Chemical Engineering 378

Special Topical Readings

CORROSION FUNDAMENTALS

by

Professor Calvin H. Bartholomew
and
William G. Pitt
Department of Chemical Engineering
Brigham Young University

Printed
July 30, 2013

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I. What is Corrosion?

A. Definition

Most materials experience some degree of degradation as they interact with their various environments. Metals undergo degradation by dissolution and/or oxidation. The first of these processes, i.e., dissolution of metals, is generally referred to as corrosion. However, since metal dissolution processes, in addition to being generally undesirable, are mostly electrochemical, we will in the context of this tutorial, define *corrosion* as *the unintended, destructive electrochemical dissolution of metals*.

B. Consequences

Corrosion of metals is a widespread and economically important phenomenon. It is estimated that about 5% of the gross domestic product is expended on prevention of corrosion or replacement of corroded materials or equipment. The important economic and technical consequences of corrosion can be illustrated by considering their role in the design and operation of a plant; these might include:

Costly plant shutdown for replacement of corroded equipment.

Increased capital and operating costs of overdesign to allow for corrosion and of operating costs for preventive maintenance.

Loss of equipment and plant efficiencies due to adjustments for corrosion, e.g., lower heat transfer rate in heat exchangers

Loss or contamination of a valuable product.

Accidents and/or unsafe working conditions, e.g. fire, explosion, release of toxics, etc. due to a sudden failure.

C. Forms of Corrosion

Electrochemical corrosion is typically classified on the basis of appearance (e.g., uniform or localized) and mechanism (e.g., macroscopic or microscopic) as illustrated in Figure 1. Macroscopic corrosion is that which is visible to the unaided eye, while microscopic attack involves unobservable, minute changes which can nevertheless aggravate serious structural damage. Several different important forms of corrosion are illustrated in Figure 2.

Uniform corrosion is the most common, easily-observed and easily-controlled form, for example, it can be controlled through use of coatings. Localized corrosion while less common is more likely to lead to unexpected failure.

The mechanisms of several corrosion types are obvious from Fig. 2. However, the mechanisms of galvanic, erosion, fretting, cavitation, stress, crevice, and pitting corrosions require some clarification. The last two are treated in a separate section. Galvanic corrosion occurs due to an inherent electrochemical potential difference at the junction of two dissimilar metals (as a result of the different half potentials for the two metals as explained in Section II); the resulting current flow causes dissolution of the more active metal. Erosion corrosion is due to enhanced metal removal by rapidly-moving corrodent (fluid); it is attributed to abrasive removal of protective surface films by the moving fluid and/or mechanical removal by fast-moving solid particles or bubbles in a slurry. Cavitation and fretting corrosion are special cases of erosion corrosion. Cavitation is caused by the formation and energetic collapse of vapor bubbles on the metal surface; the high pressure waves from collapsing bubbles remove protective films. Fretting corrosion occurs due to the repeated mechanical rubbing of two metals surfaces, which removes protective oxide layers and by addition of heat increases corrosion rate. Stress corrosion is microscopic crack formation due to the combined effects of stress and corrosion—usually at intergranular paths where metals are more active; this form of corrosion causes failure of metals which would in the absence of a corrodent not fail at the same applied stresses. While relatively little is known about the mechanisms of stress corrosion, it would be logical to speculate that since stresses affect the bonding of neighboring atoms, this would probably change the chemical and electrochemical activities of these atoms as well.

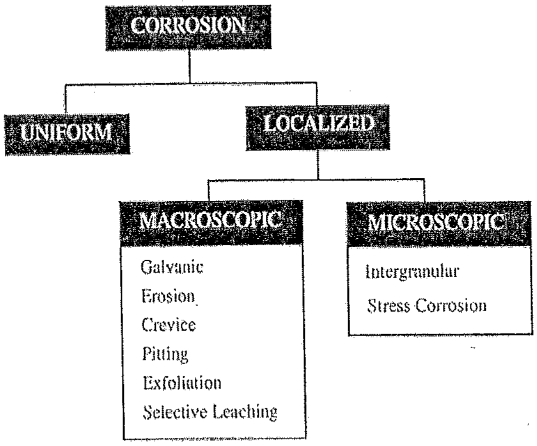


Figure 1. Types of corrosion and their classification.

II. Electrochemical Fundamentals and Thermodynamics

Since corrosion is generally electrochemical, a basic understanding of electrochemistry and some widely-used electrochemical terms is prerequisite to its study. Thermodynamics of electrochemical systems enables prediction of whether corrosion will occur, to what extent it occurs, and how the driving force for corrosion depends upon reactant concentrations and temperature. The driving force for corrosion is the cell potential which can be determined from tabulated reduction or oxidation half potentials.

A. Important Electrochemical Terms

1. Oxidation: Conversion of a metal or metal ion to a higher valence state at the anode with liberation of electrons.
2. Reduction: Electron transfer to a chemical species at the cathode.
3. Electrochemical reaction: Sum of two half reactions, one involving oxidation, the other involving reduction.
4. Galvanic couple: Two metals electrically connected in a liquid electrolyte.

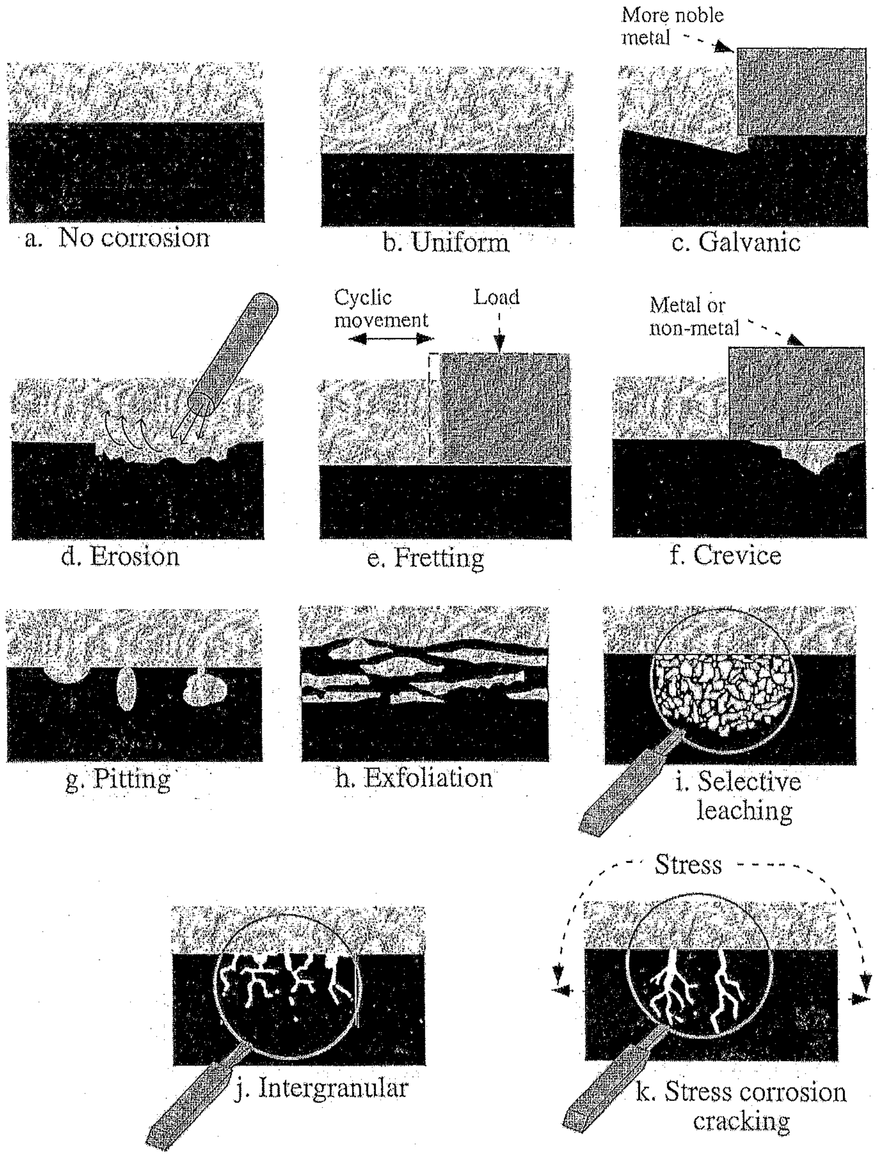


Figure 2. Different forms of corrosion [adapted from Henthorne, 1971-2].

5. Standard <u>Cell potential</u>: $\Delta E° = E_2° - E_1°$, $E_1°$ is the emf potential for oxidation; $E_2°$ is for reduction.
6. <u>Standard EMF series</u>: Standard electromotive forces (electrode potentials) for reduction of metal ions referenced to the standard hydrogen cell.
7. <u>The Galvanic Series</u>: Relative reactivities of metals and alloys in seawater.
8. <u>Corrosion Penetration Rate</u>: thickness loss of material per unit time in mils per year (mpy).
9. <u>Polarization</u>: The displacement during corrosion of each electrode potential from its equilibrium value; usually expressed as overvoltage of anode and cathode (η_a and η_c). The overvoltage is typically a linear function of the corrosion current density.
10. <u>Activation Polarization</u>: Condition wherein surface reactions control corrosion rate.

B. Requirements for a working electrochemical cell

Four things must happen simultaneously in a working electrochemical cell: (1) an oxidation half-reaction occurs at the anode surface, (2) a reduction half-reaction occurs at the cathode surface, (3) electrons flow through an external circuit, and (4) ions flow in electrolytes (anions towards the anode and cations towards the cathode). Although it is usually desirable to keep the electrolyte for each electrode separated, for the electrical circuit to be complete a pathway must be provided for ions to flow within the cell; this is typically accomplished by means of a salt bridge or ion-exchange membrane. In corrosion cells, electrolytes are often not separated, e.g. a single piece of iron in water.

C. Standard Half-Cell Potentials

1. The Standard Hydrogen Reference Cell

The reduction reaction of protons to form molecular H_2 can be written as follow:

$$2H^+ + 2\,e^- = H_2 \qquad (1)$$

The standard hydrogen reference cell is shown in Fig. 1; it is defined at 1 atm of H_2 gas bubbling on a Pt electrode in a solution of 1*M* acid. Generally, this reference cell is attached to another standard half cell for a metal to measure its standard emf, using H_2 as the zero reference as shown in Fig. 3.

