

Passivation in Steam Generating Systems

LORAINÉ A. HUCHLER, P. E., CMC[®], FIMC
MarTech Systems, Inc.
Exmore, NJ

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ABSTRACT

The term "passivation" has been applied to a wide variety of conditions, ranging from the strict electrochemist's definition of electrochemical potentials to the operator's measurement of soluble and insoluble iron in the boiler system. Other definitions include the existence of a tight, adherent iron oxide film or environmental conditions of minimum iron solubility (i.e., minimum corrosion). If the definition of passivation is the conversion of oxides to hematite, maghemite, or magnetite, then a reduction reaction must have occurred. If the definition of passivation is the creation of a tight, adherent oxide film from the substrate metal, then an oxidation reaction occurred – that's corrosion! How can passivation be both an oxidation reaction and a reduction reaction?

Despite the various descriptions, the objectives are the same: to create conditions that minimize the corrosion of iron. This paper will describe the basic chemistry of iron oxides in boiler systems, the postulated corrosion mechanisms, the thermodynamic and kinetic conditions that control iron oxide formation in boiler systems, the effects of dissolved oxygen and chemical oxygen scavengers on these system conditions, and some passivation/corrosion measurement techniques.

INTRODUCTION

Some researchers have defined passivation as the absence of corrosion, with no reference to the nature of the metal surface. Other researchers have defined passivation as the creation of a barrier to additional oxidation. If the definition of passivation is the conversion of an oxide to magnetite, then a reduction reaction must have occurred. If the definition of passivation is the creation of a tight adherent oxide film from the substrate metal, then an oxidation reaction occurred – that's corrosion! Are there two mechanisms of passivation: an oxidation reaction or a reduction reaction? The current - and sometimes contradictory - information about corrosion and passivation in steam generating systems includes the basic chemistry of iron oxides in boiler systems, postulated corrosion mechanisms, the thermodynamic and kinetic conditions that control iron oxide formation, the effects of dissolved oxygen and chemical oxygen scavengers, and some passivation/corrosion measurement techniques.

DISCUSSION

CHEMISTRY OF IRON AND IRON OXIDES - In most boiler systems, iron is in the form of carbon steel. The formation of iron oxides is a spontaneous process that occurs continuously on all steel surfaces. Environmental conditions control the conversion of iron to iron oxides and the conversion of one oxide to another oxide. Table 1 shows the four forms of iron oxides that exist in boiler water systems. (Naval Research Lab, 1969; Troy, 1978)

Ferrous hydroxide ($\text{Fe}(\text{OH})_2$) is fairly soluble; however, it can exist as a gel-like material that frequently adheres to filters. Ferrous iron dissolved in acid has a yellowish color. Adding caustic creates a green suspension of ferrous hydroxide. Ferrous hydroxide forms at temperatures below 50°C (122°F). If system conditions are favorable and the temperature is above 50°C (122°F) ferrous hydroxide can convert to magnetite.

All forms of $\text{FeO}(\text{OH})$, including goethite and lepidocrocite, have low solubilities in water and – in the absence of an underlying layer of magnetite - exist as a porous, unstable oxide layer and is easily disrupted by mechanical or chemical processes. In systems where lepidocrocite exists, particulates trapped on a submicron filter (e.g., a $0.45\ \mu\text{m}$ MF-MilliporeSigma™ filter¹) will have a yellow-orange coloration. Under certain conditions, lepidocrocite can convert to magnetite.

Table 1 – Iron Oxides in Boiler Systems

Oxide	Crystal Form	Mineral Name	Thermal Behavior
$\text{Fe}(\text{OH})_2$		Ferrous Hydroxide	Above $50\text{-}100^\circ\text{C}$ ($122\text{-}212^\circ\text{F}$), decomposes to Fe_3O_4 and $\text{H}_2(\text{gas})$; with low $[\text{O}_2]$, transforms to Lepidocrocite
$\text{FeO}(\text{OH})$	Alpha	Goethite	Above 200°C (392°F), dehydrates to hematite
	Beta	Lepidocrocite	Above 230°C (446°F), dehydrates to hematite
	Gamma		Above 200°C (392°F), dehydrates to hematite
Fe_2O_3	Alpha	Hematite	Above $1300\text{-}1457^\circ\text{C}$, dehydrates to hematite
	Gamma	Maghemite	Above 250°C (482°F), dehydrates to hematite
Fe_3O_4		Magnetite	

¹ The life science business of Merck KGaA, Darmstadt, Germany operates as MilliporeSigma in the US and Canada.
https://www.emdmillipore.com/US/en/product/MF-Millipore-Membrane-Filter-5m-pore-size,MM_NF-SMWP04700

Hematite is insoluble in water; the environmental conditions of the boiler system control the integrity of the oxide layer – from a porous and easily disrupted form to an adherent and relatively stable form. In systems where hematite exists, particulates trapped on a submicron filter will show a brick-red coloration.

While more soluble than hematite, magnetite is also relatively insoluble in water. Like hematite, magnetite may form a porous, oxide layer or a stable, protective oxide layer based on the environmental conditions. Unlike hematite, however, magnetite forms a dense matrix that closely matches the lattice structure of the underlying steel surface, minimizing the mechanical stresses at the interface.

