Introduction to corrosion prevention and control for engineers

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P. J. GELLINGS

Foreword by E. Börje Bergsman

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Foreword

Iron rusts and other metals deteriorate by different kinds of corrosion – this is so usual that it is considered natural. For technical and economical reasons it is, however, more and more obvious that serious efforts are necessary to prevent this destruction.

Corrosion defence in all forms is very well suited for international co-operation. Consequently, the European Federation of Corrosion was founded in 1955. The Federation is a voluntary association whose object is to promote co-operation in Europe between non-profit-making scientific and technical societies in the general advancement of corrosion science and materials protection. The Federation numbers 63 member societies from 18 European countries.

Education and information are extremely important parts of the fight against corrosion – quite a lot of the damage can be avoided by applying what is already known.

Accordingly a Working Party on Corrosion Education was formed within the Federation. The first task of this Working Party was to collect information on educational aids already available in English, French and German for the benefit of those wishing to learn more about corrosion, for those teaching corrosion and for those whose responsibility it is to minimize the cost of corrosion. The result of this step was a Corrosion Education Manual.

In a discussion within the Working Party in 1973 prof. A. Almar-Naess, Norway, on the basis of the Manual and personal experiences, stressed the need for a textbook suitable for engineering schools: '. . . In the universities and technical schools corrosion science and to a lesser degree corrosion technology are taught to students of chemistry and metallurgy, generally as a part of the general courses of physical chemistry, electrochemistry and physical metallurgy. It is, however, a fact that 80–90% of all metallic material produced in the world is disposed by the naval architects, civil engineers and mechanical engineers, and apart from what they may pick up in the lectures on general chemistry and materials, corrosion science or corrosion technology are not among the subjects taught to these engineers in their normal schooling . . . Many are or are soon becoming aware of their deficient knowledge of corrosion, but it is not an easy task to rectify this shortcoming, since they have great difficulties in understanding even elementary books on corrosion. They also soon discover that it is by no means easy to get advice from the chemists or the metallurgists since they talk different languages . . .'.

The Working Party unanimously shared this opinion and Prof. Dr. P.J. Gellings of the Techn. Hogeschool Twente, Enschede (Netherlands), a member of the Working Party, took upon himself the task of writing a book of the kind discussed. An editorial board was nominated, viz. Prof. A. Almar-Naess, Technical University of Norway, Trondheim, Mr. H. Arup, Danish Corrosion Centre, Copenhagen (Denmark) and Prof. J.S.Ll. Leach, University of Nottingham, Nottingham (United Kingdom).

As chairman of the Working Party 'Corrosion Education' I want to express my gratitude to Prof. Gellings and to the editorial board.

It is my sincere hope that those who are or will be responsible for the design, operation and maintenance of the many varied and often complicated systems and machinery of today's technology will take advantage of this book.

In particular I hope that those who are teaching the engineers of tomorrow will use this book to make our future engineers aware of what corrosion is and what can be done about it.

Without doubt the book helps to fill a gap on the way from theory to practice.

Stockholm, June 1976

E. BÖRJE BERGSMAN
Director
Swedish Corrosion Institute, Stockholm

Preface and guide to the use of this book

As stated in mr. Bergsman's foreword this book is primarily intended as a textbook for engineering schools. It is hoped that it will also be useful for some other purposes brought forward during the discussions in the Working Party Corrosion Education. The most important of these are the use in general chemistry courses as an illustration of the application of chemical principles and as a basis for selfstudy for engineers already working in practice. Some compromises were necessary in view of these diverse purposes.

It has been tried to write the book in such a way that it is reasonably complete and can be studied on the basis of about two years secondary school chemistry (Appendix 17 gives the chemistry knowledge necessary in terms of secondary school chemistry books of the appropriate level as used in different countries).

The book may be used at three levels:

a. *Introductory:* When only a first introduction is required the study of chapters 2 and 3 can be limited to the introductory and summary sections (sections 2.1, 2.9, 3.1, 3.5) while after the study of sections 4.1 and 4.2 only those parts of chapters 4 and 5 need be considered which are relevant to the field of interest of the student. Depending on the amount of detail included this will be equivalent with a course of 6 to 10 lecture hours.
b. *Intermediate:* When some insight into the background theory is desirable it is possible to study the main text of the book as a whole but without those appendices which go more deeply into theoretical principles. This will then correspond with a course of 14 to 18 lecture hours.
c. *Advanced:* Finally those who want to obtain a more comprehensive idea of the principles of corrosion and corrosion control may study the whole book including the more theoretical appendices. This group can with advantage use the problems added at the end of several chapters. Most of these are straightforward applications of the theory presented but some give an extension of this treatment.