2. Measurement of Standard Oxidation/Reduction Potentials

The <u>measurement of the standard half cell potential</u> E^0 is made using a voltmeter of high resistance and <u>at low current density;</u> thus, there is a net flow of electrons but at a sufficiently low rate that the <u>forward and reverse reduction and oxidation reactions at each electrode can be considered to be in near equilibrium</u>. At equilibrium the rate of oxidation is equal to the rate of reduction and can be defined as:

$$r_{ox} = r_{red} = i_o / nF \qquad (2)$$

where i_o is the exchange current density (current at dynamic equilibrium), F is the Faraday constant and n the number of electrons exchanged in each half reaction; i_o is a kinetic quantity; on the other hand E^0 is a thermodynamic quantity. Both of these parameters, however, cannot be calculated from first principles and must be determined experimentally.

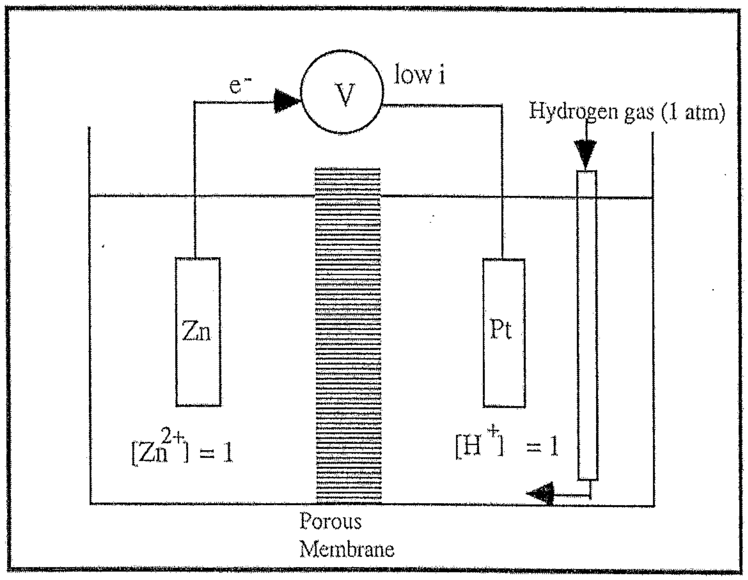
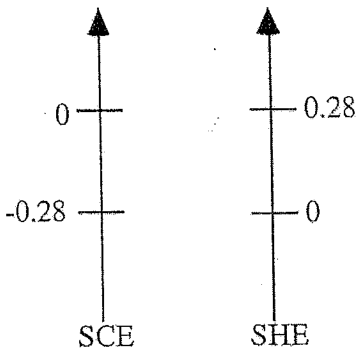


Figure 3. Schematic of electrochemical cells showing measurement of standard emf for the standard Zn electrode relative to the standard hydrogen electrode.

E^0 is independent of the surface of the electrode used to measure the half-cell potential; i_0 however, is highly dependent on surface chemistry and structure. For example, i_0 values for the standard hydrogen half-cell are 10^{-12} A/cm^2 and 10^{-3} A/cm^2 for Hg and Pt surfaces respectively. Thus, the value of i_0 is 9 orders of magnitude higher on the Pt surface. This can be attributed to the superior ability of Pt to catalyze the dissociation of molecular hydrogen, the reduction of a proton, and the recombination of hydrogen metal atoms to molecular hydrogen; Pt readily adsorbs hydrogen dissociatively, while Hg does not.

3. Note on Correction for Standard Calomel Electrode

If the potentials on a polarization curve are based on a Standard Calomel Electrode (SCE) rather than a Standard Hydrogen Electrode (SHE), the chart can be corrected to SHE by adding the standard half-cell potential of the SCE based on SHE. This follows from the definition of a standard half-cell potential referenced to hydrogen and can be illustrated schematically as follows:



It is evident that the zero on the SCE scale corresponds to 0.28 on the SHE scale (that is after all the definition of the half-cell potential based on SHE!). Accordingly $V_{SHE} = V_{SCE} + 0.28$ V.

D. Thermodynamics of Corrosion

1. Free energy for electrochemical reactions

Thermodynamics allows us to predict whether corrosion will happen. For a reaction to proceed it must have a negative free-energy change. For electrochemical reactions the change in free energy of reaction is equal to the amount of electrical work performed when n moles of electrons are transferred. Thus,

$$\Delta G = -nFE_W \tag{3}$$

where n is the number of electrons involved in the reaction, F is the Faraday constant and E is the cell potential; thus, for an electrochemical reaction to be feasible E must be positive. The change in free energy can be related to the equilibrium constant for reaction by the expression:

$$\Delta G = -(RT) \ln K \tag{4}$$

in which K is the equilibrium constant;

$$K = \Pi_i a_i^{vi}. \tag{5}$$

Π_i is the product summation, a_i is the activity of species i, and ν_i is the stoichiometric coefficient for the species i in the stoichiometric electrochemical reaction. Note that $a_i = C_i/C_i^o$ for species in solution ($C_i^o = 1$ M), $a_i = P_i/P_i^o$ for gas phase species, and $a_i = 1$ for solids, all assuming that the activity coefficients are unity.

Substituting for ΔG into Eqn 3, we obtain

$$E_W = -(RT/nF) \ln K \tag{6}$$

which is the simplest form of the Nernst equation (in some texts Q is used in place of K and is called the reactant quotient). Note that by use of this equation potential measurements can be used to determine K.

E_W can be related to the measured relative change in electrochemical potential ΔE by reference to the difference between the half-cell potentials for cathode and anode:

$$E_W = (E_c - E_c^o) - (E_a - E_a^o) \tag{7}$$

where E_c^o and E_a^o are standard reduction potentials (see Table 1) measured at standard activities (noted above just after Eqn. 5). When the electrical work in the form of potential differences from Eqn. 7 is substituted into Equation (6) and K is defined in terms of activities from Equation 5, we obtain the full Nernst equation:

$$\Delta E = E_2^o - E_1^o - (2.303\ RT/nF) \log[\Pi_i a_i^{v_i}] \tag{8}$$

If measured at standard activities, ΔE can be calculated from the standard reduction potentials. For example, for iron in acid solutions at standard activities and 25°C the cell potential is $\Delta E = E^o [H^+/H_2] - E^o [Fe/Fe^{2+}] = 0 - (-0.440) = + 0.440$ V. Hence, corrosion of iron in acid solution is predicted to be favorable at standard concentrations.

Some basic rules regarding the use of the Nernst equation and some important rules about combining half reactions are summarized in Table 2.

2. Temperature and Concentration Dependence of Cell Potential

At other than standard concentrations and 25°C, it is necessary to use the full Nernst equation to calculate E.

$$\Delta E = E_2^o - E_1^o - (2.303\ RT/nF) \log [\Pi_i C_i^{v_i}] \tag{9}$$

where R is the gas constant and T is absolute temperature; F = 96,500 C/mole. At 25°C, 2.303 x RT/F = 0.0592 volts.

It can be shown using Equation 8 that corrosion of iron is favored thermodynamically at room temperature in almost pure, neutral water (i.e., containing less than a ppm each of H^+ and Fe^{2+} and free of dissolved oxygen). Can you demonstrate that this is true?

It is important to emphasize, however, that while thermodynamics predicts whether a reaction can happen, it doesn't enable prediction of how fast it will occur.

Table 1. Standard State Reduction Potentials.

(*Source:* Therald Moeller, *Inorganic Chemistry: A Modern Introduction,* Appendix IV, New York: Wiley, 1982 © 1982 by John Wiley & Sons, Inc.)

A. Acidic Solution	$E°$ (V)
$Li^+ + e^- \longrightarrow Li(s)$	−3.045
$K^+ + e^- \longrightarrow K(s)$	−2.925
$Ba^{2+} + 2e^- \longrightarrow Ba(s)$	−2.906
$Sr^{2+} + 2e^- \longrightarrow Sr(s)$	−2.888
$Ca^{2+} + 2e^- \longrightarrow Ca(s)$	−2.866
$Na^+ + e^- \longrightarrow Na(s)$	−2.714
$Mg^{2+} + 2e^- \longrightarrow Mg(s)$	−2.363
$H_2(g) + 2e^- \longrightarrow 2H^-$	−2.25
$Al^{3+} + 3e^- \longrightarrow Al(s)$	−1.662
$Mn^{2+} + 2e^- \longrightarrow Mn(s)$	−1.185
$Zn^{2+} + 2e^- \longrightarrow Zn(s)$	−0.763
$Cr^{3+} + 3e^- \longrightarrow Cr(s)$	−0.744
$Fe^{2+} + 2e^- \longrightarrow Fe(s)$	−0.440
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.408
$Cd^{2+} + 2e^- \longrightarrow Cd(s)$	−0.403
$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}$	−0.359
$PbCl_2(s) + 2e^- \longrightarrow Pb(s) + 2Cl^-$	−0.268
$Ni^{2+} + 2e^- \longrightarrow Ni(s)$	−0.250
$Sn^{2+} + 2e^- \longrightarrow Sn(s)$	−0.136
$Pb^{2+} + 2e^- \longrightarrow Pb(s)$	−0.126
$2H^+ + 2e^- \longrightarrow H_2(g)$	0.000
$S(s) + 2H^+ + 2e^- \longrightarrow H_2S(aq)$	0.142
$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	0.15
$Sb_2O_3(s) + 6H^+ + 6e^- \longrightarrow 2Sb(s) + 3H_2O(l)$	0.152
$Cu^{2+} + e^- \longrightarrow Cu^+$	0.153
$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow H_2SO_3(aq) + H_2O(l)$	0.172
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-$	0.222
$Cu^{2+} + 2e^- \longrightarrow Cu(s)$	0.337
$SO_4^{2-} + 8H^+ + 6e^- \longrightarrow S(s) + 4H_2O(l)$	0.357
$H_2SO_3(aq) + 4H^+ + 4e^- \longrightarrow S(s) + 3H_2O(l)$	0.450
$I_2(s) + 2e^- \longrightarrow 2I^-$	0.536
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	0.564
$[PtCl_6]^{2-} + 2e^- \longrightarrow [PtCl_4]^{2-} + 2Cl^-$	0.68
$O_2(g) + 2H^+ + 2e^- \longrightarrow H_2O_2(aq)$	0.682
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.771
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg(l)$	0.788
$Ag^+ + e^- \longrightarrow Ag(s)$	0.799
$2NO_3^- + 4H^+ + 2e^- \longrightarrow N_2O_4(g) + 2H_2O(l)$	0.803
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	0.920
$NO_3^- + 3H^+ + 2e^- \longrightarrow HNO_2(aq) + H_2O(l)$	0.94
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	0.96
$Pd^{2+} + 2e^- \longrightarrow Pd(s)$	0.987
$Br_2(l) + 2e^- \longrightarrow 2Br^-$	1.065
$Br_2(aq) + 2e^- \longrightarrow 2Br^-$	1.087
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O(l)$	1.19
$2IO_3^- + 12H^+ + 10e^- \longrightarrow I_2(s) + 6H_2O(l)$	1.195