The formation of a continuous, adherent layer of magnetite is a desirable form of iron oxide in boiler systems because it protects against corrosion of carbon steel. In systems where magnetite exists, a submicron filter will show a black coloration. The conditions that favor the conversion of these oxides to magnetite are discussed in the "Magnetite Formation" section.

All iron or carbon steel surfaces have a surface layer comprised of a single oxide or a mixture of oxides. A widely-accepted description of this oxide layer is a crystalline structure that is permeable to ion transport. (Ferreira, 1991; Tjong, et al., 1981; Bloom et al., 1965; Foley et al., 1967)

One theory describes the oxide layer as being comprised of two distinct layers: a thin, adherent, homogeneous inner layer and a less dense, less adherent, heterogeneous, or homogeneous outer layer. (Potter et al., 1961; Wagner, 1973; Nagayama et al., 1962) Another theory postulates a polymeric hydrated oxide in which water acts as a binder between the polymeric oxide chains to create an amorphous, single-layer structure. (Okamoto, 1973) The conditions that favor the formation of these oxide layers are discussed in the section "The Effects of System Conditions." These oxide layers may or may not be protective, depending on the physical conditions of the system during and after the formation of the oxide layer.

CORROSION - Most definitions of corrosion include the concept of the dissolution of a metallic material by chemical or electrochemical reaction with its environment. Corrosion is considered an electrochemical reaction because electrical currents can be measured in the areas where dissolution is occurring. Electrochemical reactions result in a network of localized short-circuited electrolytic cells on the metal surface. At the anode area of the iron surface, Eq. (1) occurs. (Uhlig, 1948)



At the cathode, one or Eq. (2) and Eq. (3) occur based on the presence or absence of dissolved oxygen.



Each half-reaction has an electrochemical or oxidation/reduction (redox) potential. These redox potentials are related to the change in the free energy of the system (i.e., the thermodynamics) and are temperature-dependent. The larger the difference between the redox potentials, the higher the reaction rate. Thermodynamic principles dictate that all reactions will proceed spontaneously (automatically) toward a state of the lowest free energy or equilibrium. As Fontana states, "Corrosion will not occur unless the spontaneous direction of the reaction indicates metal oxidation." (Fontana et al., 1978)

Combining Eq. (1), Eq. (2), and Eq. (3), reactions in Eq. (4) through Eq. (7) define the corrosion process in boiler systems that have an alkaline aqueous environment and operate at saturation temperatures. Corrosion is an electrochemical reaction because water, and dissolved oxygen or

acid salts, such as chlorides and sulfates, form electrolytes that cause corrosion reactions to occur. (Flis, J., 1991) All of these reaction rates increase with increasing temperature.



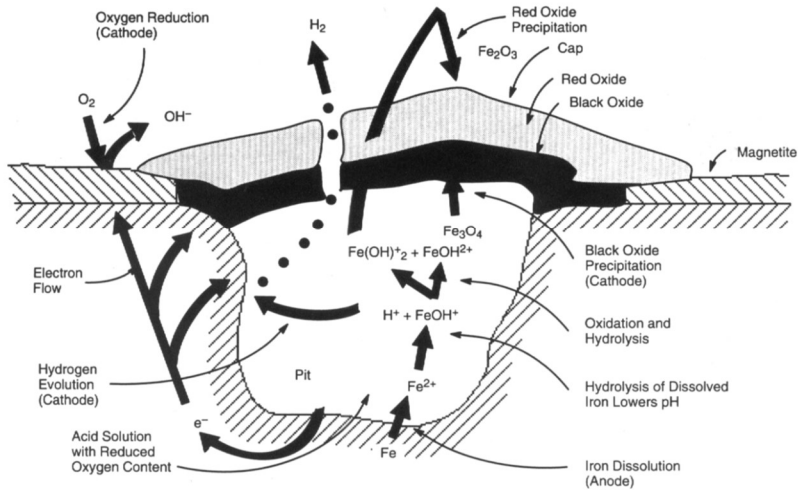
With respect to passivation, the corrosion reaction in Eq. (4) is favorable because newly-formed magnetite may be protective. The corrosion reaction in Eq. (5) may be unfavorable because hematite can be less protective than magnetite. In the presence of dissolved oxygen and/or acid salts, these corrosion reactions may occur in a very localized manner, forming stable corrosion sites known as pits. Oxygen pitting creates an oxide layer above the corrosion site (Figure 1); this oxide layer isolates the solution inside the pit from the bulk water. The corrosion process inside the pit is self-sustaining and will proceed until the removal of the oxide cap. If the concentration of acid is sufficiently high, iron ions can remain soluble, and the pits may progress without forming an oxide cap. Another type of corrosion, stress corrosion cracking (SCC) may occur across and along grain boundaries of elements or at locations where impurities substitute for the expected constituents in the crystalline lattice structure. (Flis, 1991)

A commonly-accepted mechanism for iron corrosion is a two-stage process: initiation of stable corrosion sites and progression of these microscopic pits into larger and deeper pits. (Tjong, (1981) There are several models that describe the mechanism of corrosion. (Nishimura et al., 1981; Rozenfeld et al., 1964; Heine et al., 1965; Hoar, 1965; Sato 1971, 1982) Typically, corrosion is considered a heterogeneous (i.e., two-phase) electrochemical process involving charge transfer and mass transport. (Field et al., 1965; Castle et al., 1966; Marsh, 1966) The corrosion mechanism starts with charge transfer hydrolysis (Eq. (1) and Eq. (8)): electrons moving through the solid metal substrate, the oxide layer(s), and into the aqueous layer.



