CORROSION AND SURFACE TREATMENT

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Summary

Corrosion involves electrochemical reactions of a metal with an oxidizing agent present the environment. Corrosion is of great economic importance; it limits the useful life

time of metallic objects and often presents a risk of accidents and of pollution. Corrosion reactions can be studied and understood by using electrochemical methods in conjunction with physical analysis methods of materials science. Corrosion control is an important issue for the sustainable development of human society. Decision makers should be aware of the benefits resulting from strong research and education in the field of corrosion and surface treatment.

1. Scope and economic importance of metal corrosion

Compared to other materials metals exhibit several unique properties including high strength and ductility over a wide temperature range, ease of machining and welding, electronic and thermal conductivity. In addition most metals can be easily recycled. Power plants, petroleum drilling, chemical and pharmaceutical process industries, machines, transport systems (ships, cars, railways, airplanes), information technology etc. would not be possible without metals. In nature metals (with the exception of gold) exist as minerals in their oxidized state. If left alone, metals tend to return to their natural state by reacting with oxidizing agents present in the environment: the metal corrodes. While the reduction of a mineral to a metal requires energy, the opposite reaction, the corrosion of a metal, releases energy. Because usually corrosion rates are rather small, the associated energy release is not important. However, in some cases the released energy may be substantial. A good example is that of batteries, which can be viewed as a controlled corrosion process in which metal oxidation occurs at one electrode and reduction of an oxidizing agent at the other electrode. In a lead-acid starter battery for automobiles the lead is oxidized to lead sulfate on one electrode and lead oxide (PbO_2) is reduced to lead sulfate on the other electrode. The energy supplied by these reactions is used to start the motor and drive the electric circuits. The example shows that corrosion reactions are not always damaging, but may be put to a beneficial use. It further illustrates the close relationship that exists between corrosion and electrochemistry. Indeed, corrosion reactions involve electrochemical mechanisms and they obey the basic principles of electrochemical thermodynamics and kinetics.

Corrosion science and engineering is concerned with the study and control of corrosion reactions. While all metals corrode, their corrosion rate varies enormously, depending on the nature of the metal and the properties of the environment. The corrosion resistance should not be viewed as an intrinsic property of a given metal. Rather it depends a large number of physical and chemical variables, which fall into four types: the characteristics of the metal (chemical reactivity, microstructure, mechanical strength, non-metallic inclusions), the chemical nature of the environment (acidity, oxidizing power, humidity, salinity), the mechanical forces acting on the metal (tensile stress, cyclic stress, rubbing, impacting particles or fluids), the physical conditions to which the metal is exposed (temperature cycles, wind, fluid flow, irradiation). To control corrosion one must take into account all of these variables. In other words, corrosion prevention must be based on a consideration of the metal-environment system as a whole. Further complications may arise if one or several of the critical variables change during the time of use of an equipment, for example because corrosion products accumulate or because the environment changes. All these factors complicate the prediction of corrosion rate and of the useful life-time of a metallic structure. The development of appropriate measures of corrosion control is a difficult task that requires, in addition to engineering skills, a good understanding of the underlying electrochemical mechanisms.

Corrosion and surface treatment are of great economic importance. A survey made in the early seventies in the UK evaluated the cost of corrosion and corrosion control at about 3% of gross national product and a more recent study performed in the USA also came to a figure of 3-4%. This corresponds to many billions of dollars per year. Besides the direct costs of the corroded equipment this figure includes the cost of corrosion prevention such as the application of coatings, cathodic protection, or the use of more expensive corrosion resistant materials such as stainless steels. It also includes indirect costs of corrosion such as the loss of production during plant shut down and the cost of corrosion monitoring. For example, if a pipeline must be shut down in order to repair a component of corrosion damage the indirect cost of lost oil production exceeds by far the direct cost of replacing the damaged pipes. The same applies to the lost production of a nuclear power plant that must be shut down because of corrosion of a heat exchanger. However, one should not consider corrosion only in terms of cost. Even more critical is that corrosion may threaten the safety of engineering structures and thus increase the risk of accidents. This aspect of corrosion is particularly critical for the chemical and petroleum industries, for large civil engineering structures and for transportation systems such as ships and airplanes. Corrosion may also be at the origin of environmental pollution, be it a leak in an oil pipeline because of corrosion, the wreckage of a rusted oil tanker, or release of toxic substances from inorganic pigments in a paint. Quite generally, corrosion represents a waste of natural resources including raw materials, energy and drinking water. Indeed, corrosion leaks in buried pipes of water distribution systems cause substantial losses of transported water.