A. Acidic Solution	$E°$ (V)
$Pt^{2+} + 2e^- \longrightarrow Pt(s)$	~1.2
$ClO_3^- + 3H^+ + 2e^- \longrightarrow HClO_2(aq) + H_2O(l)$	1.21
$O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O(l)$	1.229
$MnO_2(s) + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O(l)$	1.23
$2HNO_2(aq) + 4H^+ + 4e^- \longrightarrow N_2O(g) + 3H_2O(l)$	1.29
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-$	1.360
$PbO_2(s) + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O(l)$	1.455
$Au^{3+} + 3e^- \longrightarrow Au(s)$	1.498
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O(l)$	1.51
$2HClO(aq) + 2H^+ + 2e^- \longrightarrow Cl_2(g) + 2H_2O(l)$	1.63
$HClO_2(aq) + 2H^+ + 2e^- \longrightarrow HClO(aq) + H_2O(l)$	1.645
$H_2O_2(aq) + 2H^+ + 2e^- \longrightarrow 2H_2O(l)$	1.776
$O_3(g) + 2H^+ + 2e^- \longrightarrow O_2(g) + H_2O(l)$	2.07
$F_2(g) + 2e^- \longrightarrow 2F^-$	2.87
$F_2(g) + 2H^+ + 2e^- \longrightarrow 2HF(aq)$	3.06

B. Alkaline Solution	$E°$ (V)
$Mg(OH)_2(s) + 2e^- \longrightarrow Mg(s) + 2OH^-$	−2.690
$Al(OH)_3(s) + 3e^- \longrightarrow Al(s) + 3OH^-$	−2.30
$Zn(OH)_2(s) + 2e^- \longrightarrow Zn(s) + 2OH^-$	−1.245
$Fe(OH)_2(s) + 2e^- \longrightarrow Fe(s) + 2OH^-$	−0.877
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-$	−0.828
$Cd(OH)_2(s) + 2e^- \longrightarrow Cd(s) + 2OH^-$	−0.809
$Ni(OH)_2(s) + 2e^- \longrightarrow Ni(s) + 2OH^-$	−0.72
$Fe(OH)_3(s) + e^- \longrightarrow Fe(OH)_2(s) + OH^-$	−0.56
$S(s) + 2e^- \longrightarrow S^{2-}$	−0.447
$Cu_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Cu(s) + 2OH^-$	−0.358
$CrO_4^{2-} + 4H_2O(l) + 3e^- \longrightarrow Cr(OH)_3(s) + 5OH^-$	−0.13
$MnO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Mn(OH)_2(s) + 2OH^-$	−0.05
$NO_3^- + H_2O(l) + 2e^- \longrightarrow NO_2^- + 2OH^-$	0.01
$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$	0.098
$PbO_2(s) + H_2O(l) + 2e^- \longrightarrow PbO(s) + 2OH^-$	0.247
$IO_3^- + 3H_2O(l) + 6e^- \longrightarrow I^- + 6OH^-$	0.26
$ClO_3^- + H_2O(l) + 2e^- \longrightarrow ClO_2^- + 2OH^-$	0.33
$Ag_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-$	0.345
$ClO_4^- + H_2O(l) + 2e^- \longrightarrow ClO_3^- + 2OH^-$	0.36
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-$	0.401
$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-$	0.490
$MnO_4^- + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-$	0.588
$BrO_3^- + 3H_2O(l) + 6e^- \longrightarrow Br^- + 6OH^-$	0.61
$ClO^- + H_2O(l) + 2e^- \longrightarrow Cl^- + 2OH^-$	0.89
$O_3(g) + H_2O(l) + 2e^- \longrightarrow O_2(g) + 2OH^-$	1.24

Note: In some chemistry texts, particularly older American ones, you may find *standard oxidation potentials.* Such potentials are for the same standard state conditions relative to 0.000 V for the H_2/H^+ couple. The differences are that the ion-electron equations are written as oxidations (electrons on the other side) and the *signs* of the potentials are opposite. In 1953 the International Union of Pure and Applied Chemistry chose to recommend the uniform, worldwide use of standard reduction potentials, which had previously been more common in Europe. The numerical values for both sets of potentials are the same; only the signs are different.

Table 2. Important Observations and Rules Concerning the Use of the Nernst Equation

1. Notes regarding the Nernst equation:
   a. Note that the ratio of concentrations in the Nernst equation corresponds to the equilibrium constant or reactant quotient for the electrochemical reaction in question.
   b. The activity of each solid, species in solution or gas phase species is raised to a power corresponding to its stoichiometric coefficient. Thus, in Example 34.1 involving dissolution of Zn in a dilute acid, the stoichiometric reaction equation is $Zn + 2H^+ = H_2 + Zn^{2+}$ and the natural log term is $\ln[a(H_2)*a(Zn^{2+})/\{a(Zn)*a(H^+)^2\}]$ where $a(H_2) = P_{H2}/P_{H2}^o$, $a(Zn^{2+}) = C_{Zn2+}/C_{Zn2+}^o$, $a(Zn) = 1$, and $z(H^+) = C_{H+}/C_{H+}^o$.
   c. The common definitions for activities of species are: 1) any solid has an activity of 1; 2) the activity of a species in solution is the molar concentration divided by the standard state molar concentration, which is usually 1M; 3) the activity of a gas is the partial pressure divided by 1 atm. Thus in this example, the activity of Zn is unity, while the activity of H_2 is unity only at a partial pressure of 1 atm. Since zero potential is defined at a hydrogen partial pressure of 1 atm; thus, it follows that the reactant quotient for the Nernst equation must include ratios of gas pressures in atmospheres and ratios of solution species concentrations in molar units, e.g. moles/L.

2. Some important rules about combining half reactions:
   a. While it is often necessary in determining the overall electrochemical reaction to multiply the half-reaction equations by whole numbers to equalize the number of electrons gained and lost, The E^o values are not multiplied by these same factors when a cell potential is calculated from electrode potentials. The standard potential difference is, by definition, the potential difference between 1M solutions, pure substances, or gases at 1 atm partial pressure. The quantity of solution or gas or the size of the electrode doesn't influence this potential. Consider common batteries A, AA, C, and D; while these batteries differ in size, they each have a 1.5 V potential. Thus, we simply add the E^o values for the half reactions.
   b. It is possible to combine half potentials to obtain a new half potential reaction. However, in this case the E^o value is not the simple sum of the two E^o's; rather it is necessary to account for the number of electrons transferred in each of the known half reactions by multiplying each known E^o by the number of electrons in the electrode reaction and dividing their sum by the total number of electrons in the new electrode reaction (Hess's law).
   c. Don't forget to reverse the sign of E^o (standard reduction potential) for the oxidation half reaction.
   d. The potentials have no bearing on how fast a potential electrochemical reaction might occur.

III. Kinetics of Corrosion

A. Corrosion Rate

The rate of an electrochemical reaction, e.g. corrosion, depends upon the rate of current flowing between anode and cathode. Intensive corrosion rate can be defined in terms of current density (A/area) using Faraday's laws:

$$r_c = i_c/nF \qquad (10)$$

where r_c has units of mole/cm^2-s, i_c has units of amps/cm^2, and F is 96,500 C/mol.

The current density or current is related to cell potential through Ohms law ($I = E/R$). Accordingly, at infinite resistance or very large resistances, I (and i) will be zero or near zero. Thus, the rate or corrosion under these circumstances is zero or near zero. This emphasizes the importance of isolating anode and cathode by a large resistance (e.g. by means of a passive film or insulating gasket) in order to minimize the rate of corrosion.

In general, the current flowing between the anode and cathode of an electrochemical or corrosion cell is given by (Ohms law):

$$i = (E_c - E_a)/RA \qquad (11)$$

where $i = I/A$ is the current density, R is the total resistance of the electrochemical cell (metal, solution, and films), A is the electrode area, E_c and E_a are the cathode and anode potentials, respectively. It was mentioned previously that under conditions for which standard half cell potentials are measured, the resistance is high, E_c and E_a are E_c^o and E_a^o respectively. And it was also shown than under these conditions the current density is very low and equal to the exchange current density i_o. Under these low current conditions there is essentially negligible corrosion.

However, in a typical corrosion cell (see Fig. 4), the resistances are generally very low (the electrodes are for all practical purposes short-circuited) and the values of E_c and E_a approach each other (E_c-E_a becomes small) as predicted by Equation 11 (i.e. $E_c - E_a = iRA$ where R is very small). This is also illustrated in Figure 5; this figure also shows that as resistance decreases, current flow increases dramatically (remember current density is on a log scale). It is also apparent from this figure that as resistance in an electrochemical cell is decreased allowing current to flow at higher rates, the potential of the anode increases, while that of the cathode decreases, thus approaching each other. This change in potential or *polarization* ($\eta = E - E^o$) is due to *activation polarization*, the mechanistic aspects of which are discussed in the next subsection. Thus, in a typical corrosion cell, the resistance is typically low enough that for all practical purposes the corrosion potential is defined by a single $E_{corr} \approx E_a \approx E_c$ defined at the intersection of the anodic and cathodic polarization curves and by a corresponding i_{corr} of relatively large magnitude.

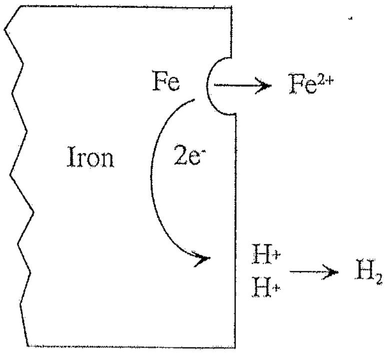


Figure 4. Typical corrosion cell showing dissolution of metal and the path of current flow.

