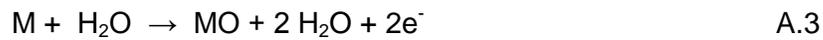
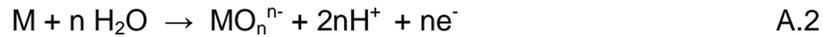


A.3 Corrosion Basics

Corrosion of metals in aqueous environments involves various electrochemical and chemical reactions at, or close to, the material/environment interface. For instance simplified reaction equations may be formulated for the electrochemical oxidation of a metal atom to form either (a) a solvated metal cation (Equation A.1) or (b) in alkaline solutions, a metal anion (Equation A.2); or (c) an oxide may be formed directly on the surface (Equation A.3) by electron transfer. Alternatively, the oxide may also form adjacent to, and then deposit onto, the surface via a precipitation reaction (Equation A.4).



Extensive research and development over many decades has focused on the kinetics and thermodynamics of such reactions since they are central to the development of corrosion mitigation actions used in numerous industries; such actions include, for instance, anodic and cathodic protection, development of various inhibitors and paint schemes, alloy development, water chemistry control, etc. Discussion of such developments and the science behind them is outside the scope of this present discussion, and the reader is directed towards appropriate textbooks, such as References 1-6, for such details.

Under equilibrium conditions the change in Gibbs free energy, ΔG , associated with those surface reactions involving electron transfer (Equations A.1-A.3) will have a related electrode potential, E , at that surface (Equation A.5) with the value of that potential being a function of temperature, metal cation or anion activity (for Equations A.1 and A.2) and pH (for Equations A.2 and A.3).

$$E = -\Delta G/zF \quad A.5$$

where F is Faradays constant (96,500 coulombs/equivalent), and z is the number of electrons (or equivalents) exchanged in the reaction.

Again the reader is referred to corrosion textbooks [1-6] for details of these electron transfer relationships, and the derivation (and measurement) of the electrode potential that exists at the metal/solution interface. The equilibrium stability of the precipitated oxide in Equation A.4 will be dependent on the interactions between temperature, pH and oxide solubility.

These fairly basic concepts lead to the construction of a Pourbaix diagram [7], which denotes the potential/pH combinations where various species (M , MO , M_{aq}^{z+} , MO_n^{n-}) are thermodynamically stable or metastable at a given temperature. Such diagrams are of extreme value in predicting corrosion events and in determining E/pH combinations where the metal is, (a) thermodynamically immune from corrosion or, (b) where it is possible that the surface may be protected by an oxide (or salt) which may, depending on its structure, confer "passivity" or, (c) where the metal may undergo active corrosion. With this knowledge, mitigation strategies associated with, for instance, water chemistry specifications or alloy choice can be formulated. The Pourbaix diagram for the iron-water system, at 25°C and activities of dissolved species of

10^{-6} gm-equivalents/L, is shown in Figure A.1 as an illustration of these concepts. It is seen that, at lower potentials, there is a region in potential-pH space where the oxidation reactions (Equations A.1-A.3) are not possible thermodynamically, and iron is immune from corrosion. However, corrosion is possible at more positive potentials corresponding to the general oxidation Equations A.1 and A.2 where the dissolved species are Fe^{2+} or Fe^{3+} in acid solutions and HFeO_2^- in alkaline solutions.

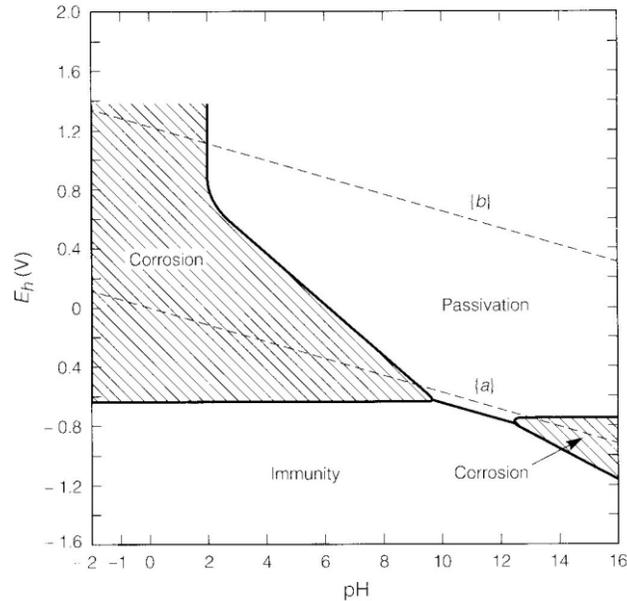


Fig. A.1 Pourbaix diagram for the iron- water system at 25°C, Activities of dissolved species of 10^{-6} gm-equivalents/L [7] (© NACE International 1974)

