽¹⁵⁾ apparently guided a certain amount of the KAPL studies reported by Fowler et al.;⁽²³⁾ these investigations studied the behavior of carbon steel in deoxygenated water, in water of initially low oxygen content, or in systems with a hydrogen overpressure. Studies with corrosion inhibitors (lithium hydroxide or boric acid) were also reported. WAPD^(11, 12) also studied the behavior of steel by operating carbon steel loops at 600°F (316°C) and circulating water containing ammonia with an hydrogen overpressure; other carbon steel loops circulated degassed feed-water of high pH (lithium and ammonium hydroxides) and hydrogen atmospheres. All such tests in high-temperature degassed or hydrogenated water showed that carbon steel was relatively little attacked.^(11, 12, 51) Other work was undertaken to simulate pressurizer operation with a view to the possible use of an unclad carbon steel vessel; the results showed serious corrosion of carbon steel with air-pressurization whereas steam-pressurization (up to 2 to 6 cc of oxygen per kilogram of water) did not produce excessive attack by demineralized degassed water at about 335°C.⁽¹⁰⁾

Two symposia on the corrosion by high-purity water at high temperature were held in 1955.^(56, 57) The basis for both symposia was the use of high-purity water in nuclear reactors. All eight of the technical papers considered carbon steel only in water of relatively low oxygen content, generally degassed and/or hydrogenated.

The known behavior of carbon steel in high-temperature water appeared suitably attractive enough for the Babcock and Wilcox Company to proceed with the design of a carbon steel reactor system. Sufficient knowledge of the critical environmental factors (chiefly, alkalinity and low oxygen concentrations) were believed available to put such a design into practice.^(6, 7)

At least two in-pile tests investigating the behavior under irradiation of carbon steel in water have been completed. The first was undertaken by the Naval Research Laboratory⁽³⁵⁾ which operated a carbon steel loop in the

Materials Test Reactor for 79 days at a water temperature of 575 to 600°F (302 to 316°C) and a pressure of 2200 psi and with flow velocities up to 30 fps. Deionized and deoxygenated water was used, but hydrogen was not added deliberately at any time. However, analyses of dissolved gases showed that the major gas constituent was hydrogen (probably produced both by radiation decomposition of water and by corrosive action); there was considerable disagreement in the analyses for oxygen, but it was believed likely that the concentration was not greater than 0.2 cc/l for the entire run. The pH of the water during normal operation was about 8 and varied from about 7 to 10 for various reasons on several occasions. From the standpoint of weight-change corrosion data, deposition of corrosion products, water purification and accessibility (due to radioactivity in the system), carbon steel appeared to suffer no serious disadvantage compared to stainless steel.

The second in-pile test⁽³⁾ consisted in the operation of three mild steel loops for from 2 to 9 months in the NRX reactor (Chalk River, Ontario) at a water temperature of 85 - 95°F (29 - 35°C) and at flow velocities less than 3 fps. The lowest corrosion rates were obtained when the water was maintained at pH 10.5 with or without oxygen being present; a general attack occurred with no pitting. Severe pitting was observed with pH 7 water containing some oxygen; with oxygen absent, the corrosion rate was several times smaller. The results were summarized by listing the aqueous systems tested in order of increasing corrosiveness: high pH with or without oxygen < pH 7 with oxygen absent and continual purification < no pH control, no purification and oxygen absent < pH 7 with 3 - 5 ppm oxygen.

In conjunction with the carbon steel program at WAPD, in which the feasibility of substituting carbon steel for stainless steel in reactor components was being investigated out-of-pile, screening tests of corrosion inhibitors were undertaken.^(9, 68) These tests were carried out at 600°F (316°C) with A 212 Grade B carbon steel discs rotating at 2 fps peripheral velocity in inhibitor solutions made from demineralized and degassed water (< 0.05 ppm O₂). Most of the inhibitors investigated were not beneficial under the experimental conditions for one reason or another; many simply did not demonstrate inhibitory action. Although morpholine was decomposed by neutron-irradiation and so would not be useful during reactor operation, it did show good inhibition under certain

experimental conditions, although pitting of the metal was observed in many cases. Chromate was also "decomposed" (reduced) at the elevated temperature without irradiation, but the presence of 1 ml O_2 /kg water improved its stability and led to inhibition. Pertechmetate was reduced to TcO_2 under the experimental conditions (including the mechanical failure of the testing facility). Although Brown⁽⁹⁾ listed inhibitors considered to be most effective under the experimental conditions employed, it would appear that if the experimental conditions were modified slightly, other inhibitors not listed would also qualify; thus, anodic inhibitors (e.g. most of those tested) are known not to function in the absence of oxygen.^(26, 37b, 58)