Corrosion prevention and control is an important issue for the sustainable development of human society. Unfortunately, this is often not sufficiently recognized by decision makers. Corrosion impacts on many priority areas of sustainable development such as preserving the environment, providing an adequate supply of energy, maintaining human health, and providing for efficient access to information (Figure 1).

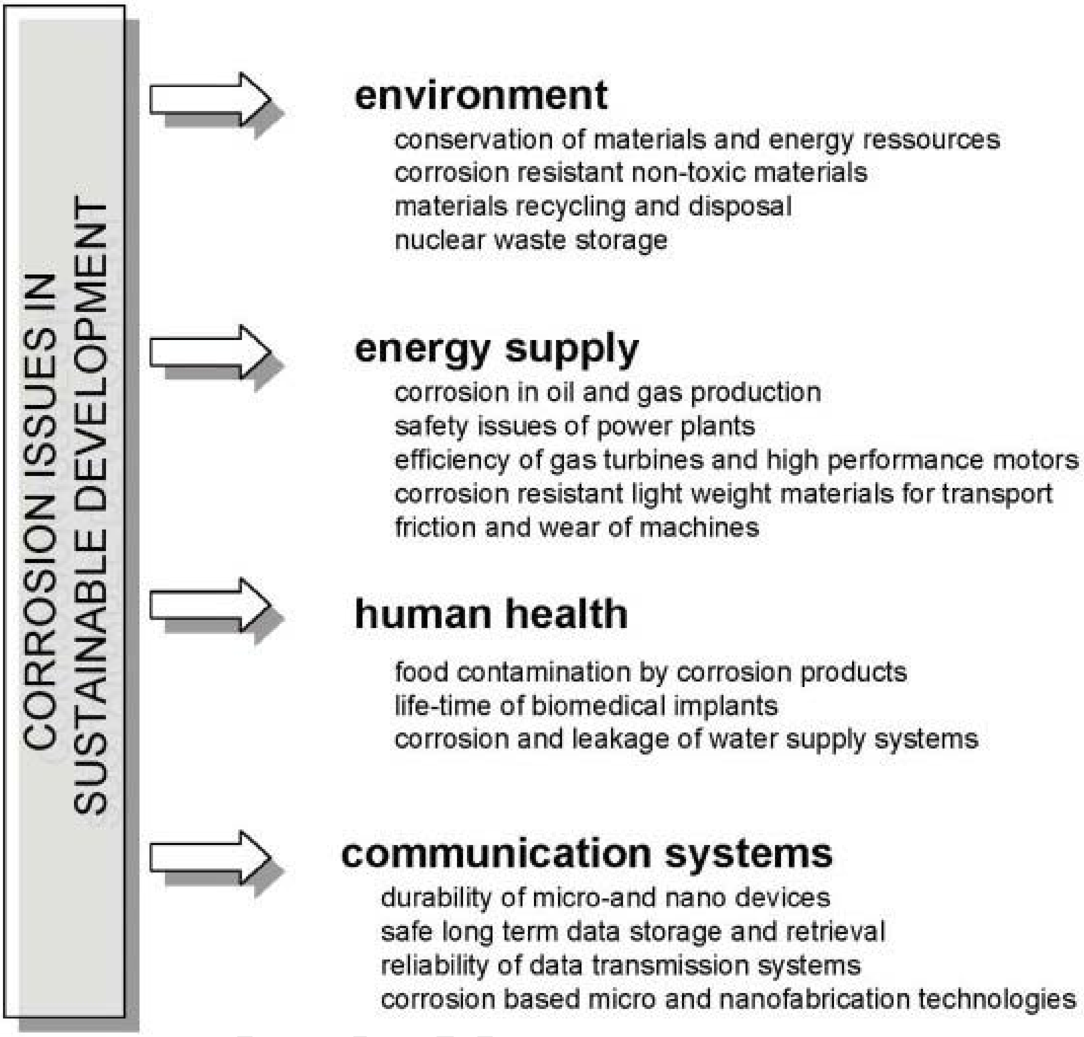

Figure 1. Impact of corrosion science and engineering on sustainable development

2. Why Metals Corrode

2.1. Corrosion Reactions

From a chemical point of view the corrosion of metals involves the oxidation of a metal and the reduction of an oxidizing agent that is present in the environment. The two most important oxidizing agents in terms of corrosion are the hydrated proton H^+ present in acid solutions and oxygen present in air.

Corrosion in acid media

Corrosion in presence of acids results form a reaction of the metal with hydrated protons. The corrosion reaction can be written as follows, where M stands for metal and the subscript aq signifies a species in aqueous solution:

$$\mathrm{M} + \nu \mathrm{H}^{+}_{(\mathrm{aq})} \rightarrow \mathrm{M}^{n+}_{(\mathrm{aq})} + (\nu/2)\mathrm{H}_2 \qquad (1)$$

In this equation ν is the stoichiometric coefficient of the protons. Its value is the same as the charge $n+$ of the metal ion formed. The overall reaction (1) can be decomposed into two *partial reactions*, namely the partial oxidation reaction (2) and the partial reduction reaction (3):

$$\mathrm{M} \rightarrow \mathrm{M}^{n+}_{(\mathrm{aq})} + n\mathrm{e} \qquad (2)$$

$$\nu \mathrm{H}^{+}_{(\mathrm{aq})} + n\ \mathrm{e} \rightarrow (\nu/2)\mathrm{H}_2 \qquad (3)$$