Oxides (Fe_3O_4 , Fe_2O_3) are stable at intermediate pH values via oxidation reactions (Equation A.3) or dissolution/ precipitation reactions (Equation A.4) and may, depending on the oxide structure confer corrosion protection. Alloying may significantly affect the oxide structure and the degree of protection or “passivation,” which is conferred at various E/pH conditions. A simple example of this is shown in Figure A.2 where the stability region for $\text{Cr}(\text{OH})_3$ is superimposed onto the Pourbaix diagram for the iron-water system. It is seen that the passivity region is considerably expanded, with the possibility of improved corrosion resistance in ferritic stainless steels (Fe-Cr alloys) and austenitic stainless steels (Fe-Cr-Ni) due to the formation of mixed spinel oxides on the metal surface. Again the reader is guided to the corrosion handbooks that refer to numerous papers that focus on the details of these phenomena.

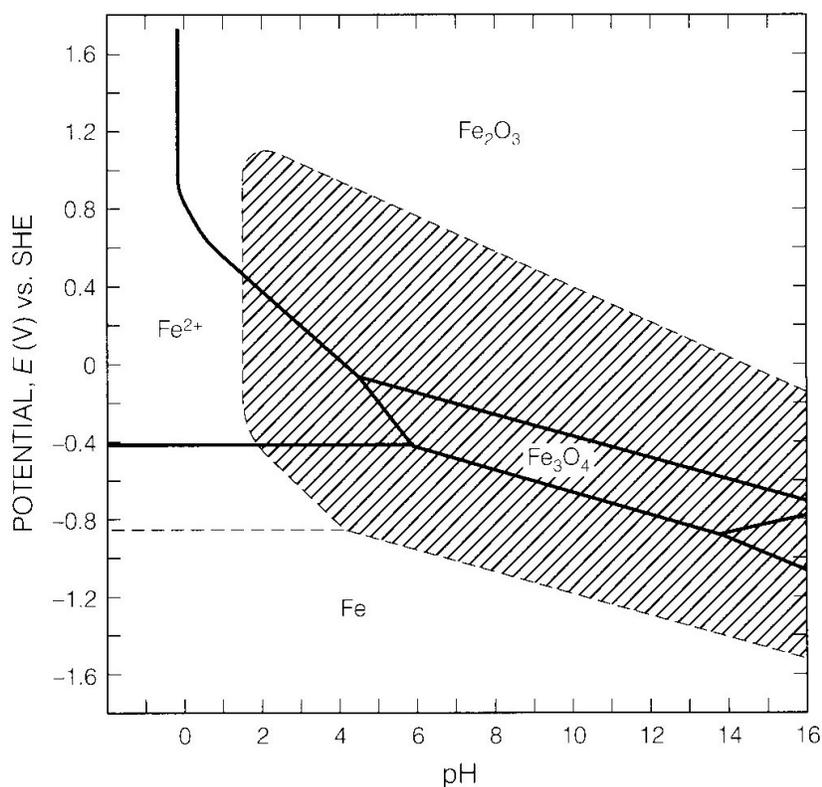


Fig. A.2 Superimposition of Cr(OH)₃ stability region onto the Pourbaix diagram for the iron-water system at 25°C and activities of dissolved species of 10⁻⁶ gm-equivalents/L. [4; adapted from 7]. Note that the alternate Cr₂O₃ phase has a similar outline but with reduced stability regions in the acid and alkaline regions. (Reprinted by Permission of Pearson Education, Inc., Upper Saddle River, NJ.)

Pourbaix diagrams may also be used for the prediction of corrosion degradation modes other than general corrosion, since many of these are dependent on the conjunction of reactions such as Equations A.1- A.4. Such a use is discussed in Appendix B relative to the E/pH combinations known to be relevant for various submodes of stress corrosion cracking of nickel-base alloys in PWR steam generators [see Appendix B.7].

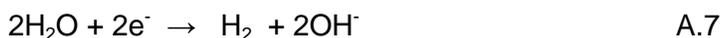
Finally, in discussing the thermodynamics of the various species at the metal – environment interface, it is important to point out that the Pourbaix diagram sets bounds on the kinetics of formation of those species. For example, metal dissolution (Equation A.1), cannot occur, even at extremely slow rates at potentials more negative than the reversible potential for that reaction. The rate of dissolution at potentials above the reversible potential will depend on various factors that are discussed below.