3. High-Temperature Water Studies in Toroids.

From the discussions in the previous section, it is apparent that the behavior of carbon steel in high-temperature water has been studied much more critically when the oxygen content has been very low (degassed, deoxygenated and/or in the presence of hydrogen) than in the presence of high concentrations of oxygen.

Theoretically and experimentally at low temperatures, it appears that very high concentrations of oxygen in pure water can passivate carbon steel (19a, 19d, 59) while the experiments by Breden⁽⁸⁾ and English⁽¹⁸⁾ at elevated temperatures support these observations. The results reported by Reed and Compere^(47, 48) for the behavior of carbon steel in oxygenated aqueous thorium oxide slurries are also in general accord with these other observations, although, the presence of suspended solids may affect the results. Furthermore, the results obtained by circulating aqueous thorium oxide slurries in toroids with oxygen⁽³⁷⁾ gave attack rates for carbon steel indistinguishable from those for stainless steel and titanium.

All of these considerations seemed to demand at least a cursory investigation in toroids of the effect of varying oxygen concentration on the behavior of carbon steel in distilled water at 250°C. Actually, two runs were carried out; the first (Run No. 111) was undertaken in stainless steel toroids previously used to circulate aqueous thorium oxide slurries while the second run (No. 112) employed unused titanium toroids in order to reduce the Cr (VI)

contamination (and, therefore, possible inhibition by chromate) and to avoid the presence of undesirable solids (such as thorium oxide). These runs are summarized in Tables II and III; A 212 Grade B carbon steel was used in both runs.

The presence of solids not arising from the corrosive process (viz., thorium oxide), of the relatively significant amounts of chromate, and of the varying acidity made Run No. 111 not suited to unique interpretation. On the other hand, Run No. 112 did not suffer from these difficulties. Photographs of the pins, as removed from the toroids after Run No. 112, are shown in Figures II through V; of the four A 212 Grade B pins in each toroid, the two pictured show the extremes in appearance. The carbon steel exposed to high-temperature water containing relatively little oxygen (Figures II and III) produced heavy scales of corrosion products which were easily removed, and were identified as being predominantly Fe_3O_4 ; the corrosion rate was 5 to 16 mpy. In contrast the films produced in high-temperature water containing relatively large amounts of oxygen (Figures IV and V) were thin and very adherent, so much so that only a very small amount could be removed for analysis; these films analyzed more $\alpha\text{-Fe}_2\text{O}_3$ than those in the lower oxygen systems. The corrosion rates ranged from 3 to 6 mpy.

It is of interest that in these toroid tests with aqueous systems of varying oxygen content, both a decrease in corrosion rate and a change in appearance of corrosion products were observed for systems very high in oxygen; the two observations are undoubtedly related, of course. Similar observations were reported by Braden⁽⁸⁾ and English⁽¹⁸⁾ for high-temperature systems and by many investigators in room temperature studies.^(22, 24, 34) The discovery of the nature of "films", in general, has been one of great theoretical and practical attention and consequently, a great deal of effort has been devoted to their study. Since a large amount of published work exists describing these studies, a literature review becomes impossible at the present time; the following comments do seem pertinent and within the scope of this memorandum, however.

Many reviews, when discussing corrosion of iron and its alloys, (for example, references (19) and (20)) attempt to describe the appearance of corrosion products and to determine their chemical and physical compositions.^(19f)

FIGURE II

A 212 Grade B Carbon Steel Pins After Exposure for 237 Hr in Circulating (26 fps) Distilled Water at 250°C in Titanium Toroids Containing Approximately 6 psi Oxygen.