Some of the problems are chosen in such a way that even those going only to level *a* or *b* can solve them. In my experience solving problems is a great help in getting a quick grasp of a subject and in fact saves studying time.

Nevertheless learning about any subject, and corrosion is no exception, takes time and work. There is no magical way of solving corrosion problems without at least some understanding of how corrosion occurs and of the principles of corrosion prevention and control.

It is hoped that the important gains to be achieved by a better insight in the possibilities of corrosion prevention and control, some of which are indicated in chapter 1, will more than repay the work involved in this study.

Many corrosion problems are so complex that even a knowledge of everything presented in this book is not sufficient to obtain a solution and a corrosion expert has to be consulted. However, the knowledge gained by the study of this book will lead to better recognition of the cases where more expert advice is necessary, to a better understanding of the proposed solutions and to a more fruitful discussion. The choice of a practical and economically acceptable solution is in most cases only possible through close cooperation between the engineer or designer and the corrosion expert.

I should like to acknowledge the help of all members of the Working Party on Corrosion Education for the sound advice given during the discussions about this book. In particular I am very grateful to the members of the editorial board, who read most of the manuscript, for their valuable comments. Professor J.S.Ll. Leach read the whole manuscript and did his best to turn the language written by the present author into good english. If this has not been completely successful this is certainly not due to a lack of effort on his side but to the selfconceit of the author.

Enschede, June 1976 P.J. GELLINGS

1. Definition and importance of corrosion

1.1. DEFINITION OF CORROSION

Perhaps the most common example of what is called corrosion is the reaction between ordinary steel and its environment during which a voluminous and porous layer of rust is formed. There are many well-known examples of this from everyday life such as the perforation by rusting of silencers and exhaust systems of cars, of car bodies and of various kinds of structural steelwork. In fact rusting and corrosion are sometimes considered to be synonymous.

In order to give a more precise background to this subject it is desirable to use a more exact and general definition of corrosion. In the Corrosion Education Manual of the European Federation of Corrosion [1] the following definition is given:

> 'Corrosion: attack on a material by reaction with the environment with a consequent deterioration of properties. When no reference is made to the material it is normally understood that a metal is involved, and that the valency of the metal is increased; an exception is the dissolution of a metal in a liquid metal or in a fused salt. The term corrosion may refer either to the process or to the damage caused. Implicit in the concept of corrosion as a process is the rate per unit area of the corrosion reaction; implicit in the damage caused is the extent and nature of the damage in relation to the function of the component concerned'.

From this definition we see that purely mechanical or physical attack on a material, such as wear, erosion, cavitation or swelling of polymers fall outside what we define as corrosion. Similarly only when the deterioration is caused by reaction with the environment do we speak of corrosion; internal reactions such as tin-pest (change of crystal structure from white to grey tin upon cooling below about 15°C) are excluded. As we shall see later there are some combined forms of attack where two processes, e.g., erosion and corrosion or cavitation and corrosion are combined and occur simultaneously causing attack much greater than that of either of the processes independently.

It will be clear from the definition that the aim of preventing or controlling corrosion is to minimize either the attack on the metal or the damage caused by that attack.

1.2. IMPORTANCE OF CORROSION

The general corrosion of steel and other metals converts large tonnages of these metals into corrosion products with a consequent slow deterioration of their properties. On the other hand there exist several types of localized corrosion, e.g., pitting, which may have very serious consequences, even though the actual amount of metal corroded is very small. Thus the failure of a heat-exchanger tube by pitting could result in the shutdown of a power station, maybe leaving half a city without electricity and central heating in midwinter. Similarly perforation of an underground pipeline, used for transporting natural gas, water or oil, may lead to losses of product and extensive damage to the environment. Sometimes the influence of corrosion is less direct such as in the loss of efficiency due to the accumulation of corrosion products decreasing heat transfer or preventing the proper functioning of equipment, e.g., by jamming of moving parts.