Eq. (8) liberates hydrogen ions, reducing the pH of the aqueous solution inside the corrosion pit. Eq. (9) produces hydrogen gas that may travel through the oxide layer (tubercule) and evolve into the bulk water.

Figure 1 – Corrosion Pit in the Presence of Oxygen



The corrosion mechanism proceeds with mass transport, reacting ferrous hydroxide ions with iron hydroxide to form magnetite. This magnetite layer is forming under low pH conditions due to the evolution of hydrogen ions as shown in Eq. (10). Practitioners know that the black appearance of an oxygen pit is empirical evidence of active corrosion; a grey appearance is empirical evidence of past corrosion activity.



Depending on the system, the rate-controlling reaction for pitting corrosion might be the charge transfer step, hydrolysis, or mass transfer steps.

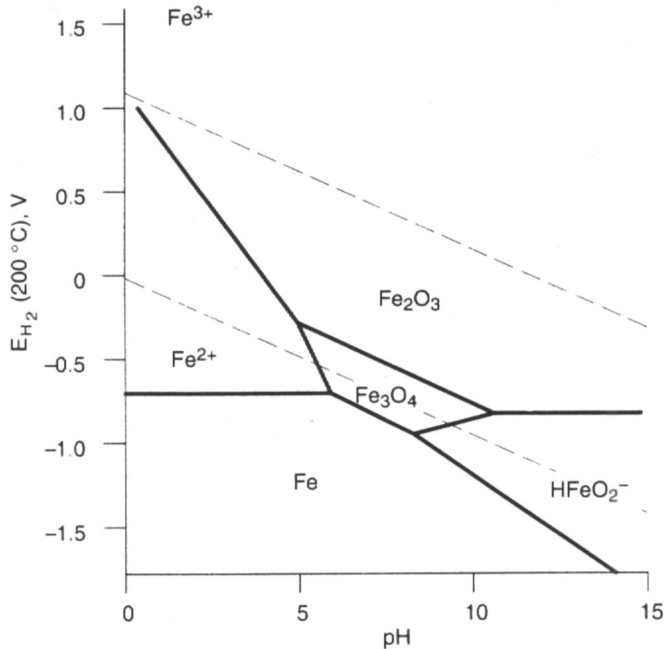
In most areas of the boiler system, the charge transfer is the limiting factor for the corrosion rate because the mass transfer rate is high. Consequently, the recirculating boiler water removes the corrosion reaction product, ferrous hydroxide, from the surface. As the concentration of the corrosion products decreases at the corrosion site, the thermodynamic forces re-establish equilibrium concentrations of the reactants, driving the reaction in Eq. (10) to the right and increasing the corrosion rate. (Castle et al., 1966).

This type of corrosion is known as erosion-corrosion or flow-assisted corrosion. The corrosion rate or kinetics of erosion-corrosion depends on the flow velocity, water chemistry, temperature, and chemical composition of the steel. (Huijbregts, 1984) The corrosion rate also depends on the magnetite film thickness. (Flis, 1991) Various investigators have postulated mechanisms describing the method of dissolution and diffusion between the iron substrate, inner layer, outer layer, and aqueous phase. (Bessone et al., 1975; Bech-Nielsen, 1976; Engell, 1977; Bonhoeffer, 1953; Weil et al., 1955)

To illustrate the principles of thermodynamics as they apply to corrosion phenomena, Dr. M. Pourbaix created electrochemical potential-pH plots. These plots, known as Pourbaix diagrams, show the oxidation states and oxide compositions that are thermodynamically stable, (i.e., have the lowest free energy) as a function of pH, electrochemical potential, and temperature. Figure 2 shows the equilibrium iron-water system at 200°C (414°F). These Pourbaix diagrams enable the prediction of the spontaneous direction of chemical reactions and an estimate of the composition

of reaction products. These diagrams also enable the prediction of environmental changes, such as the pH, that impact the direction of the reactions, i.e., the creation or dissolution of the metal and metal oxides.

Figure 2: Pourbaix Potential-pH Diagram, 200°C²



These Pourbaix diagrams do not predict the integrity of the oxide film or the kinetics (reaction rate).¹² As described in the section, "The Effects of Reducing Agents," system conditions such as pH and dissolved oxygen concentration influence the integrity of the film and the kinetics. For example, the rate of Eq. (2) will increase with decreasing pH ($\text{pH} = -\log[\text{H}^+]$) because pH measures the concentration of hydrogen ions. Likewise, the rate of the cathodic reaction (Eq. (3)) will increase with increasing concentrations of dissolved oxygen. However, these diagrams do not contain any information about the severity of the corrosion, i.e., pitting or SCC, or any information about corrosion mechanisms.