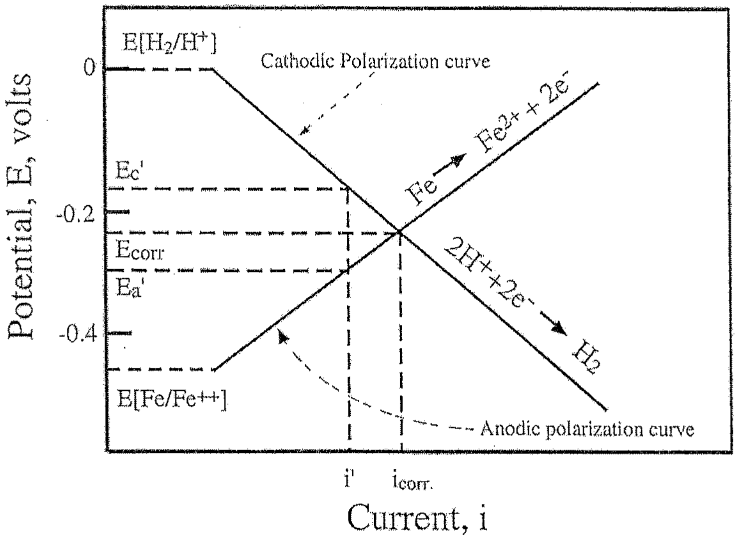


Figure 5. Changes in electrode potentials for iron in acid solution with increasing current density (decreasing resistance) due to polarization; corrosion occurs at E_{corr} and i_{corr}.

Mathematically, the relationship between anodic overvoltage and current density during corrosion under conditions of activation polarization is described by the following equation:

$$\eta_a = E_a - E_o = \pm \beta_a \log(i/i_{oa}) \qquad (12)$$

where β is the slope of the plot of overvoltage versus log i and i_{oa} is the exchange current density for the anode defined as the current density at which the rate anodic oxidation is equal to the rate of anodic reduction, i.e. $r_{red} = r_{ox} = i_o/nF$ (note this is a dynamic equilibrium); the slope is positive for oxidation and negative for reduction. A similar equation can be written for the cathode overvoltage. The corrosion potential E_c and current i_c are found at the intersection of the curves for E_a and E_c (i.e., $E_a = E_c$) as shown in Figure 5.

B. Activation Polarization

What causes the observed changes in electrode potentials with increasing current density? In this region of moderately large current density, surface electrode reactions control the rate of the electrochemical reaction. At each electrode there is a sequence of elementary steps which determines the steady-state concentration distribution of various intermediates, e.g. electrons and various hydrogen species, i.e., $H^+(l)$, $H^+(s)$, $H(s)$, and $H_2(s)$, $H_2(g)$ (l = liquid, s = surface, g = gas) at the hydrogen electrode; moreover, the overall rate of reaction at each electrode will be determined by the slowest or rate-determining step. Fast steps quickly remove intermediates leading to low steady-state concentrations of reactants, while slow steps cause build-up of reactant species to high steady-state levels. At a fixed current density, the steady-state concentrations of species at each electrode will be constant with time; that is after all the definition of steady-state. However, as current density increases, the relative rates of different steps change leading to a new distribution of surface intermediates at each electrode. Note that these changes do not lead to accumulation of any given species with time; nor does this imply that the overall rate of oxidation is different than the overall rate of reduction. Otherwise, the system would not be at steady-state.

What is the implication of these different distributions of surface electrode species with different current density? Namely, that the surface potential of each electrode is a function of the species surface concentrations--especially surface electron concentrations.

Consider as an example the simple cathodic reduction of protons in an acidic solution. The first elementary step at this electrode is adsorption of protons on the surface.

$$H^+(l) \rightarrow H^+(s) \tag{13}$$

The second is the reduction of protons with electrons

$$H^+(s) + e^-(s) \rightarrow H(s) \tag{14}$$

At low hydrogen ion concentrations and/or if the metal surface is passivated with an oxide, the corrosion rate is zero (see Fig. 6a). However, at higher $[H^+]$ in the presence of a clean metal surface, the corrosion cell resistance is lowered and current density increases. At progressively higher current densities, hydrogen atoms reach higher surface concentrations, especially if the recombination of the hydrogen atoms to molecular hydrogen is a slow step. At high steady-state surface hydrogen concentrations, adsorption sites for protons are blocked, i.e., protons are prevented from reaching the surface to react with electrons; thus, the steady-state concentration of electrons on the Pt electrode is increased, thereby changing the electrode surface potential relative to lower current densities and lowering the cathode potential as illustrated in Figure 6b.

The large decrease in cathodic potential with increasing current density is referred to as *cathodic polarization*, since the decrease is substantially larger than the increase in anodic potential. The overall effect is a lowering of the corrosion rate.

However, if air or oxygen is now added above the solution of the cell, oxygen is adsorbed on the cathode surface, reacts with adsorbed hydrogen atoms to produce water, thereby depleting the surface of hydrogen atoms, and depolarizing the cathode. This results in both increased corrosion potential and current (see Fig. 6c). Thus, acidic solution and oxygen combine to greatly increase corrosion rate.

Electrode kinetic parameters for operation in the active region in which surface electrochemical reactions control rate (i.e., in the region of activation polarization) are listed in Table 3. It is evident that i_o, β_a, and β_c are functions of acid, base and metal ion concentrations. These parameters are useful in estimating corrosion rates for various corrosion environments.

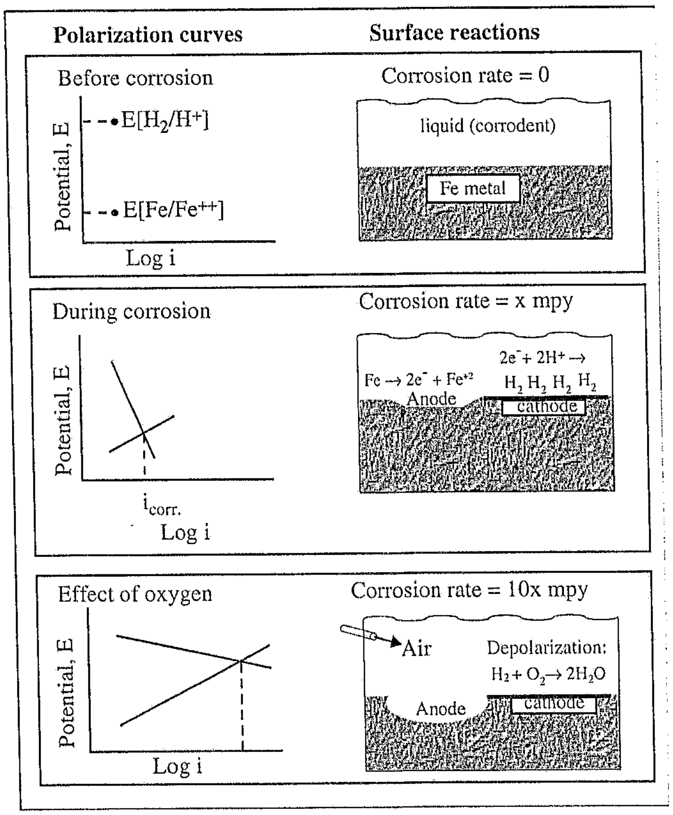


Figure 6. a. Absence of polarization at exchange current density levels; b. cathodic polarization during corrosion of iron in acid (no air); c. depolarization during corrosion in acid with air present [adapted from Henthorne, 1971-2].

Table 3. Electrode Kinetic Parameters, 20-25°C.

Electrode	Solution	i_o (A/cm^2)	β_c (V)	β_a (V)
Reaction:	**$2H^+ + 2e^- \rightarrow H_2$**			
Pt	1 *N* HCl	10^{-2}	0.03	
	0.1 *N* NaOH	0.7×10^{-3}	0.11	
Pd	0.6 *N* HCl	2×10^{-3}	0.03	
Mo	1 *N* HCl	10^{-5}	0.04	
Au	1 *N* HCl	10^{-5}	0.05	
Ta	1 *N* HCl	10^{-4}	0.08	
W	5 *N* HCl	10^{-4}	0.11	
Ag	0.1 *N* HCl	5×10^{-6}	0.09	
Ni	0.1 *N* HCl	8×10^{-6}	0.31	
	0.12 *N* NaOH	4×10^{-6}	0.10	
Bi	1 *N* HCl	10^{-6}	0.10	
Nb	1 *N* HCl	10^{-6}	0.10	
Fe	1 *N* HCl	10^{-5}	0.15	
	0.52 *N* H_2SO_4	2×10^{-5}	0.11	
	4% NaCl, pH 1-4	10^{-6}	0.10	
Cu	0.1 *N* HCl	2×10^{-6}	0.12	
	0.15 *N* NaOH	10^{-5}	0.12	
Sb	2 *N* H_2SO_4	10^{-8}	0.10	
Al	2 *N* H_2SO_4	10^{-9}	0.10	
Be	1 *N* HCl	10^{-8}	0.12	
Sn	1 *N* HCl	10^{-7}	0.15	
Cd	1 *N* HCl	10^{-6}	0.20	
Zn	1 *N* H_2SO_4	2×10^{-10}	0.12	
Reaction:	**$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$**			
Pt	0.1 *N* H_2SO_4	9×10^{-11}	0.10	
Reaction:	**$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$**			
Pt	0.1 *N* NaOH	4×10^{-12}	0.05	
Au	0.1 *N* Na OH	5×10^{-12}	0.05	
Reaction:	**$Cl_2 + 2e^- \rightarrow 2Cl^-$**			
Pt	1 *N* HCl	5×10^{-3}	0.11	0.13
Reaction:	**$M \rightarrow M^n + + ne^-$**			
Fe	0.52 *N* H_2SO_4	10^{-7}		0.060
	0.52 *N* H_2SO_4	10^{-10}		0.039
	0.63 *N* $FeSO_4$	3×10^{-9}		0.060-0.075
	4% NaCl, pH 1.5			0.068
	0.3 *N* H_2SO_4			0.10
	0.5 *M* $FeSO_4$	3×10^{-10}		0.030
	0.1 *M* Na HSO_4			
	Perchlorate			0.030
Cu	0.001 *N* $Cu(NO_3)_2$	10^{-9}		

Source: Adapted from H.H. Uhlig and R.W. Revie, Corrosion and Corrosion Control, 3rd ed., Wiley, P. 44, 1985. Reprinted by permission John Wiley and Sons, New York

C. Concentration Polarization

Given a sufficiently acidic solution, high oxygen concentration, and large enough metal surface area, the rate of the surface electrochemical reaction may be high enough that it no longer controls the overall rate, but rather it is controlled by the rate of diffusion of hydrogen ions to the cathode surface (see Fig. 7a). The depletion of hydrogen ions at the electrode surface causes a precipitous drop in cathode potential (i.e. concentration polarization) as shown in Fig. 7b. The extent of this diffusional limitation at any given current density depends upon the degree of mixing or flowrate of solution near the electrode, which affects the thickness of the quiescent liquid film surrounding the electrode through which the hydrogen ions must diffuse.