There are also other important aspects of corrosion damage. The conjoint action of stress and corrosion may in certain cases lead to fracture of a metal at stresses well below its yield point with catastrophic consequences when vital parts are concerned. Thus many lives have been lost in automobile and aeroplane crashes which afterwards were attributed to the occurrence of stress-corrosion.

It is always difficult, and impossible when the loss of life is considered, to calculate accurately the costs of corrosion and protection, but it is estimated that in industrialized countries these costs amount to £ 20–30 per capita per annum, corresponding to 2.5 to 3.5% of the gross national product [2]. Some of these costs are unavoidable such as those due to the higher price of more corrosion resistant materials or the cost of painting or other protective measures. However, it has become quite clear that doing something about corrosion is in most cases cheaper than just letting it run its course, if only by avoiding unplanned outages of equipment. It has also been estimated [2] that about 25% of the present corrosion costs could be saved by the application of *existing* knowledge of corrosion prevention and control, i.e., by using better protective systems, by improving design and materials selection. In Appendix 1 this is presented in more detail.

The estimates of costs and of possible savings only relate to the so-called *direct* corrosion costs, i.e., those due to higher investment, maintenance and repair costs. In many cases the *indirect* costs, e.g., due to production or product loss, are even higher although in general also more difficult to estimate.

Apart from the immediate economic or technical consequences, corrosion is also a serious problem because it contributes to the depletion of our natural resources. The increasing industrial development of many countries means that the competition for and the price of metal resources will increase as these become more scarce.

Finally it should be mentioned that corrosion control also contributes to the conservation of energy. The manufacture of all materials consumes a large amount of energy, e.g., steel 55 to 70 x 10^6 $J.kg^{-1}$, aluminium 200 to 250 x 10^6 $J.kg^{-1}$ and similar amounts for most other metals. An average car has an energy content of about 1.3 x 10^{11} J of which at the most 33% can be recovered by recycling. Extending the lifetime of cars thus makes it possible to save large amounts of energy.

1.3. CORROSION RESISTANCE AND MATERIALS SELECTION

When a material has to be selected for a particular application a large number of factors affect this choice, as shown schematically in Fig. 1.1. [3]. Only one of these is the corrosion resistance. This itself is also dependent upon a number of other factors, the most important of which are given in schematic form in Fig. 1.2.

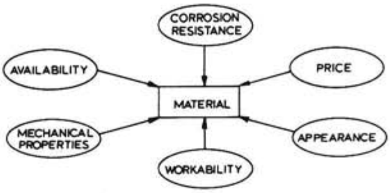

Fig. 1.1. Factors affecting the choice of a material.

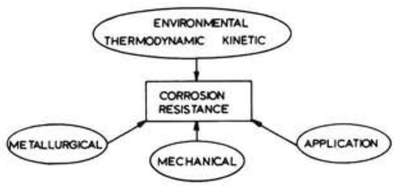

Fig. 1.2. Factors influencing the corrosion resistance of a material.

From this it is seen that corrosion resistance is not an intrinsic property of a metal such as its modulus of elasticity or electrical resistivity. It is impossible to define 'the' corrosion resistance of a metal as this is very sensitive to the influence of the environment. A metal may be nearly completely corrosion resistant in one medium (e.g. aluminium in the atmosphere), while it corrodes rapidly in another (e.g. aluminium in alkaline solutions). Stainless steel type AISI 316 (18% Cr, 10% Ni, 2% Mo) is in many environments found to be more corrosion resistant than type AISI 304 (18% Cr, 9% Ni) and therefore 316 is sometimes chosen in preference to 304 for safety's sake. Although in chloride containing solutions this is correct, in nitric acid and in other acid, oxidizing solutions 316 is definitely inferior to 304.

Furthermore the application and desired lifetime also play a decisive role. Even if the lifetime of a certain material is acceptable as such, its corrosion resistance may be insufficient for example if the (small) amount of corrosion product formed is unacceptable. This may occur when these products lead to unacceptable contamination or disturb the process or proper working of the equipment. For example some enzymatic reactions used in the synthesis of antibiotics are strongly inhibited by traces of copper or certain other heavy-metal ions at concentrations as low as 0.1 to 2 ppm (ppm = parts per million, e.g., mg per 1).

1.4. GENERAL PLAN OF THE BOOK

Because corrosion processes are just specific examples of chemical or electrochemical reactions, the usual thermodynamic and kinetic considerations are applicable and thus have an important bearing on corrosion resistance as indicated in Fig. 1.2.