MAGNETITE FORMATION - Various mechanisms have been postulated to describe the formation of magnetite. There are two categories of mechanisms: *in-situ* conversion of the existing substrate to magnetite versus oxide transport and conversion to magnetite. System thermodynamics control the probability of the formation of magnetite while kinetics control the rate of formation of magnetite. Optimizing system conditions such as temperature, pH, concentration of reactants, and dissolved oxygen will improve both the thermodynamics and kinetics - and the probability and rate of formation of magnetite.

Under thermodynamically-favorable conditions, magnetite formation is spontaneous through the oxidation of the iron surface, as described by Eq. (11). "Spontaneous" formation does not necessarily imply a fast process; the kinetics will control the rate of the reaction.

² Corrosion Science, Volume 10, H. E. Townsend, 343 (1970), Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, UK



There are several different mechanisms proposed for the formation of magnetite from iron or other oxides. The best-known mechanism for the reduction of ferrous hydroxide to magnetite above 100 °C is the Schikorr Reaction (Eq. (12)). (Schikorr, 1933)



Investigators at the Naval Research Laboratory (NRL, 1956) proposed a mechanism for the formation of ferrous hydroxide through the corrosion of iron metal (Eq. (13)).



The conversion of hematite or maghemite to magnetite can occur through slow heating, with minimal or no oxygen present (Eq. (14)). (Troy, 1978)



This *in-situ* conversion of the existing substrate to magnetite occurs under thermodynamically-favorable conditions. Electrochemical potential describes the conditions that thermodynamically favor the formation and maintenance of magnetite. Pourbaix graphically illustrated all reactions that are theoretically possible and impossible for various electrode potentials and pH conditions for iron and iron oxides (Figure 2).

Although Pourbaix's diagram shows all of the reactions that are thermodynamically possible, not all reactions will necessarily occur due to a large "over-potential" or electrochemical energy barrier. Even if the system conditions (i.e., electrochemical potentials) are favorable to the formation of magnetite, the degree of protection against corrosion depends on the kinetics of the reactions and on the physical nature of the magnetite layer (e. g. density, oxide integrity, and thickness). As Pourbaix states, (Pourbaix, 1966) "passivation thus does not necessarily imply the absence of corrosion."

In boiler systems, oxides such as ferrous hydroxide and hematite may precipitate onto a surface; under favorable system conditions, these oxides may convert to magnetite. (Hoar, 1949) Several Russian researchers (Margulova et al., 1983; Moskvina et al., 1989) have suggested a mechanism for epitaxial growth of a protective oxide film at temperatures above 250°C (482°F). The decomposition of a specific ligand forms secondary compounds (oxides of iron), followed by a protective two-layer oxide film on the surface of pearlitic steels. The inner layer of magnetite forms by contact between the decomposing chelate and steel. The outer layer forms by contact of the iron chelate with the inner layer.

One of the conditions for the formation and maintenance of a dense, protective magnetite layer is that the system conditions must be at the minimum solubility of magnetite. A practical application of this concept of magnetite solubility is congruent or coordinated pH/phosphate control for high-purity boiler water. The specification ranges for pH on the coordinated pH/phosphate control chart are consistent with the minimum solubility of magnetite in water as a function of temperature (i. e. operating pressure). Similarly, EPRI's guidelines for the specification ranges for dissolved oxygen and pH of feedwater, condensate, and boiler water are also consistent with the system conditions of minimum solubility of magnetite.

THE EFFECTS OF SYSTEM CONDITIONS - The environmental conditions of a specific system can significantly impact the corrosion rate or degree of passivation. There are several categories of environmental effects: mechanical, thermal, and chemical.

Mechanical stresses can affect the integrity of the oxide layers. For example, high-velocity flows,