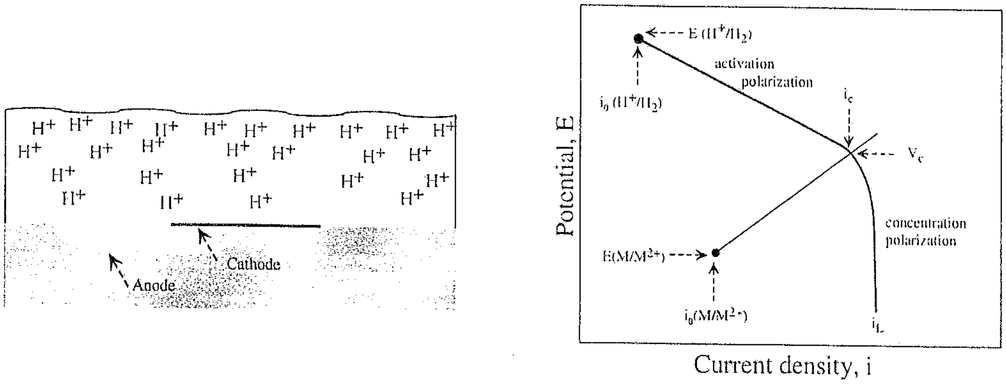


Figure 7. a. Depletion of hydrogen ion concentration due to concentration polarization (i.e., film mass transfer limitation); b. precipitous drop in cathodic potential due to concentration polarization at high current density.

D. Passivity

Corrosion rate depends greatly on environmental conditions, i.e., pH, metal ion concentration, and temperature, Depending on these conditions a number of metals and alloys may be active or relatively inactive (passive) towards corrosion. Passivity typically occurs when conditions favor formation of a thin, but highly-adherent oxide. For example, stainless steels are passive over a wide range of conditions due to formation of very stable chromium, molybdenum, and nickel oxide films; similarly aluminum is highly corrosion-resistant due to the formation of a highly passive alumina surface film.

Passivity is experimentally observed as a region of low and essentially constant anodic current density over a relatively wide range of potential (see Fig. 8). If cathodic conditions are mild, the corrosion cell operates at this low current density (Point A in Figure 8). At values of potential lower than this range, the oxide film is reduced and the metal becomes active for corrosion. Thus, if highly reducing conditions are favored at the cathode (more negative potential), the corrosion cell will operate in the active region at a much higher current density (e.g. Point B in Figure 8). Under highly oxidizing conditions, i.e., at values of cell potential above the passive range (e.g., due to addition of Cl_2), current density increases greatly with increasing potential. In this *transpassive* region *pitting* (a phenomenon discussed in the next subsection) is observed.

Passivity is affected by alloy composition, chloride concentration, inhibitors, and temperature. For example, addition of Mo to stainless steels increases the potential range for passivity, while addition of chromium decreases the current density of the passive region. Addition of chlorides decreases the range of cell potential in the passive region and increases passive current density (see Fig. 9); increasing temperature has a similar effect.

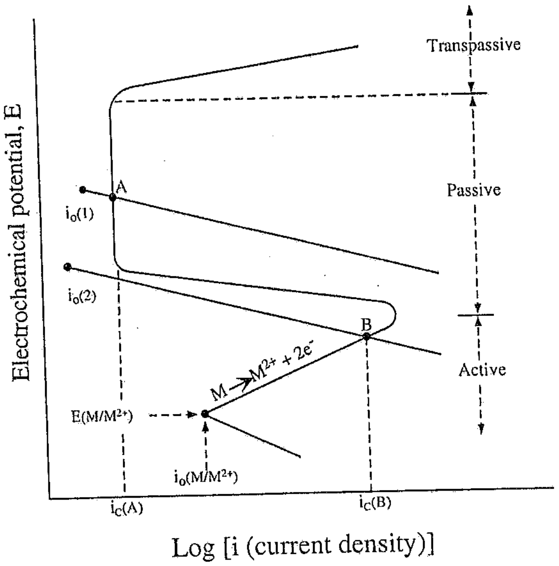


Figure 8. Polarization curve for a metal that displays an active-passive transition.

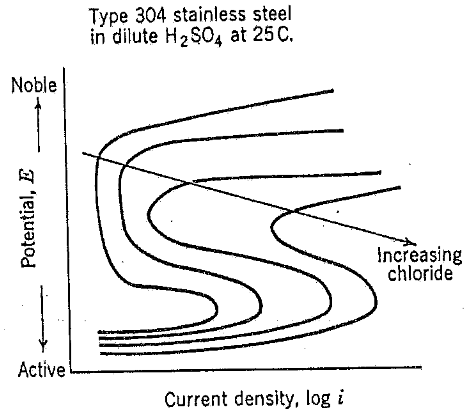


Figure 9. The influence of chloride concentration on anodic polarization [Henthorne, 1971].

IV. Mechanisms of Crevice and Pitting Corrosions

A. Introduction

Crevice and pitting corrosion involves localized corrosion at high rates due to (1) a depletion oxygen (in a crevice), (2) a surface defect, or (3) loss of coating. These types of corrosion are due to a concentration cell in which high concentrations of HCl are developed.

B. Crevice Corrosion

The mechanism for crevice corrosion is illustrated in Figure 10. In the cathodic area accessible to oxygen the principle reaction is:

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \tag{15}$$

The hydroxide reacts with the metal surface to form a surface hydroxide, e.g. iron hydroxide, which contributes to cathodic passivity. In the anodic, oxygen-depleted region, the metal surface is readily oxidized to form metal ions:

$$M \rightarrow M^{n+} + n\,e^- \tag{16}$$

For example, iron metal is oxidized to Fe^{2+}. In the absence of oxygen, water may also be oxidized to hydrogen ions:

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \tag{17}$$

To maintain charge balance in the oxygen-depleted region, anions must diffuse from the oxygen-rich to the oxygen-depleted region. Since chlorides, especially NaCl, are ubiquitous in the atmosphere and on the surface of solids, the most likely ions to diffuse into the crevice are chloride ions. Thus the combination of Reaction 17 and the diffusion of Cl^- causes a build-up of concentrated HCl at the anode, which accelerates corrosion by attacking protective surface films. For example, Figures 9 and 11 show how the passive region for Type 304 stainless steel is diminished and shifted to higher current density by increasing Cl- concentration.

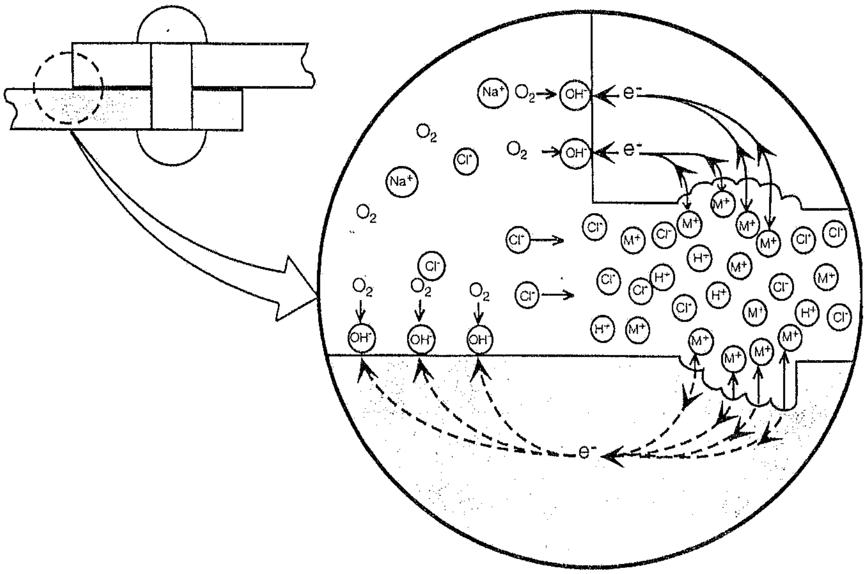


Figure 10. Mechanism of crevice corrosion [Fontana , 1986].

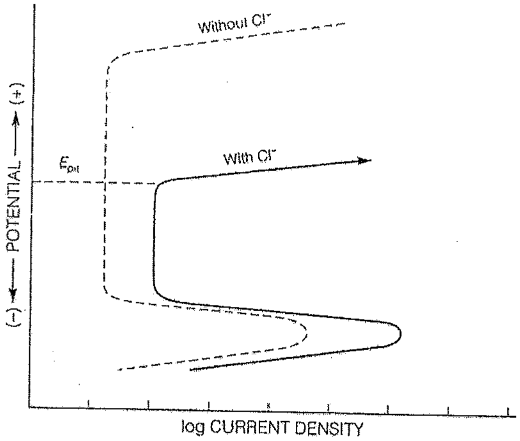


Figure 11. Schematic showing the critical pitting potential for anodic polarization [Jones, 1992].

C. Mechanism of Pitting and Effects of Chloride Ion

Figures 9 and 11 shows how the transpassive or pitting region is shifted to a lower potential by addition of chloride ion. Note that in this region, the current density increases orders of magnitude with increasing potential. Thus, what might be a passive region of operation at a moderate potential in the absence of chloride ion becomes a highly-corrosive pitting region with its addition. Corrosion pitting potentials for various alloys along with maximum and minimum corrosion potentials are listed in Table 2. It is evident that pitting potentials are substantially lower than the maximum corrosion potentials for these metals.