A 212 Grade B Carbon Steel Pins After Exposure for 237 Hr in Circulating (26 fps) Distilled Water at 250°C in Titanium Toroids Containing Approximately 30 psi Oxygen.

FIGURE III

A 212 Grade B Carbon Steel Pins After Exposure for 237 Hr in Circulating (26 fps) Distilled Water at 250°C in Titanium Toroids Containing Approximately 90 psi Oxygen.

FIGURE IV

A 212 Grade B Carbon Steel Pins After Exposure for 237 Hr in Circulating (26 fps) Distilled Water at 250°C in Titanium Toroids Containing Approximately 400 psi Oxygen.

FIGURE V

TABLE II

SUMMARY OF TOROID RUN (NO. 111) STUDYING THE EFFECT OF
OXYGEN CONCENTRATION ON THE BEHAVIOR OF CARBON AND
STAINLESS STEELS IN HIGH-TEMPERATURE WATER.

Conditions: Distilled water
250°C
26 fps
192 hr
Type 347 stainless steel toroids (used)

Water Analysis

pH	6.2
Spec. Cond. $\times 10^5$, ohm ⁻¹ cm ⁻¹	0.38
Cl, mg/l	< 1
SO ₄	< 1
Cu	< 1

Toroid	N	O	P	M
ml H ₂ O ₂ (a)	0.0	0.0	1.0	5.0
Atmosphere at 250°C (initial)	H ₂ (b)	O ₂ (c)	O ₂ (+ air)	O ₂ (+ air)
Approximate Pressure, psi/250°C (d)	30	30	90	400
Attack - 347 SS				
mpy (e)	0.3, 0.6	+, +	+, 0.4	+, 0.0
Appearance	Black	Gold to purple	Blue-purple	Blue
Attack - A 212 B				
mpy (e)	5.5, 7.4	4.0, 4.5	8.2, 9.4	4.3, 4.4
Appearance	Gray	Darkened	Very rough surface (due to deposit?)	Brown Mottled
Solution (f)	Colorless	Sl. yellow	Yellow	Very yellow
pH	4.6	3.9	3.2	3.0
Spec. Cond. $\times 10^5$, ohm ⁻¹ cm ⁻¹	6	11	30	35
Cr, mg/l	< 1	8	37	80
Ni	1	2	3	9
Cl	3	2	2	3

- (a) 281 mg H₂O₂/ml.
 (b) Hydrogen gas bubbled through water and toroid.
 (c) Oxygen gas bubbled through water and toroid.
 (d) Calculated assuming zero gas solubility in water.
 (e) Based on defilmed weight of corrosion pins and total elapsed operating time.
 (f) A slight quantity of black solids was present in each solution: X-ray diffraction analysis gave patterns of ThO₂, MoS₂ and SiO₂.

TABLE III

SUMMARY OF TOROID RUN (NO. 112) STUDYING THE EFFECT
OF OXYGEN CONCENTRATION ON THE BEHAVIOR OF A 212
GRADE B CARBON STEEL IN HIGH-TEMPERATURE WATER

Conditions: Distilled water
250°C
26 fps
237 hr
Titanium 75A toroids (new)

Water Analysis

pH	5.5
Spec. Cond. $\times 10^5$ ohm ⁻¹ cm ⁻¹	0.41
Cl, mg/l	< 1
SO ₄	< 1
Cu	< 1
Total solids	3