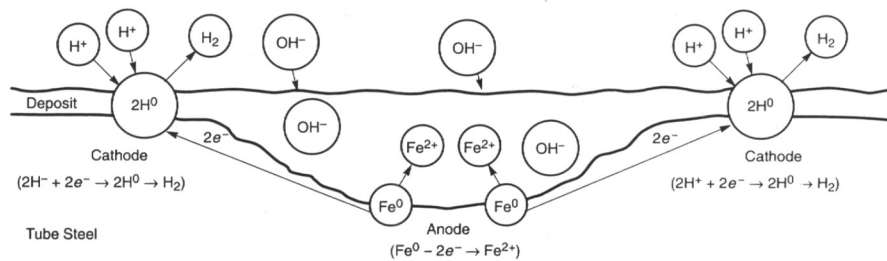
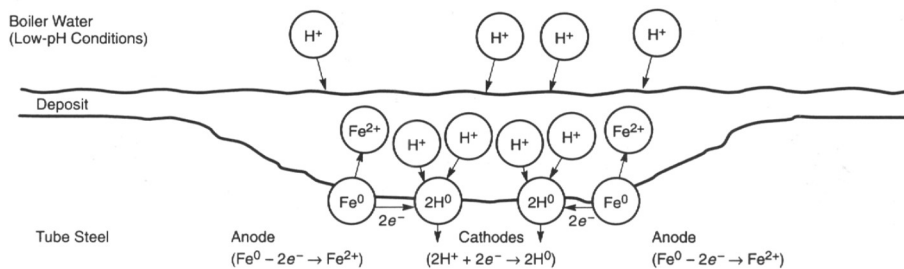
especially in the feedwater and condensate circuits, can cause erosion of the iron oxide layer by the mechanisms of flow-assisted corrosion (FAC) or erosion-corrosion. The loss of a non-protective oxide layer, such as ferrous hydroxide, prevents the conversion to a more protective oxide layer under future, favorable environmental conditions. The kinetics of the FAC process increase when the concentration of dissolved oxygen is below the minimum “safe” specification limit. European practitioners often intentionally increase the concentration of dissolved oxygen to reduce the rate of the erosion-corrosion process by matching the local mass transfer coefficient to the rate of erosion of the surface. (Woolsey et al., 1986) Mechanical effects can also result from unrelieved stresses created during the manufacture or repair of structural steel. These stresses physically disrupt the protective metal oxide layers, creating sites where corrosion may occur.

The temperature of the system strongly influences the speed of the passivation reaction. As described by the Schickor reaction (Eq. (12)), magnetite formation occurs through a reduction reaction at temperatures above 50-100°C (122-212°F). When the system temperature is too low, the formation of magnetite is imperceptibly slow, if it occurs at all.

Thermal effects can occur in conjunction with mechanical stresses. For example, rapidly changing steam loads cause temperature fluctuations in the boiler system metallurgy. This phenomenon, known as thermal cycling, causes the heat transfer rates and surface temperatures to rapidly change, resulting in the expansion and contraction of the steel boiler tubes. Predictably, the steel substrate expands and contracts at a rate that is different from that of the iron oxide layers, causing exfoliation. Superheaters are especially vulnerable to the effects of thermal cycles, creating excessive growth of oxide layers (including magnetite) and subsequent exfoliation. (Dooley, 1978) There are also chemical effects that can contribute to corrosion. All oxide layers, including a protective magnetite layer, have some porosity. When boiler water diffuses through the magnetite layer to the iron layer, Eq. (15) occurs.



The consumption of the water molecules that have diffused through the magnetite layer results in a localized concentration of any other species in the surrounding solution. These ionic species (hydrogen, hydroxides, sodium, chlorides, carbonates, nitrates, sulfates, phosphates, and dissolved oxygen) create an electrochemical circuit that allows large currents to flow through a highly conductive magnetite layer, initiating localized corrosion. (Field et al., 1963) As shown in Figure 3, localized high concentrations of caustic can cause a type of corrosion known as “caustic gouging.” Upsets in boiler water chemistry that result in a pH depression may cause corrosion by hydrogen ions (Figure 4).

Figure 3: Caustic Corrosion³Figure 4: Hydrogen Ion Corrosion⁴

For high-pressure boiler systems using ultra-purified feedwater European researchers developed “Oxygenated Treatment.” These boiler systems require precise control of the concentration of dissolved oxygen and very low concentrations of ionic contaminants in the boiler feedwater to convert iron and iron oxides to a protective layer of hematite or a mixture of magnetite and hematite. Eq. (16) shows that the reaction of oxygen with iron produces hematite.



The goal of this treatment is to prevent the reductive dissolution of magnetite by maintaining a hematite-rich outer layer. However, failure to strictly control the concentrations of ionic species and dissolved oxygen can degrade protective oxide layers, resulting in carbon steel corrosion and the formation of non-protective iron oxides. The requirement for strict control of concentrations of ionic species and dissolved oxygen in the boiler system makes oxygenated treatment inappropriate for most industrial boilers. Consequently, the guidelines for industrial boilers specify very low concentrations of dissolved oxygen in the feedwater (ASME, 1994).

THE EFFECTS OF REDUCING AGENTS - The purpose of reducing agents, more commonly known as oxygen scavenger chemicals, is to reduce, but not eliminate, the concentration of dissolved oxygen in the boiler feedwater system. Creating and maintaining a protective magnetite oxide layer requires a very low concentration of dissolved oxygen to create the optimal

³ Electric Power Research Institute. EPRI CS-3945. Manual for Investigation and Correction of Boiler Tube Failures. ©1985.

⁴ Ibid.

thermodynamic conditions in the boiler feedwater system. The performance of oxygen scavengers depends on several parameters: the reducing power of the scavenger chemical, the kinetics of the reaction (e.g., temperature, pH, reactant concentrations), the catalyst, and the reaction rate.

Oxygen scavengers react with dissolved oxygen through a reduction reaction. Corrosion by dissolved oxygen is an oxidation reaction. Thus, the electrochemical (thermodynamic) measure of these reactions, or the redox potential, can be measured to identify the favored reactions. The redox potential of an oxygen scavenging reaction is known as the reducing power of that oxygen scavenger. The reducing power is one of several factors controlling the rate of reaction and subsequent reduction in the rate of corrosion.

