

The Ni cathode is obviously highly polarized in contrast to the steel anode. This leads to increased corrosion near the contact point on the steel and decreased corrosion near the contact point in the Ni.

Concentration Cells:

Corrosion is often affected by concentration cells. Differential aeration with different concentrations of dissolved oxygen on a single metal surface or on electrically connected surfaces are common. Such cells are especially important for Fe and carbon steels. Acid chloride concentration cells are important for the initiation and growth of pitting and crevice corrosion in stainless steel.

A laboratory setup of a differential aeration cell is shown in figure 6.23. Two iron electrodes are immersed in 0.1 N NaCl on both sides of a porous diaphragm, allowing charge transfer, but not sufficient mass transfer to affect the dissolved oxygen content.

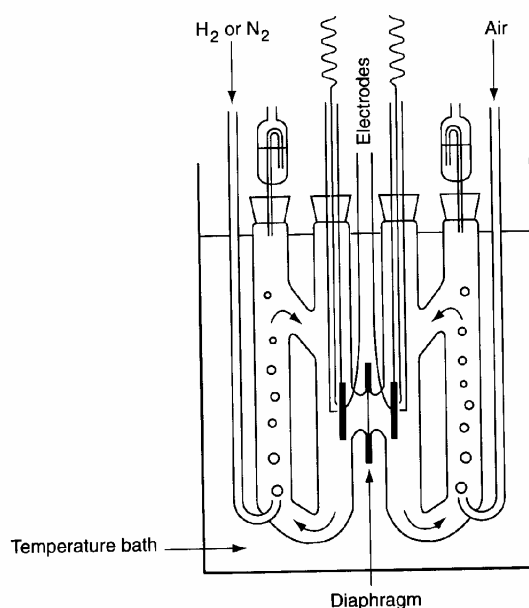
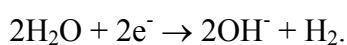
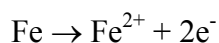
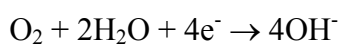


FIGURE 6.23 Differential aeration cell. (From H. Grubitsch, cited by U. R. Evans, *The Corrosion and Oxidation of Metals*, Arnold, London, p. 129, 1960.)

For uncoupled electrodes the anodic and cathodic reactions on the nitrogen side are



As there is hardly any dissolved oxygen, reduction of dissolved oxygen as the cathodic reaction is impossible. On the aerated side the anodic reaction is still the oxidation of Fe, but the cathodic reaction is the reduction of the dissolved oxygen by



The corrosion rate of the uncoupled cathode is controlled by concentration polarization and diffusion of dissolved oxygen at $I_{L,C}$. The uncoupled corrosion potential on the aerated electrode is $E_{\text{corr},C}$ as shown in figure 6.24.

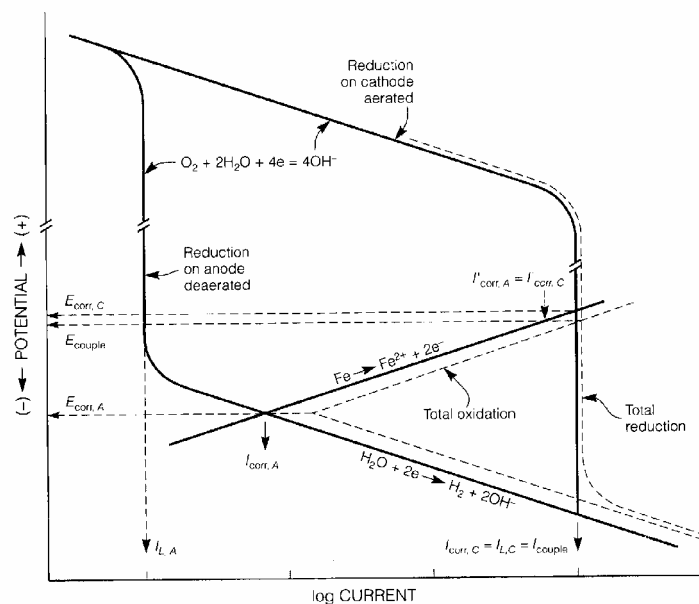
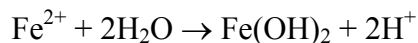


FIGURE 6.24 Mixed potential analysis of the differential aeration on identical iron electrodes of equal area, assuming uniform constant solution concentration and current distribution.

When the two sides are coupled one finds the couple potential between the two initial potentials. The potential distributions on the surface again lead to increased attack near the junction. On the aerated side the reduction reaction leads to an increase in pH, whereas at the deaerated side the Fe^{2+} ions react with water leading to a decrease in pH by the reaction



Increased alkalinity passivates the cathode and increased acidity increases the activity of the anode. This additional effect is shown schematically in figure 6.25.