The extent of corrosion, or the mass of metal oxidized per unit area, is the faradaic equivalent of the oxidation charge density passed in Equations A.1-A.3. However, in order to conserve charge under open circuit conditions (i.e., the metal does not have an imposed current on it as would be the case with anodic or cathodic protection), the release of electrons in such oxidation reactions must be balanced by an equal consumption of electrons by reduction reactions. In LWRs such reactions commonly involve reduction of hydrogen cations (Equation A.6), water

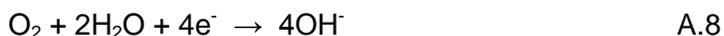
(Equation A.7), or dissolved oxygen (Equation A.8), or may be associated with other reactions associated with reduction of hydrogen peroxide, cupric cations, etc.



in acid solutions or, in neutral or alkaline solutions



and



The fact that reduction reactions must also occur on the metal surface has an impact on the regimes on the Pourbaix diagram that are applicable for a given system. For instance, Equation A.6 is an appropriate reduction process in deaerated water, and the line “a” in Figure A.1 indicates the equilibrium potential/pH relationship for that process. Thus, in order to have reduction according to Equation A.6 in conjunction with oxidation of iron by Equations A.1-A.3, the relevant potential/pH area lies below line “a.” By contrast in aerated water, where a relevant reduction reaction would be Equation A.8 (whose equilibrium potential / pH relationship is given by line “b” in Figure A.1), the relevant potential/pH area on the Pourbaix diagram where metal oxidation or corrosion can occur is considerably increased. Thus there is a thermodynamic reason why, in general, corrosion problems are potentially more significant in aerated vs. deaerated solutions.

As shown schematically in Figure A.3 the oxidation and reduction reactions may take place on adjacent areas of the material surface, but this is not always the case, especially for localized corrosion modes when the “anodic” and “cathodic” sites (where the oxidation and reduction reactions respectively occur) may be separated for geometric or metallurgical inhomogeneity reasons.

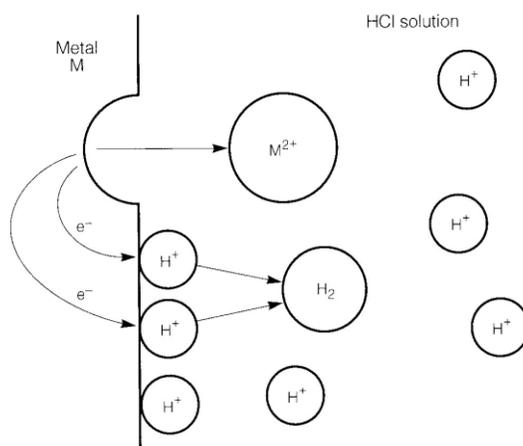


Fig. A.3. Oxidation and reduction reactions occurring on adjacent areas of surface [4]
(Reprinted by Permission of Pearson Education, Inc., Upper Saddle River, NJ.)

The kinetics of the oxidation and reduction reactions for the simple case of zinc dissolving in an acid solution are shown in Figure A.4 in order to illustrate the concept of the equilibration of oxidation and reduction reaction rates. It is seen that the oxidation, or dissolution, rate for zinc, quantified by the current density for the reaction,



increases exponentially with the extent that the surface potential is increased from the potential associated with equilibrium for that oxidation reaction (i.e. approximately -0.75V vs. SHE); this difference between the equilibrium potential and the surface potential is known as the overpotential. Similarly the reduction rate of hydrogen cations (Equation A-6) occurring on the adjacent metal surface also increases exponentially with increasing overpotential from the equilibrium potential (i.e. 0V vs. SHE) for that reduction reaction. At a surface potential denoted as the corrosion potential, E_{corr} in Figure A.4 the rate of oxidation equals the rate of reduction, and the zinc corrosion rate is defined by the Faradaic equivalent of the corrosion current density, i_{corr} . Note that in terminology generally used in corrosion in nuclear systems, E_{corr} is usually termed the electrochemical corrosion potential, or ECP.