Overfeeding any oxygen scavenger creates a reducing environment that can inhibit the *in-situ* formation of a non-porous, adherent magnetite layer from hematite or iron. Researchers have proven that one class of oxygen scavengers (hydrazine and carbohydrazide) will directly interact with iron and iron oxides to form magnetite; however, the results are less conclusive with other oxygen scavengers. (Schmidt, 1984)

The kinetics of the oxygen scavenging reaction determines the rate of reaction. Adjusting the temperature, pH, catalyst, and concentrations of the reactants and products will change the kinetics. As temperatures decrease, the reaction rate of all oxygen scavengers decreases. Reductions in the reaction rate risk increasing the dissolved oxygen concentration and the subsequent corrosion rate because boiler feedwater systems have a fixed residence time. Kinetics also control the rate of magnetite formation. At temperatures below 100°C (212°F), the rate of magnetite formation decreases dramatically. Thus, the reaction rate or kinetics is another factor directly limiting corrosion and increasing the rate of magnetite formation.

Options for optimizing the kinetic conditions include the addition of a catalyst, changing the system temperature or pH, choosing an alternate scavenger that has a higher rate constant, and/or increasing the scavenger concentration to reduce the concentration of dissolved oxygen and reduce the rate of oxygen-related corrosion. Changing the system conditions to improve the reaction kinetics will change the electrochemical potential (thermodynamics) to a certain degree. The laws of thermodynamics, however, are inviolable: system changes that improve the kinetics cannot overcome unfavorable thermodynamics.

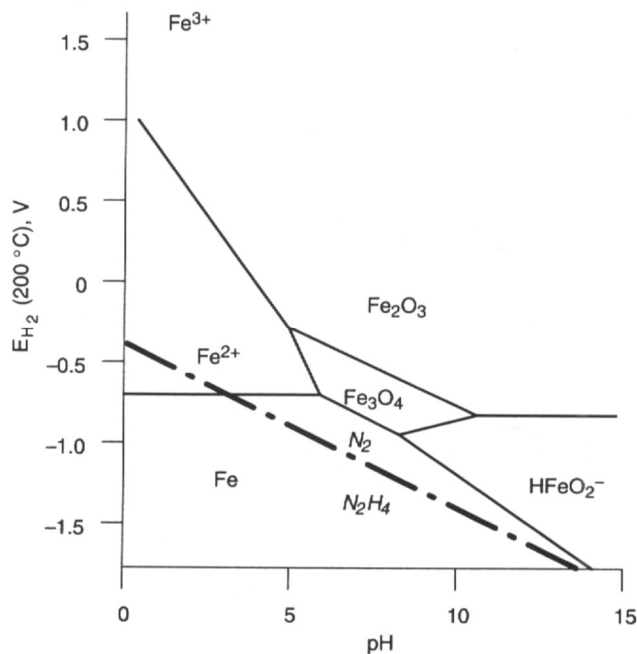
For industrial feedwater systems, the presence of an oxygen scavenger, consistently low concentrations of dissolved oxygen, and subsequent reduction in the corrosion rate seem like a reasonable definition of passivation; however, the evidence is mostly indirect. As described earlier, the Pourbaix diagram in Figure 2 shows the thermodynamic conditions that favor the conversion of the iron oxides to magnetite. Figure 5 shows that, in the presence of the oxygen scavenger hydrazine, the electrochemical potential increases, thereby improving the thermodynamic condition or driving force that favors the conversion of iron oxides to magnetite. Straub has documented the reaction of hydrazine with ferric oxide and its hydrated forms to form magnetite (Eq. (17)). (Straub, 1957) This reaction can occur in the presence of dissolved oxygen if the electrochemical potential and pH of the system are in the region where the Pourbaix diagram predicts the formation of magnetite.



The rate of the reaction in Eq. (17) may depend on the crystal structure and the degree of hydration of the oxide. In other words, the kinetic conditions control the oxide conversion rate. Under the optimal conditions, the reduction of hematite to magnetite is rapid above 140°C (284°F). (Straub, 1957) Researchers have not proven that the magnetite formed in the presence of hydrazine is always protective in a boiler system. However, given favorable thermodynamic conditions, these

observations support the conclusion that passivation can occur due to the presence of hydrazine. Thus, the primary role of oxygen scavengers is to reduce the concentration of dissolved oxygen to the optimal concentrations to control oxygen-related corrosion. The secondary role is to directly – or indirectly – enhance the conversion of iron oxides to protective oxides such as hematite, maghemite and magnetite. Controlling the concentration of oxygen scavengers is especially important in areas of the boiler like the condensate and feedwater systems where dissolved oxygen is present or the rate of magnetite conversion is not optimal due to temperature. Oxygen scavengers are not as important in areas such as the boiler drum that has a very low concentration of dissolved oxygen and/or operates at high temperatures (e. g. above 140°C (284°F)).