TABLE 2 Corrosion Potential Data Compared with Pitting Potentials (Volts vs. SCE)

		Corrosion Potential	
Alloy Designation	**E_{pit}**	**Maximum**	**Minimum**
Type 430 stainless steel	-0.130	0.230	-0.310
Type 304 stainless steel	-0.020	0.280	-0.140
Type 316 stainless steel	0.100	0.385	0.090
Carpenter 20 Cb	0.050	0.520	0.120
Incoloy 825	0.525	0.530	0.180
Hastelloy C	>0.900	0.530	0.530

From B.E. Wilde and E. Williams, J. Electrochem. Soc., Vol. 117, p. 775, 1970. Reprinted by permission, The Electrochemical Society.

The mechanistic role of chlorides in pitting corrosion is explained as follows. In the absence of chloride ions, the passive hydroxide film dissolves slowly to form ferric ions:

$$FeOOH + H_2O \rightarrow Fe^{3+} + 3\,OH^- \qquad (18)$$

It is proposed [Jones, 1992] that chloride ion catalyzes the liberation of Fe^{3+} by displacement of the outer layers of the passive film:

$$FeOOH + Cl^- \rightarrow FeOCl + OH^- \qquad (19)$$

$$FeOCl + H_2O \rightarrow Fe^{3+} + Cl^- + 2\,OH^- \qquad (20)$$

Chloride also reacts with the Fe^{2+} corrosion products in a hydrolysis reaction to produce HCl, thus contributing to the buildup of a high chloride, low-pH microenvironment:

$$Fe^{2+} + 2\,H_2O + 2\,Cl^- \rightarrow Fe(OH)_2 + 2\,HCl \qquad (21)$$

Fe^{2+} also diffuses from the oxygen-deficient anodic region to the exterior where it is oxidized to $Fe(OH)_3$ and produces a porous cap of ferric hydroxide.

The mechanism for this process is shown schematically in Figure 12. The cap impedes easy escape of Fe^{2+} but is sufficiently porous to permit easy migration of chloride ions into the pit. Note that Cl^- is consumed in Reaction 15 but regenerated in Reaction 16 and also appears on both sides of Reaction 17; thus, it acts as a catalyst for dissolution of Fe and formation of $Fe(OH)_2$. In the case of stainless steels, additional anodic reactions for nickel and chromium also occur.

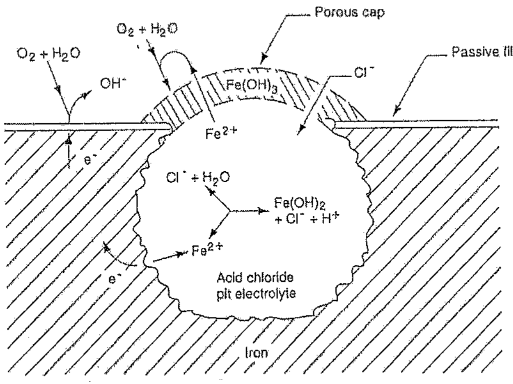


Figure 12. Schematic of processes occurring at an actively growing pit in iron [Jones, 1992].

V. Corrosion Protection

A. Cathodic Protection

1. Principles of cathodic protection

Cathodic protection involves the application of a current in the direction opposed to the corrosion in order to lower the corrosion rate. In the limit it effectively converts the metal to a cathode under reducing conditions so that it cannot corrode. Thus the reactions shown in Figures

4 and 6b are reversed, i.e., at the cathode, $M^{2+} + 2\ e^- \rightarrow M$ and at the anode $H_2 \rightarrow 2\ H^+ + 2\ e^-$.

To understand how this works, consider a metal corroding in acid solution in the presence of iron metal (Fig. 13). Suppose a current density i_{app} is applied to the cathode causing electrode potential to shift negatively from E_{corr} to E, then

$$E_c = E - E_{corr} \qquad (22)$$

where E_c is defined as the cathodic overpotential. The excess electrons from the applied current reduce the current density of the anodic oxidation reaction from i_{corr} to i_a and similarly increase the cathodic reduction current density from i_{corr} to i_c. The principle of conservation of charge (i.e., which excludes build-up of charge on an electrode) requires that the difference between the increase in the cathodic reduction rate and the decrease in the anodic oxidation rate (prompted by the cathodic overpotential E_c) must be equal to the applied current. Thus,

$$i_{app} = i_c - i_a \qquad (23)$$

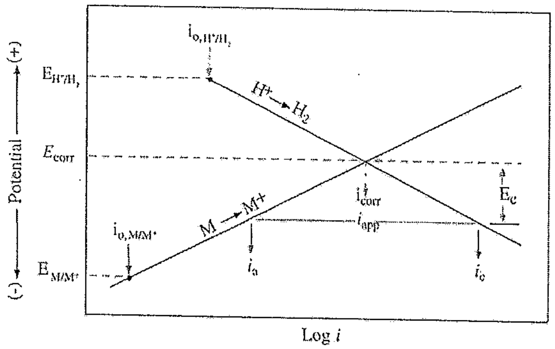


Figure 13. Changes in anodic and cathodic current densities caused by application in the opposing direction of a current density i_{app}. Note that potential is reduced from E_{corr} by the amount E_c, while the corrosion current is reduced from i_{corr} to i_a.

The decrease in corrosion rate due to an applied current (which occurs at the anode) is illustrated in Figure 14. The unpolarized corrosion rate is 10^3 μA/cm² or 460 mpy. Application of a cathodic polarization of about 120 mV reduces corrosion rate (at the anode) by three orders of magnitude to $i_a = 1$ μA/cm². However, note that the corresponding applied current density requirement of 1.5×10^{-2} A/cm² is prohibitively high, since only 1 m² of exposed area would require 150 A for protection! Since coatings to reduce current requirements are generally not acid resistant, cathodic protection in acid solution is usually not practical.

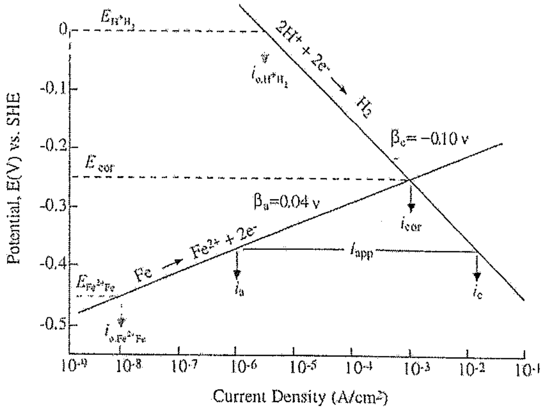


Figure 14. Cathodic protection for steel in acid solution with an impressed current of 1.5 x 10^{-2} A/cm^2; the corrosion rate is reduced by three orders of magnitude.

Relative amounts of current that must be purchased for partial, complete, and safe cathodic protection are shown in Figure 15. The amount of current purchased is shown on the plot, and the current must be purchased at the voltage shift shown (from E_{corr}). The total cost in watts is $Power = \Delta E \cdot i \cdot area$, where $area$ is the area of the corroding surface. For safe protection, the potential should be pushed at least about 0.1 V past the open circuit half-cell potential.

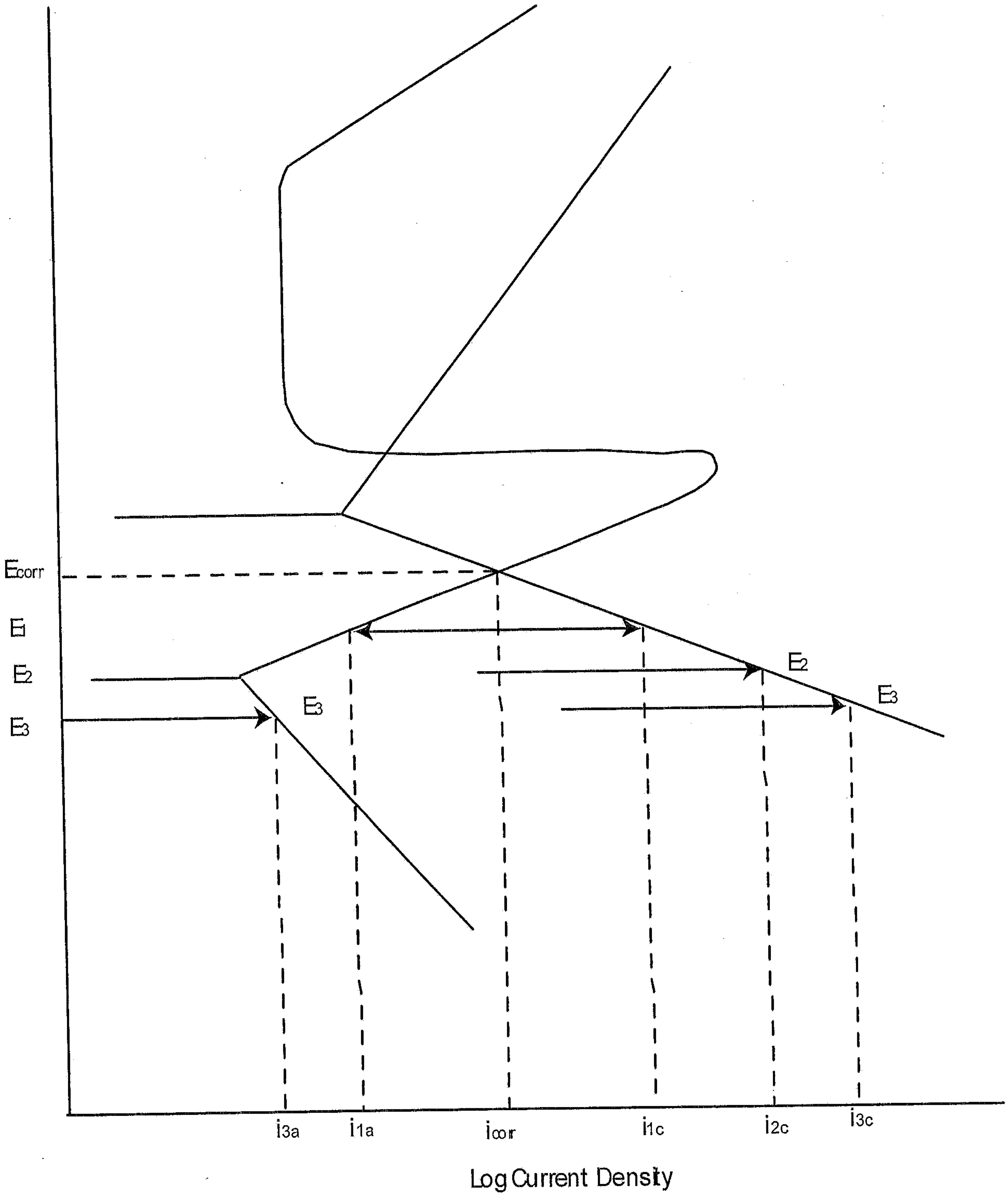


Figure 15. The concepts and costs (in current) of cathodic protection.