In these equations e designates the electron and n is the charge number which corresponds to the number of electrons transferred. The charge number n may be viewed as the stoichiometric coefficient of the electrons transferred. The charge transfer between the metal and the protons takes place at the metal-electrolyte interface. Such reactions are referred to as electrode reactions. The overall corrosion reaction (1) includes two electrode reactions, the anodic partial reaction (2) and the cathodic partial reaction (3). The equilibrium conditions and the rate of these reactions are described by the well known principles of electrochemical thermodynamics and electrochemical kinetics.

Corrosion in neutral and alkaline media

In neutral media exposed to air corrosion usually results from a reaction of the metal with oxygen. The formation of dissolved metal ions then follows the overall reaction:

$$\mathrm{M} + (\nu/4)\ \mathrm{O}_2 + (\nu/2)\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{M}^{\nu+}_{(\mathrm{aq})} + \nu\mathrm{OH}^{-}_{(\mathrm{aq})} \qquad (4)$$

The overall reaction (4) includes the following partial oxidation and reduction reactions:

$$\mathrm{M} \rightarrow \mathrm{M}^{n+}_{(\mathrm{aq})} + n\ \mathrm{e} \qquad (5)$$

$$(\nu/4)\ \mathrm{O}_2 + (\nu/2)\mathrm{H}_2\mathrm{O} + n\ \mathrm{e} \rightarrow \mathrm{OH}^{-}_{(\mathrm{aq})} \qquad (6)$$

If the solubility limit of hydroxide at the surface is exceeded a precipitation reaction may occur that results in the formation of a loose hydroxide film:

$$\mathrm{M}^{\nu+}_{(\mathrm{aq})} + \nu\mathrm{OH}^{-}_{(\mathrm{aq})} \rightarrow \mathrm{M(OH)}_{\nu} \qquad (7)$$

Another type of corrosion reaction between a metal and oxygen leads to the formation of metal oxide:

$$\mathrm{M} + (\nu/2)\ \mathrm{O}_2 \rightarrow \mathrm{MO}_{\nu} \qquad (8)$$

In dry air under ambient conditions, the growing oxide film forms a barrier between the metal and the environment that effectively inhibits further corrosion after a thickness of some one to three nanometers has been reached. In humid air because an aqueous electrolyte may form on the surface the reactions between the metal and oxygen are generally more complicated, leading to reaction products that may or may not be protective. These reactions will be discussed in more detail in Section 4.