Figure 5: Potential-pH Diagram, 200 °C with Hydrazine⁵



MEASUREMENT OF CORROSION/PASSIVATION PHENOMENA - There are several laboratory and field measurement methods for corrosion/passivation phenomena in boiler systems. The laboratory methods include measuring the chemical composition, physical configuration, and electrochemical characteristics of the oxide layers both *in-situ* and *ex-situ*. The field methods include system-wide measurements of the corrosion and passivation reaction products of the iron/water system and *in-situ* evaluation of corrosion rates.

Researchers generally agree that an oxide layer's resistance to corrosion is partially dependent on the nature of the crystalline structure. The more perfect the lattice, the more protective the film. There are a variety of techniques to evaluate the crystalline structure and chemical composition of oxide films. These *ex-situ* techniques use samples removed from the boiler or simulated boiler system. Electron diffraction (Cohen, 1952, 1974; Foley et al., 1967) is a common method to determine the specific oxides of iron and the crystalline structure of oxide films. The primary limitation of electron diffraction is the inability to discriminate between magnetite and gamma-

⁵ Ibid.

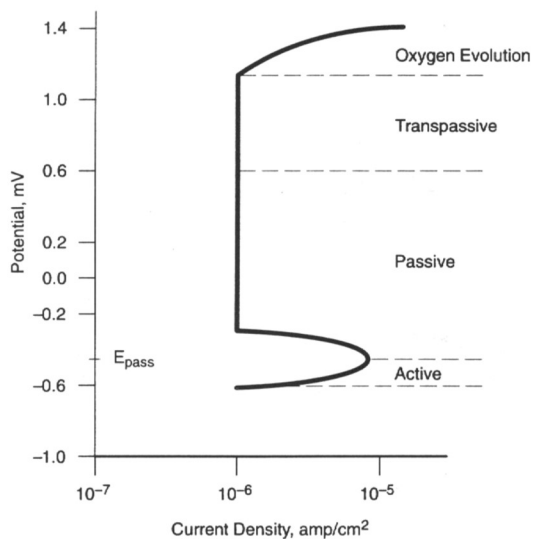
hematite; however, researchers have shown that they can qualitatively evaluate the integrity of the crystalline structure. (Szklańska-Smiałowska, 1986)

Ellipsometry is an optical method that evaluates the integrity of an oxide layer. This analytical technique uses the change in the states of polarization of light reflected from a surface to indirectly measure the thickness and crystalline structure of the oxide layer. Researchers have conducted extensive *ex-situ* studies of the optical spectra of a variety of iron oxide films. (NRL, 1989) This surface measurement is suitable for various aqueous system conditions or as an *in-situ* method to evaluate the time-dependent and temperature-dependent changes in the oxide layer thickness. While this method can distinguish the type of oxide (i.e., Fe_3O_4 , Fe_2O_3), it cannot verify that the oxide layer is protective against corrosion.

Potentiodynamic polarization is an analytical method that evaluates the resistance to electron flow (current) as a function of a change in the electrochemical potential. The corrosion process requires the movement or flow of electrons. The higher the resistance to electron flow, the more limited or polarized the rate of the corrosion reaction. (Fontana et al., 1978) Thus, the rate of change of the current correlates to the degree of oxide layer protection, i.e., the oxide thickness and integrity.

A typical scan of a perfectly passivated surface is shown in Figure 6. (NRL, 1989) In the region labeled active, the behavior of the material is identical to the base metal. No oxide film is present and metal dissolution (corrosion) will occur. As the potential is increased, the current and hence the corrosion rate peaks rapidly and falls at the boundary of the passive region. This initial oxidation corresponds to the formation of an oxide layer that is protective against further oxidation (corrosion) as the potential increases through the passive region. As the potential increases through the transpassive region, the oxide layer is no longer a physical barrier to corrosion and the corrosion rate will increase. (Fontana et al., 1978) As the potential is increased, additional oxygen evolution will occur on the outside of the film. (Dooley, 1978) Thus, the higher the potential required to enter the transpassive region, the more protective the oxide. Researchers often use potentiodynamic polarization in conjunction with ellipsometry to characterize the protectiveness of the oxide layer. (NRL, 1979)

Figure 6: Potentiodynamic Polarization Curve, Perfectly Passivated Surface⁶



⁶ M. Nagayama and M. Cohen, J. Electrochem., Volume 109, 781(1962)

Researchers have studied the dynamics of the growth of oxide layers using electron diffraction, X-ray emission techniques, and ellipsometry. (Brundle, 1977) Other techniques for measuring the chemical and crystalline structure of oxide films include Auger and LEED-Augur spectroscopy, and ESCA (Electron Spectroscopy for Chemical Analysis). Researchers have also used an *in-situ* technique, Mossbauer spectroscopy, to study the crystalline structures of protective oxide films. (Simmons et al. 1973; O'Grady et al., 1973)

These studies of oxide layers have an important limitation: researchers must conduct these measurements under laboratory conditions, instead of field conditions. Consequently, the test results will reflect changes in the oxide layers relative to a set of standard conditions. Although the studies of passivation phenomena in aqueous solutions with a high ionic concentration in the laboratory are common techniques, researchers should cautiously extrapolate the laboratory results to specific boiler systems.