2. Practical aspects of cathodic protection

Cathodic protection has been used for over 150 years to protect metals against corrosive electrolytes. Common applications include protection of underground pipelines, cables, and tanks against soil corrosion and of cables, piers, and ships against marine corrosion. There are two approaches to cathodic protection: (1) application of a current to reverse corrosion and (2) galvanic protection using a sacrificial anode which is more active than the metal being protected. The application of these two approaches to protection of an underground pipeline are illustrated in Figure 16. Metals used as sacrificial anodes include magnesium, zinc, aluminum and their alloys. Galvanic protection can be used where current requirements are modest (e.g. in the case of smaller structures) and the resistivity of the soil is low (e.g. $< 10^4$ ohm-cm).

Cathodic protection has a number of advantages over anodic protection: (1) it is applicable to all metals, (2) sacrificial electrodes can be used where no source of power is available, (3) installation costs are generally lower, (4) methods are well-established. However, cathodic protection suffers from the following limitations: (1) application of large currents may be required at a large operating, (2) stray currents may induce corrosion of neighboring structures (this may be a difficult problem in a large plant consisting of complex structures), (3) hydrogen produced at the cathode may cause hydrogen blistering and/or embrittlement of metals, and (4) design and operation may be complicated by variable resistivity of soils and bacterial action in a corrosion system. It should be emphasized that cathodic protection is a usually a long-term control method; application to a failing system is rarely economical.

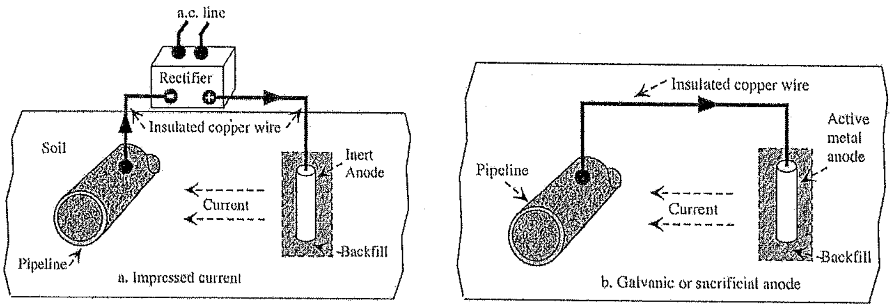


Figure 16. Cathodic protection for an underground pipe: a. applied current; b. sacrificial anode.

B. Anodic Protection

1. Principles of anodic protection

Anodic protection involves application of a current in the direction of the corrosion current to shift the potential quickly through a region of greater activity (more anodic) into into a region of passivity where the corrosion rate is lower than without protection. From the previous discussion of passivity it follows that in order to shift from an active to a passive region, it is necessary to deliver a current to the critical value (i_{crit}) required to passivate the surface and pass the nose of the active region into the passive region (see Fig. 17); i_{crit} is determined by shifting the potential up until it reaches the nose of the active region; the additional amount of current that we must purchase (i_{max}) for a short period to clear the nose is measured by a horizontal line between the cathode curve and the nose. However, upon passage in the passive region the corrosion current is reduced by orders of magnitude to i_{app}. It is also apparent from Figure 18 that anodic protection can sometimes require substantially less applied current and hence operating cost relative to cathodic protection. This depends upon the shape of the cathodic and anodic reaction.

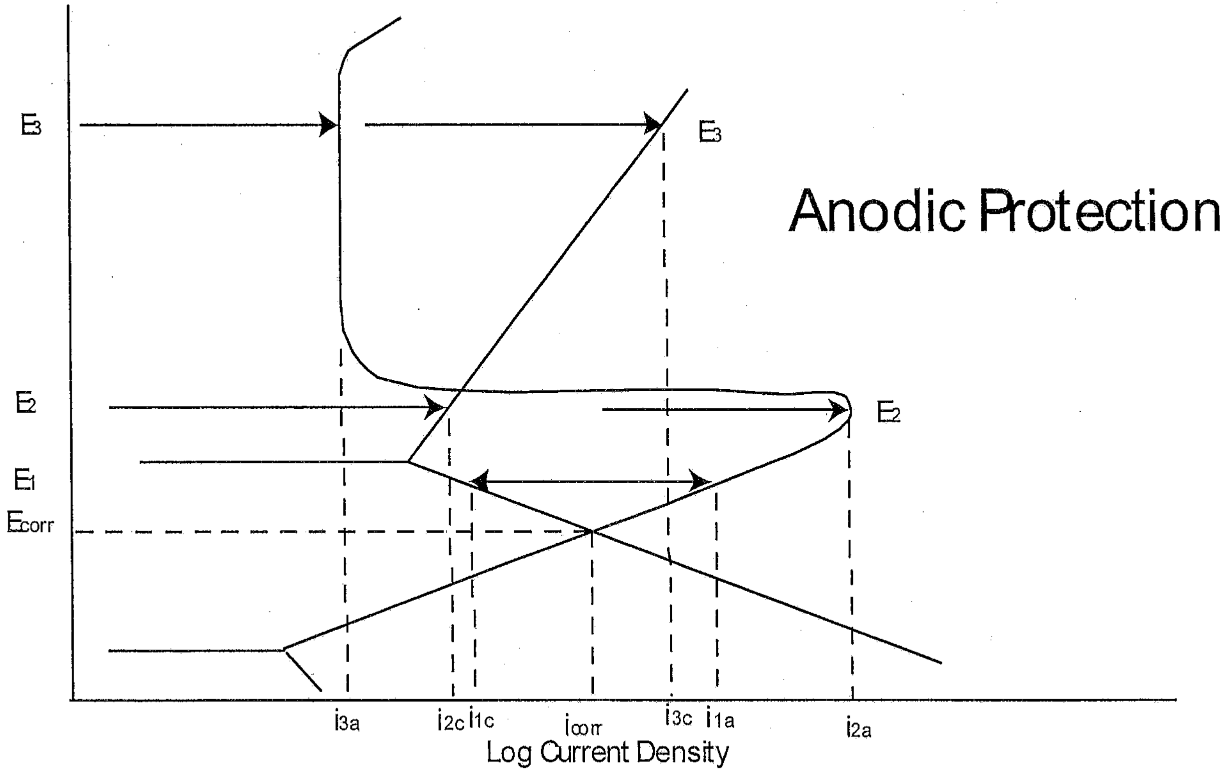


Figure 17. Graphical determination of the applied potential and current density necessary for shifting from operation in the active region to safe operation in the passive region. $i_{crit} = i_{2a} + i_{2c}$ = minimum current density to pass from the active to the passive region; i_{3a} = minimum current density to maintain anodic protection, but it must be accompanied by purchase of i_{3c} current also; *Thus* cathodic protection can sometime be very expensive and impractical.

For some stainless steels under mild conditions (free of chloride ion), i_{app} and i_p (passivation current) are not significantly different since the lower limit of i_{3a} (on a log scale) is close to zero. There are, however, situations in which the value of applied current density may be significantly less than i_p (if i_p is large) Such a case is illustrated in Figure 18.

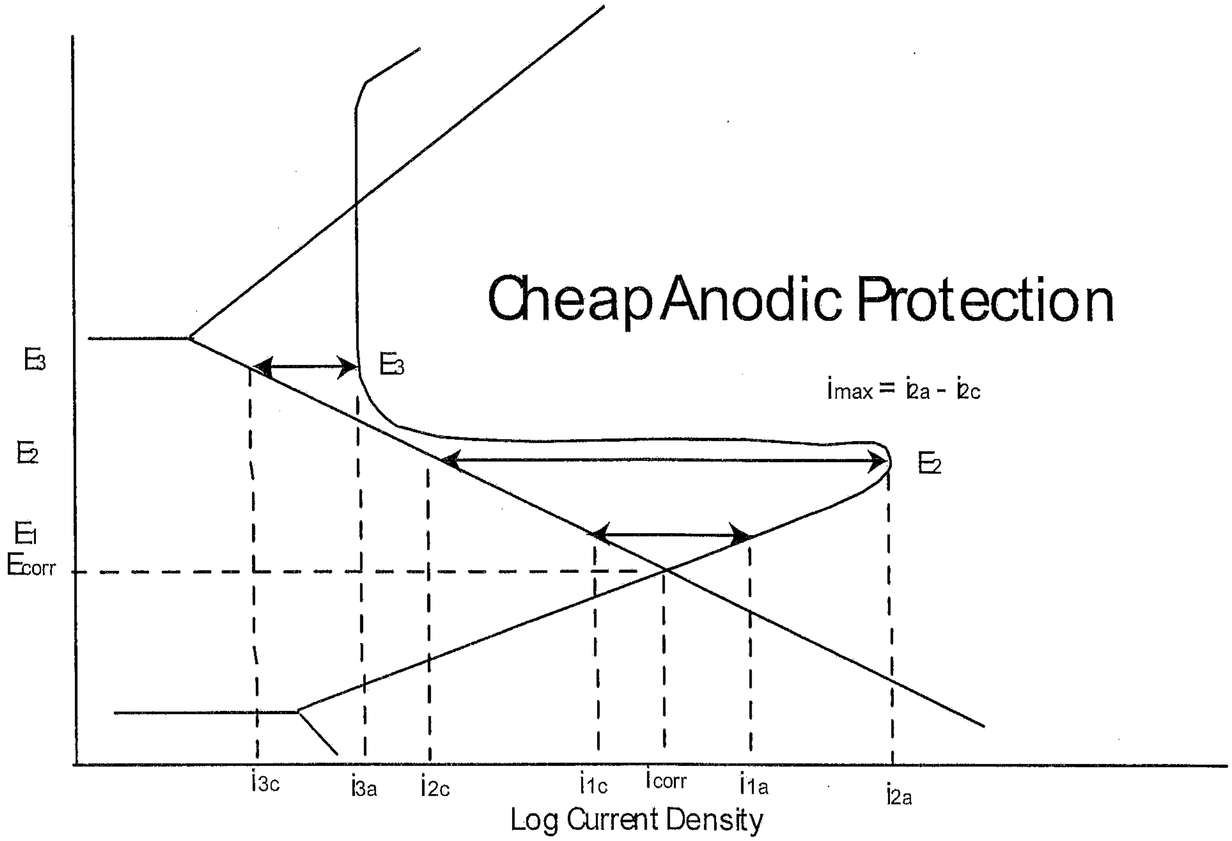


Figure 18. Graphical determination of the applied potential and current density necessary for shifting from operation in the active region to safe operation in the passive region for the case in which not much current is required to keep the metal protected.