2.2. Nernst Equation

Chemical reactions spontaneously proceed towards an equilibrium state that is energetically most favorable. The quantitative description of equilibrium conditions is the subject of the field of chemical thermodynamics. Similarly, electrochemical thermodynamics deals with the equilibrium conditions at electrodes. The equilibrium potential E_{rev} of an electrode varies with the concentration of the reactants and products (more precisely, with their activity) and it obeys the Nernst equation. In general way, an electrode reaction can be written

$$\sum \nu_{\text{ox},j}\, B_{\text{ox},j} + n\,\text{e} = \sum \nu_{\text{red},j}\, B_{\text{red},i} \qquad (9)$$

In this equation, B_j designates the different species that participate in the reaction and ν_j their stoichiometric coefficient. The subscripts ox and red indicate whether a species j corresponds to the "oxidized" or to the "reduced" state; in other words, whether it stands to the left or to the right of the equality sign of the reduction reaction (9). The Nernst equation for reaction (9) reads:

$$E_{\text{rev}} = E^0 + \frac{RT}{nF} \ln \frac{\prod a_{\text{ox},j}^{\nu_{\text{ox},j}}}{\prod a_{\text{red},j}^{\nu_{\text{red},j}}} \qquad (10)$$

Here E^0 is the standard potential of the electrode reaction and the symbol Π indicates the multiplication product of the activities of participating species to the power ν_j; R is the universal gas constant (8.31 J/mol K), T is the absolute temperature (K) and F is the Faraday constant (96480 Coulomb mol^{-1}). Numerical values of standard potentials can be found in many reference works and physical chemistry textbooks. Table 1 gives a selection of standard potentials of electrode reactions that are of particular interest in corrosion. All values refer to the standard hydrogen electrode, the potential of which by convention is zero volts.

The equilibrium between metallic copper and cupric ions serves to illustrate the use of the Nernst equation:

$$\text{Cu}^{2+} + 2\text{e} = \text{Cu} \qquad (11)$$

The standard potential of this electrode reaction is E^0 = 0.340 V. The Nernst equation then becomes:

$$E_{\text{rev}} = 0.340 + \frac{RT}{2F} \ln a_{\text{Cu}^{2+}} \qquad (12)$$

The term RT/F has the dimension of Volts. For 25°C, and converting the natural logarithm to base 10, yields: $2.3(RT/F)$ = 0.059V. Equation (13) valid for 25°C thus reads:

$$E_{\text{rev}} = 0.340 + \frac{0.059}{2}\log\ a_{\text{Cu}^{2+}} \qquad (13)$$

Electrode	**E°/V**
$\text{Li}^+ + \text{e} = \text{Li}$	- 3.045
$\text{Mg}^{2+} + 2\text{e} = \text{Mg}$	- 2.356
$\text{Al}^{3+} + 3\text{e} = \text{Al}$	- 1.676
$\text{Mn}^{2+} + 2\text{e} = \text{Mn}$	- 1.18
$\text{Cr}^{2+} + 2\text{e} = \text{Cr}$	- 0.90
$\text{Cr}^{3+} + 3\text{e} = \text{Cr}$	- 0.74
$\text{Zn}^{2+} + 2\text{e} = \text{Zn}$	- 0.763
$\text{Fe}^{2+} + 2\text{e} = \text{Fe}$	- 0.440
$\text{Cd}^{2+} + 2\text{e} = \text{Cd}$	- 0.403
$\text{Ni}^{2+} + 2\text{e} = \text{Ni}$	- 0.257
$\text{Sn}^{2+} + 2\text{e} = \text{Sn}$	- 0.136
$\text{Pb}^{2+} + 2\text{e} = \text{Pb}$	- 0.125
$2\text{H}^+ + 2\text{e} = \text{H}_2$	0
$\text{Cu}^{2+} + 2\text{e} = \text{Cu}$	0.340
$\text{O}_{2\,(g)} + 2\text{H}_2\text{O}_{(l)} + 4\text{e} = 4\text{OH}^-$	0.401
$\text{Cu}^+ + \text{e} = \text{Cu}$	0.520
$\text{Ag}^+ + \text{e} = \text{Ag}$	0.799
$\text{O}_{2\,(g)} + 4\text{H}^+ + 4\text{e} = 2\text{H}_2\text{O}_{(l)}$	1.229
$\text{Au}^+ + \text{e} = \text{Au}$	1.83

Table 1. Standard potentials of electrode reactions

For the partial electrode reaction (14) responsible for the formation of cuprous oxide,

$$\text{Cu}_2\text{O} + 2\text{H}^+ + 2\,\text{e} = 2\,\text{Cu} + \text{H}_2\text{O} \qquad (14)$$

one gets for 25°C:

$$E_{\text{rev}} = 0.471 - 0.059\ \text{pH} \qquad (15)$$

Here the definition $\mathrm{pH} = -\log a_{\mathrm{H}^+}$ was used and the activity of pure solids and of water was taken as unity. One may note that the standard potential for the formation of cuprous oxide differs from that of cupric ions. The standard potential for the formation of cupric oxide,

$$\mathrm{CuO} + 2\mathrm{H}^+ + 2\,\mathrm{e} = \mathrm{Cu} + \mathrm{H_2O} \qquad (16)$$

is again different and has a value of 0.570V. Standard potentials always refer to a specific reaction stoichiometry. For oxide formation its value also depends on the particular crystal structure and the state of hydration of the oxide.

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Biographical Sketch

Dieter Landolt was born near Zurich, Switzerland. He got a Diploma in Chemical Engineering from the Swiss Federal Institute of Technology in Zurich in 1962 and a Ph.D. from the same institution in 1965. From 1966 to 1968 he worked as a postdoctoral researcher at the Lawrence Berkeley Laboratory and the Department of Chemical Engineering of the University of California Berkeley. He then joined the University of California Los Angeles (UCLA) as Assistant Professor at the School of Engineering and Applied Science. In 1972 he was appointed Professor of Materials Science and Head of the Laboratory of Metallurgical Chemistry at the Swiss Federal Institute of Technology in Lausanne (EPFL), a position he held until his retirement in 2003. At EPFL he contributed decisively to the development of teaching and research in materials science. At present he is Professor Emeritus at the Institute of Materials of EPFL. The research of Dieter Landolt embraces the general area of corrosion, electrochemistry and applied surface science. He authored or coauthored some three hundred papers and book chapters, dealing in particular with electrochemical engineering and materials aspects of electrochemical metal deposition and dissolution, thin passive oxide films, applied surface analysis by spectroscopic methods, organic and inorganic coatings and chemical aspects of wear (tribocorrosion). He authored a textbook entitled Corrosion and Surface Chemistry of Metals. His research contributions were recognized by several international awards including the Cavallaro medal and the EFC medal of the European Federation of Corrosion, the Castner medal of the Society of Chemical Industry London, the Research Award of the Electrodeposition Division of the Electrochemical Society (ECS), the AESF Scientific Achievement Award of the American Electroplater and Surface Finishers Society and the Grande médaille of CEFRACOR, the French Corrosion Society. He served as Secretary General and as President of the International Society of Electrochemistry (ISE) and as Chairman of the International Corrosion Council (ICC). For a number of years he chaired the Science and Technology Advisory Committee (STAC) of the European Federation of Corrosion. He is a Fellow of ECS and Honorary member of ISE.