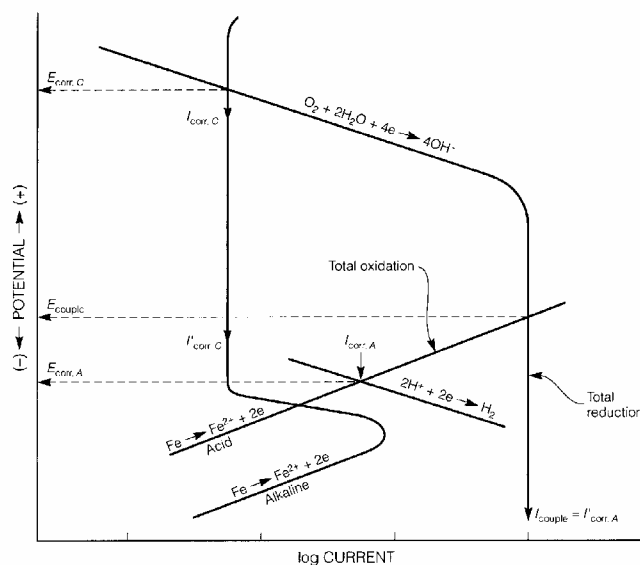


FIGURE 6.25 Mixed potential analysis of a differential aeration cell on iron with passivated cathode and acidified anode.

This effect can be clearly seen at waterline corrosion on steel and zinc. Corrosion depletes the water from dissolved oxygen, which is easiest replaced near the surface of the water in an unstirred solution. Depleted oxygen creates the anode at greater depth and the cathode formed at the waterline by reduction of the excess dissolved oxygen. This is schematically shown in figure 6.26.

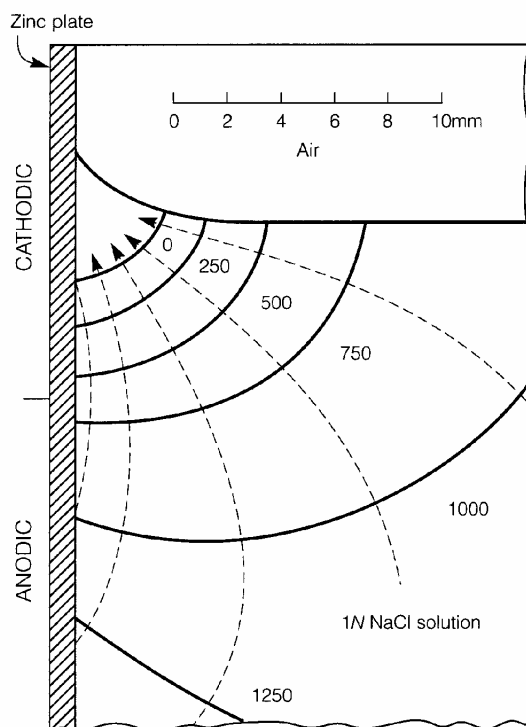


FIGURE 6.26 Potential (solid) and current (dashed) distributions on a vertically immersed zinc plate at the water line. (From J. N. Agar and U. R. Evans, cited by Kaesche¹⁸.)

The surface at the waterline is passivated by formation of local alkalinity from reduction of dissolved oxygen. But the metal is strongly attacked nearby, where dissolved oxygen is less accessible, but solution resistance is minimized between adjacent surfaces. This process can be shown by putting a drop of saltwater on an abraded steel surface. In the water small amounts of phenolphthalein and ferricyanide indicators show cathodic areas pink (OH^- formation) and anodic areas blue (liberation of Fe^{2+}). The initial and final surface distributions are shown in figure 6.27. Similar concentration cells can also form when the metal is fully immersed. One has found concentration cell corrosion in both agitated and quiescent solutions. But in full immersed experiments the formation of the concentration cells takes longer times up to several days. So anodic and cathodic areas can form at a surface even if the solution flows, which one would think should lead to a homogeneous aeration of the solution.

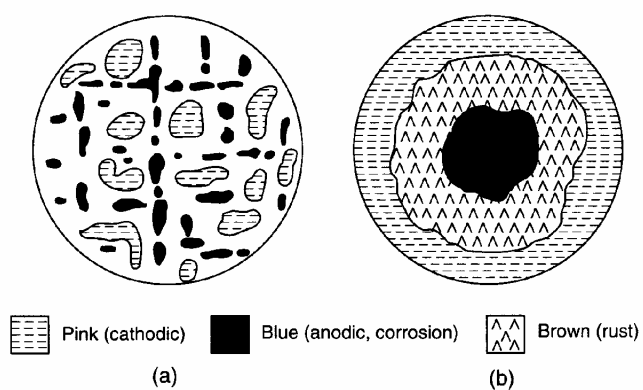


FIGURE 6.27 Initial (a) and final (b) distribution of anode and cathode in a water drop on a horizontal iron surface. (From U. R. Evans, *An Introduction to Metallic Corrosion*, Arnold, London, p. 36, 1981. Reprinted by permission Edward Arnold Publishers Ltd.)