2. Practical aspects of anodic protection

Anodic protection is only applicable to metals and alloys that show active-passive behavior; for example, it can be used to protect steels, stainless steels, titanium, aluminum and chromium, although the greatest emphasis has been on protection of steels and stainless steels. One of the most common applications is protection of large steel tanks of simple geometry containing sulfuric acid or other acidic materials, although anodic protection can be used to protect more complex structures in a large plant by appropriate placement of the cathode. For example, anodic protection has also been used to protect stainless steel heat exchangers in sulfuric acid plants.

Figure 19 illustrates a relatively simple anodic protection system for a tank; it consists of an auxiliary electrode (cathode), reference electrode for measuring potential, a potentiostat which feeds a potential controller (not shown) which in turn drives the DC power source to the cathode. The cathode is clad with a corrosion-resistant material such as platinum, while reference electrodes are typically silver or platinum.

The principal advantages of anodic protection include its: (1) low operating costs, (2) applicability to a wide range of severe corrodents, (3) high throwing power for protection of large complex structures, (4) predictability and designability based on laboratory experiments, and (5) capacity to directly monitor corrosion rate from the applied current. Limitations of anodic protection include its (1) limited application to systems exhibiting passivity, (2) high installation costs, (3) potential difficulties in avoiding crevice-corrosion problems, and (4) potential for high corrosion rates if the system controls fail. It should be emphasized that anodic protection is relatively ineffective for chloride-containing corrodents.

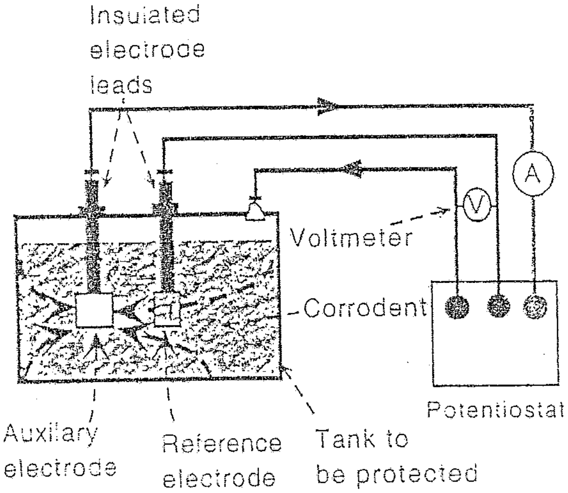


Figure 19. Typical anodic protection system for tanks.

C. Protection by Design

Logically, the best way to deal with corrosion is to prevent or minimize its occurrence. Keys to prevention include (1) careful design of equipment, (2) minimizing the contact of equipment with corrodents, (3) minimizing where possible the severity of the corrodent, and (4) using coatings and inhibitors (see Section D). Some basic principles of design include the following:

1. Minimize crevices by using welds properly (see Fig. 20).
2. Minimize galvanic corrosion through: (a) use of metals close in galvanic series, (b) avoiding low anodic areas, (c) insulation, (d) maintaining coatings (especially anode), and (e) putting a third active sacrificial metal in contact with others.
3. Minimize erosion corrosion by increasing pipe diameter, using baffles and or flared tubing; don't direct inlet tubes at walls.
4. Minimize stress corrosion by avoiding high localized stresses and maintaining smooth, clean surfaces.
5. Maximize drainage of corrodents from equipment, since small amounts of stagnant residue can be highly corrosive (see Fig. 21).

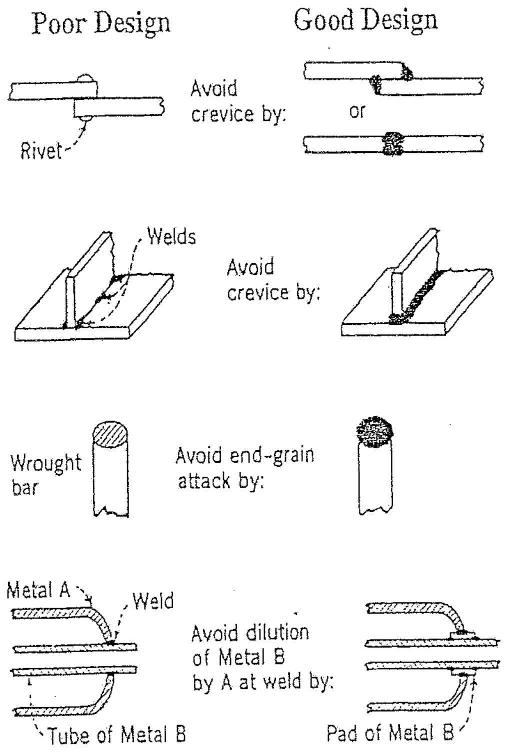


Figure 20. Minimizing corrosion by proper welding of joints and end pieces.

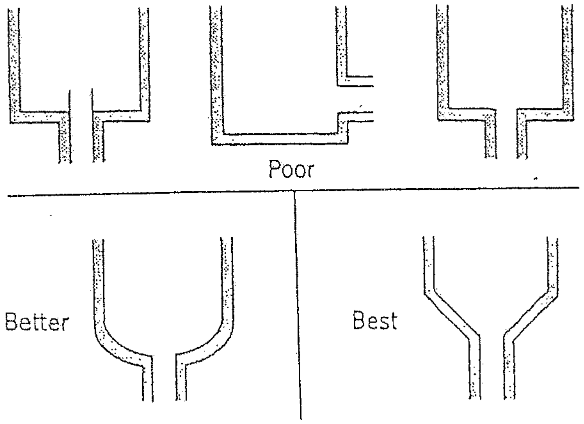


Figure 21. Drainage of corrosive liquids is important in preventing corrosion.

D. Coatings and Inhibitors

1. Coatings

Application of a coating to a metal is the most commonly used method for preventing metal corrosion. This approach operates on the principle of minimizing contact of active metals with corrodents. Generally, coatings do not fare well in the presence of highly-corrosive chemicals; rather, they are most effective for protection against natural media in the atmosphere, water, or soil. Hundreds of different kinds of coatings are available. The most common classes of coatings are (1) metallic, (2) inorganic compounds, and (3) organic compounds, including paints. Details on selection of and application of coatings are provided in Henthorne (1972).

2. Inhibitors

Inhibitors are substances that reduce corrosion rate when added to the corrodent in small quantities. They are typically classified according to composition (organic or inorganic), form (solution or vapor-phase) and mechanism of action (anodic or cathodic control).

Anodic inhibitors retard the anodic reaction (see Fig. 22a). They include (1) oxidizing agents that promote passivity, e.g. chromates, nitrates, ferric salts, etc. and (2) film formers that precipitate insoluble films on the anode, e.g., alkalis, phosphates, silicates, etc. There is significant risk in using anodic inhibitors, since they must completely protect the anodic area to be effective.

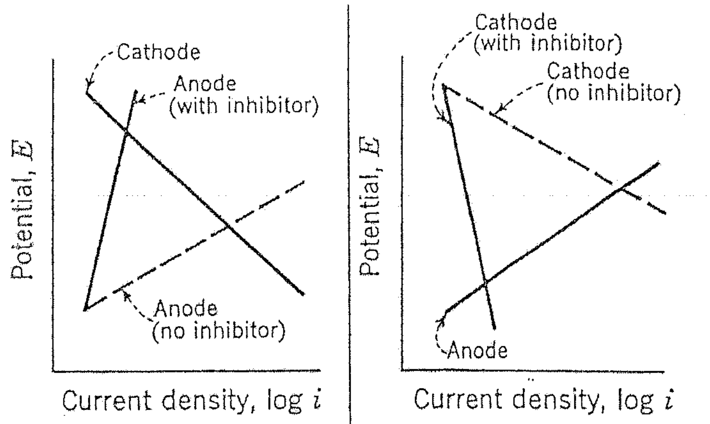
Cathodic inhibitors (Fig. 22b) can be catagorized into three types:

1. Oxygen scavengers that remove oxygen from solution and thus prevent depolarization of the cathode. Examples include sodium sulfite and hydrazine.
2. Poisons for hydrogen evolution, e.g. arsenic, antimony, bismuth, and sulfur.
3. Insoluble films that form on the cathode and reduce its effective area, e.g. addition of calcium bicarbonate to produce insoluble calcium carbonate.

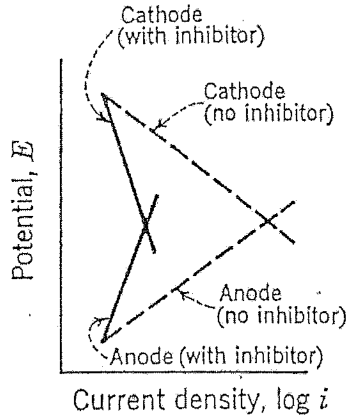
Adsorption inhibitors are used to control both anodic and cathodic reactions, especially in acid solutions. Polar organic compounds which adsorb strongly on metals, e.g. amines, are typical adsorbates.

Vapor inhibitors are typically compounds having high vapor pressures which adsorb through the gas phase on metal surfaces; examples are amine salts, morpholine, and sodium benzoate.

While use of inhibitors is a well-established and often effective method of minimizing corrosion, a number of precautions are advised: (1) some inhibitors are toxic materials, (2) product contamination is possible (this is particularly true in dealing with foodstuffs), and (3) inhibitors may find their way into another part of the plant, causing contamination or increasing corrosion.



a. Anodic inhibition **b. Cathodic inhibition**



c. Anodic and cathodic inhibition

Figure 22. Effects of inhibitors on electrode polarization.

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