All of the laboratory methods are able to measure the nature and integrity of the oxide layer and evaluate the degree of protection or passivation. In contrast, all the field measurements are direct measurements of system corrosion rates and indirect measurements of the integrity of the passive oxide layer. Field test methods that are very familiar to boiler operators include measurements of particulate (insoluble) iron, soluble iron, and corrosion coupons in the boiler feedwater, condensate, and boilerwater. All field test methods of water chemistry require sampling systems that provide a representative, cooled water sample to obtain an accurate test result. The specific design and operation of these systems are beyond the scope of this manuscript.

Some professionals advocate the use of the measurement of dissolved hydrogen gas concentrations as evidence of active corrosion because some corrosion reactions will liberate hydrogen gas. ((Eq. (18) and Eq. (19)).



Some reduction reactions of iron and iron oxides create protective oxides and evolve hydrogen gas; one example is the Schickor Reaction (Eq. (12)). Consequently, conducting hydrogen tests in the boiler water is not a reliable measurement of corrosion because both corrosion and passivation reactions can produce hydrogen gas.

A common field test measurement of particulate (insoluble) iron concentrations is an empirical method that requires filtering a standard volume of water through a 0.45-micron filter. Boiler manufacturer Babcock and Wilcox developed standard charts that correlate the color of the iron oxides on the filter to the type of oxide, e.g., magnetite, hematite, or a mixture of these oxides. These charts also correlate the intensity of the color with the concentration of iron oxides. MilliporeSigma™ sells these Color Standards Charts through various distributors.

Other field analytical methods include colorimetric and spectrophotometric techniques that measure soluble and reactive iron. Measurement of reactive iron is different than particulate (insoluble) iron. The test method for reactive iron uses a standardized aliquot of an acidic reagent to dissolve iron particulates. The kinetics of the iron dissolution reaction depends on the concentration, size, particulate morphology, and oxide type. Professionals should select the field test for insoluble iron based on site-specific requirements.

Common laboratory spectroscopic techniques include atomic absorption (AA) and inductively-coupled plasma (ICP)). Sample preparation such as acid digestion will allow direct measurement of total iron concentrations by these methods. The difference between the total and soluble iron concentrations is the concentration of insoluble iron. Guidelines from the American Society of

Mechanical Engineers (ASME) (ASME, 1994, 2006) and the Electric Power Research Institute (EPRI) (EPRI, 2020) provide specification limits for the concentration of total iron and sampling methods.

As described earlier, corrosion is a localized phenomenon. Measurements of soluble, reactive, and particulate iron are system-wide parameters. Consequently, professionals can make only limited conclusions regarding the specific location of corrosion based on these test methods.

The last field method to evaluate the degree of corrosion within a boiler system is a corrosion coupon. The ideal configuration is a bypass rack that allows adjustment of the sample flow rate. The coupons should match the materials of construction of the components in the boiler system (e. g. iron, copper, copper alloys, stainless steel). The objective of a coupon test will determine the location of each bypass rack. These coupon tests are semi-quantitative tests because they lack the mechanical and thermal stresses and the evaporation of boiler water under deposits. The ideal purpose of corrosion coupons in the feedwater, boiler, or condensate systems is to measure the relative corrosion rates or changes in corrosion rates over time.

CONCLUSIONS

Passivation has many descriptions, including the measurement of electrochemical potential, the reduction of iron oxides, the oxidation of an iron substrate, the absence of corrosion, and the indirect measurement of soluble and insoluble iron oxide concentrations. Most of the passivation mechanisms postulate the formation of a protective iron oxide film, usually magnetite. The presence of magnetite, however, is not sufficient evidence that passivation has occurred.

The formation of magnetite depends on the thermodynamic state (electrochemical potential) of the boiler system; the rate of oxide formation is dependent on the kinetics. Improving the thermodynamics and, consequently, the kinetics, requires changing the conditions of the system (temperature, pH, dissolved oxygen concentration) and/or adding a reducing agent. Both laboratory and field techniques measure the electrochemical potentials and the thickness and integrity of iron oxide layers with some limitations.

The definition of corrosion is the destruction of a metal by a chemical or electrochemical reaction with its environment. Corrosion descriptions include the location (or geometry) and contributing factors (e. g. mechanical, operational, thermal, and chemical). Like passivation, the rate of corrosion depends on the thermodynamic state of the boiler system while the kinetics of corrosion depend on the system conditions. The addition of oxygen scavengers in boiler systems to reduce corrosion may not create thermodynamic conditions that are more favorable for passivation. The most common corrosion measurement techniques are soluble, reactive, and insoluble iron oxide concentrations and direct examination of metal surfaces. Predicting corrosion based on measurements of dissolved hydrogen is a challenge because hydrogen can evolve from both corrosion and passivation reactions.

Passivation is a very complex phenomenon with many unknowns. Each of the various definitions of passivation is appropriate to a specific set of circumstances or observations. The challenge is to define and conduct measurements of passivation phenomena that have wide acceptance and clear application to boiler systems.

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