Toroid	A	D	C	B
ml H ₂ O ₂ (a)	0.0	0.0	1.0	5.0
Atmosphere at 250°C (initial)	Air (b)	O ₂ (c)	O ₂ (+ Air)	O ₂ (+ Air)
Approximate pressure, psi/250°C (d)	6 (O ₂)	30	90	400
Attack - A 212 B				
mpy (e)	5.1, 5.3, 6.9, 12.1	6.4, 7.1, 11.1, 16	2.7, 3.5, 3.6, 6.1	3.0, 3.6, 4.2, 4.8
Appearance	Black scale strongly magnetic	Brown deposits strongly magnetic	Red-brown film less than A and D, thin, adherent; magnetic?	Black film, thin, adherent; possibly red- brown under Teflon, magnetic?
X-ray (f)				
% Fe ₃ O ₄	> 90	60-90	30-70	5-15
% α -Fe ₂ O ₃	-	10-40	30-70	60-90
See Figure	II	III	IV	V
Solution	Colorless	Colorless	Yellow	Yellow
pH	7.1	7.6	7.1	5.2
Spec. Conc. $\times 10^5$, ohm ⁻¹ cm ⁻¹	16	17	15	12
Cr, mg/l	< 1	< 1	8	6
Cl	3	4	1	2
Solids	Black	None	Green-gray	Green-black
Spectrographic (g), %	Fe >>10 Al 0.4 Ti 0.4 Si 0.4 Mo 0.3 Mn 0.2	-	Ti >>5 Si 10 Mo 3 Fe 2 Cr 1 Al 0.6 Ca 0.3 Mg 0.3	Ti >>5 Fe 4 Mo 4 Si 2 Cr 1 Al 0.6 Ca 0.4

FOOTNOTES FOR TABLE III

- (a) 286 mg H_2O_2 /ml.
- (b) Air-saturated.
- (c) Oxygen gas bubbled through water and toroid.
- (d) Calculated assuming zero gas solubility in water.
- (e) Based on defilmed weight of corrosion pins and total elapsed operating time.
- (f) By H. W. Dunn. Samples also sent to T. E. Willmarth.
- (g) Molybdenum probably resulted from contamination of the solution with Liqui-Moly lubricant at the end of the run.

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The identification of corrosion products has been the object of much research: one of the NACE technical committees has recently published a selected bibliography which abstracts much of the work on the identification and composition of corrosion products on stainless steel, zinc, zirconium, titanium and iron and steel.⁽⁴²⁾ Another NACE committee⁽⁴¹⁾ has prepared a bibliography pertaining to methods of identification of corrosion products based on crystal structure and has collected X-ray diffraction pattern data. Much of this work is concerned with the products formed by the reaction of metal and gas and only a portion is devoted to that formed in aqueous exposures, however.

"Film" has been used here in a generic sense to include all surface layers or skins that occur on or at the interface between a metal or alloy and its environment; such "films" range in thickness from monomolecularly adsorbed (by physical or chemical forces) gases to thick oxide scales. The difficulty in distinguishing experimentally between thick oxide films (acting predominantly as a diffusion barrier between the metal and its environment) and chemisorbed films (to which passivity has been ascribed as measured by corrosion resistance and a noble potential) has been described by Uhlig.⁽⁶²⁾ He regards the thick oxide films (isolatable from the base metal) to have arisen subsequent to the formation of adsorbed films and, thus, to be of secondary importance in accounting for passivity and to be unnecessary to any observed corrosion resistance.

From this point of view, the establishment of the nature of the bulk film may actually be immaterial. Ultimately, it would seem that one desired knowledge about both "mechanical" and "electro-chemical" passivity; this terminology is perhaps more aptly descriptive of the gross mechanics of the passivity than others,⁽⁶⁰⁾ although they are fundamentally very closely related. The study of the bulk films, constituting more descriptively the features of mechanical passivity, has been undertaken by many investigators.^(1, 19f, 41, 42, 66) The other extreme is the concept offered by Uhlig⁽⁶²⁾ who considered passivity to be due to a chemisorbed film; the phenomenon of adsorption of gases by solids has been treated extensively.⁽²⁾ The point of view of Uhlig is likely the basis of the concept of electrochemical passivity; however, such an adsorbed film may be of theoretical significance only, since its existence may be essential only for what next occurs upon the exposure of metal and adsorbed film in a realistic environment. Although Uhlig considers such an event of secondary importance in