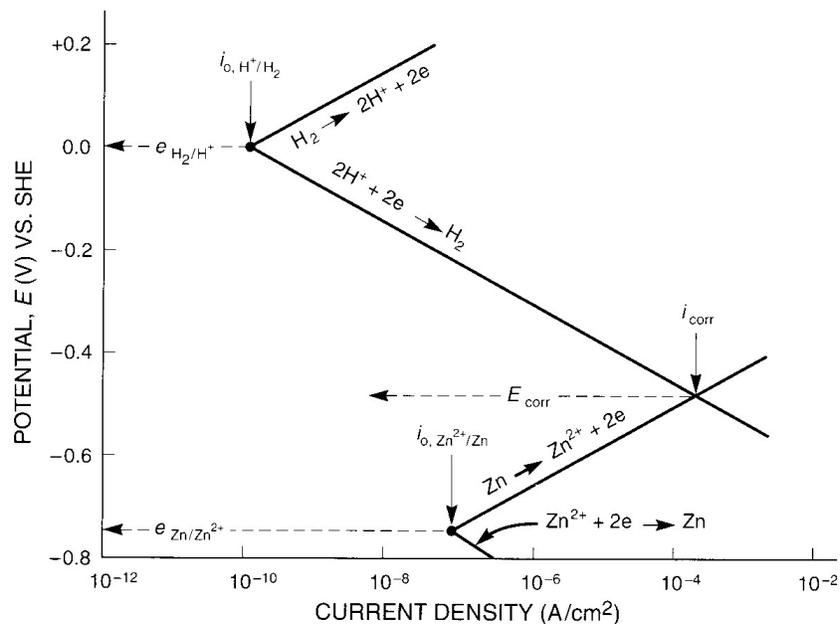


Fig. A.4 Schematic “Evans” diagram indicating the equilibration of the oxidation and reduction rates for the dissolution of zinc in 1N HCl solution, and the associated “corrosion current, (i_{corr})” and “corrosion potential, (E_{corr})”. [4] (Reprinted by Permission of Pearson Education, Inc., Upper Saddle River, NJ.)

This simple kinetic system may become more complicated when, as mentioned above, the “anodic” and “cathodic” sites are separated for geometric or metallurgical inhomogeneity reasons, or where the areas on the metal surface associated with oxidation and reduction reactions are markedly different. These are particularly important in localized corrosion events, and will be discussed later in the appropriate section.

In order to control corrosion product (or “crud”) release in the reactor coolant system, alloys are used that operate in the region of the Pourbaix diagram where surface protection is provided by the presence of a protective oxide film. The effect of the formation of such a film on the kinetics of oxidation is shown schematically in Figure A.5. As the overpotential for oxidation is increased so the corrosion rate may increase exponentially under “activation control” until a potential, predictable from the Pourbaix diagram, is reached when an oxide may form. This potential is denoted by E_{pp} in Figure A.5. Thereupon the oxidation rate decreases by a factor of 10^4 or more dependent on the structure, composition, and solubility of the surface oxide. The increased corrosion resistance may be maintained over a considerable potential range until, at more positive potentials, the oxide may lose its protective properties, either due to the onset of localized breakdown associated with the presence of aggressive impurity anions (such as chloride) leading to pitting [8, see Appendix B.9,] or, at more oxidizing conditions, to the dissolution of the passive film. This latter condition is known as “transpassivity” and an example would be dissolution of Cr_2O_3 -rich surface oxides to HCrO_4^- .

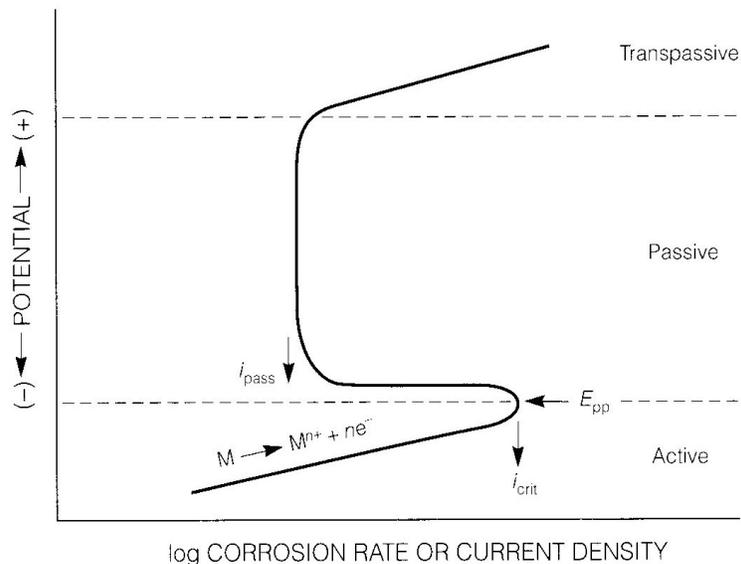


Fig. A.5 Schematic oxidation current density vs. electrode potential diagrams, indicating, for the oxidation reactions, transitions from activation control, to onset of passivation, to oxide break down due to transpassivity or pitting. [4] (Reprinted by Permission of Pearson Education, Inc., Upper Saddle River, NJ.)

The prediction of the kinetics of corrosion reactions is further complicated by the fact that many of the oxidation and reduction reactions occurring on the metal surface may be ultimately controlled by the transport of either reaction products away from the surface, or by the transport of reactants to the metal surface. This is especially the case for material geometries, such as crevices and cracks; these situations will be discussed in the appropriate sections on localized corrosion later in this Appendix and in the topical reports in Appendix B. An example of such a complication due to mass transport under general corrosion conditions is shown schematically in Figure A.6 where the kinetics for the reduction of dissolved oxygen (Equation A.8) are superimposed on the metal oxidation kinetics from Figure A.5. In this situation it is seen that the “activation controlled” reduction kinetics increase exponentially with overpotential to a limiting value when the reduction rates become potential-independent. This limitation corresponds physically to the point when dissolved oxygen cannot arrive fast enough to the reacting surface to satisfy