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accounting for passivity,⁽⁶²⁾ it may be the event of primary importance in establishing the resistance of the metal to the aggressive action of the environment. This, then, is the point where a great deal of work is currently being undertaken. Intuitively, it seems that changes in the environment might alter the integrity of the film; this was suggested by Evans^(19g, 19h, 30) and has been borne out in efforts by many others (for example, see references 36, 45, and 46). Of particular note here is the work of Hackerman who has investigated conditions of film formation and studied their subsequent behavior in corrosive media;⁽⁵²⁾ it was such a study that led to the postulate that rapid initial attack resulted in the deposition of a film composed of fine particles which was relatively less permeable to the medium and, therefore, showed the lowest continuing corrosion rate.^{(27)*} Other fundamental studies of this nature resulted in proposals of ions chemisorbed on an undetectable oxide film⁽²⁸⁾ and of adsorbed anions associated with passive metals.⁽⁴⁴⁾ The concept of "competitive adsorption" was suggested to occur on metal^{oxide} surfaces by Hackerman^(28, 44) and on the metal surface itself by Uhlig.⁽⁶³⁾ Cartledge⁽⁵⁸⁾ has pursued the hypothesis of competitive adsorption even further by considering the relative inhibition of XO_4^{n-} inhibitors and has proposed a specific behavior for chloride ions upon adsorption to account for enhanced corrosion. The investigations of Kraus, et al.,⁽³²⁾ on the ion exchange properties of hydrous oxides should be recalled when considering the competitive adsorption hypotheses that have been advanced to explain the enhancement and inhibition of attack of metals. It appears that both "ion exchange" and "competitive adsorption" may be terms describing no innate difference in mechanism but may arise solely from a different emphasis on end results.

4. Resume'

The behavior of carbon steel in high-temperature water has been well defined.^(19, 59) Much of the knowledge has stemmed from work associated with water-boiler systems^(29, 53, 54) and especially the influence of the components

* J. C. Griess has noted that this concept could account for the results of Table II and Figures II through IV; more adherent films and lower long-term rates were obtained for carbon steel exposed to high-temperature water of relatively great oxygen content compared to low oxygen systems possibly due to more rapid initial attack and the deposition of less porous finer-particle films.

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of the feed-water on the corrosion of steel.⁽⁵⁵⁾ More recently, the use of structural steel in reactor applications has been considered⁽⁵⁷⁾ and this work quite naturally made use of the experience gained in operating water boilers.

Normally, metals or alloys other than carbon steel have been considered for reactor applications especially if water was to be used as the primary heat exchange medium; under radiation, water would be expected to decompose to generate continuously small amounts of oxygen, which would produce a system for which carbon steel would be unsuited. However, carbon steel has been used quite satisfactorily as a material of construction for pump loops circulating high-temperature water both out-of-radiation^(11, 12) and in-pile.⁽³⁵⁾ These studies utilized neutral or mildly alkaline water of very low or zero oxygen content; even in-pile the oxygen concentration of the water was always very small and hydrogen was the major constituent of the dissolved gases. It therefore appears possible to utilize carbon steel in a high-temperature water reactor and thereby gain the advantages of initial economy and availability, ease of construction and fabrication without sacrifice of corrosion resistance.⁽⁷⁾

Such developments have overshadowed the indications that carbon steel possessed good resistance to high-temperature water containing very high oxygen concentrations.^(8, 18) To summarize qualitatively some of the information currently available on systems of carbon steel in water, experimental evidence and theoretical predictions have been reviewed for the systems containing large amounts of oxygen. High-temperature experiments with water^(8, 18) (Section 3) and aqueous thorium oxide slurries^(37, 40, 47, 48) were consistent with previous experimental results at lower temperatures,^(19, 24, 59) in general, the results have shown that carbon steel possessed good resistance to highly-oxygenated water.

A system composed of carbon steel in high-temperature highly-oxygenated water is not one commonly considered and emphatically is not one which eliminates all corrosion problems. The substitution of carbon steel for austenitic stainless steel may merely trade problems related to stress-corrosion cracking induced by chloride ions with cracking induced by hot caustic solutions (so-called, caustic embrittlement). Differential aeration cells or crevice corrosion may be another problem not encountered in other systems while the possibility of

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pitting attack by chloride must also be considered. Some of these problems can perhaps be solved by proper selection of pH⁽³⁾ or inhibitors^(26, 58) or other variables.^(16, 27) The utility and limits of such a system can be established only through extended experimentation.

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