Thermodynamics tells us when a reaction may occur spontaneously and the application to corrosion reactions will be the subject of Chapter 2. Even when thermodynamic arguments suggest that a metal should corrode it is found in many cases that it corrodes very slowly or not at all. This means that we also have to study reaction rates, which is the subject of kinetics and this is treated in Chapters 3 and 4.

These general principles are then applied in the description of characteristic forms of corrosion in Chapter 5 and to a number of important methods for corrosion control and prevention in Chapter 6. In these chapters emphasis is laid on what is generally called electrochemical corrosion (sometimes, but not quite correctly, also called 'wet' corrosion) even though many of the principles also apply to purely chemical corrosion ('dry' corrosion) which is treated in more detail in Chapter 7.

At the end of the book a number of appendices are collected. These are of two types:

a. those giving numerical data;

b. those going more deeply into certain parts of the theoretical background.

The reading of the second group of appendices is not necessary for a first introduction in this field.

1.5. REFERENCES

1. *Corrosion Education Manual.* Prepared by the Working Party on Corrosion Education of the European Federation of Corrosion, 2nd international edition, Swedish Corrosion Institute, Stockholm (1974).
2. *Report of the Committee on Corrosion and Protection*, Chairman T.P. Hoar, London, H.M.S.O., 1971.
3. M.G. Fontana and N.D. Greene, *Corrosion Engineering*, New York, McGraw Hill, 1967.

1.6. PROBLEMS

For numerical data and conversion factors see Appendix 2 and 3.

1. List some cases of corrosion you have met and try to estimate the costs caused by these.
2. In a cylindrical copper tank, diameter 1 m, a reaction mixture is kept during 8 hours. If the depth of the reaction mixture is 1.5 m and the corrosion rate is such that the copper wall thickness decreases 0.1 mm/year calculate the concentration of copper in the reaction mixture (in ppm) after one 8 hour period.
3. If the maximum permissible tin content in a certain beverage is 5 ppm calculate the maximum permissible corrosion rate in mm/year if the size of the tin-plated container is 10 cm diameter by 15 cm high and the average storage life is three months.

2. The driving force for corrosion reactions

2.1. INTRODUCTION

It is a well known fact that an iron object, when placed in water, tends to corrode and rust is formed. On the other hand when a noble metal, like silver, is put into water it remains unchanged, which is just the reason why it is called noble. Thus iron is unstable under those circumstances whereas rust and silver are stable.

However, if a silver object is put into a solution containing sulphides, e.g., an egg, it is rapidly tarnished, that is covered with a dark-coloured layer of silver sulphide. Thus under these circumstances silver is unstable and corrodes with the formation of stable silver sulphide.

There are many similar observations about the stability of metals under different circumstances. Some metals are unstable, and thus corrode, under nearly all conditions. Other metals, like silver in the example given above, sometimes are stable but become unstable in suitable circumstances. Very few metals, practically only gold and platinum, are stable under nearly all conditions. However, even these can be made to dissolve under extreme circumstances.

We will now try to put this rather vague notion of 'stability' on a firmer basis using the methods of thermodynamics.

Stability is clearly connected with tendencies for change in a system. If no change tends to occur we say that the system is stable. If, however, a spontaneous change is observed this makes the system move to a more stable state.

A well known tendency in nature is for systems to move towards a state of minimum internal energy. A simple example is a falling object: the fall leads to a decrease of its potential energy. Similarly in the burning of a fuel such as coal the energy is decreased by the formation of strong chemical bonds between the atoms of the fuel and of oxygen and this energy is liberated as heat. Strictly speaking for processes occurring at constant pressure, which include most corrosion reactions, the proper quantity to use is the *enthalphy* H instead of the *energy* U. In practice the difference can very often be neglected (see problem 1).

On the other hand there are also spontaneous processes in which the internal energy increases, e.g., the dissolution or melting of a crystal. There the attractive energy between the atoms or molecules of the crystal is lost. This corresponds to a second tendency in nature to move to a state of maximum randomness. In a crystal we find nearly perfect order, but in the dissolved or molten state the atoms or molecules are free to move, which means a large increase in randomness. This tendency towards randomness becomes more important with increasing temperature. The randomness of a system is expressed in a quantity called the *entropy* S. This is small in ordered systems, e.g., crystals and large in disordered systems, e.g., solutions, melts, vapors.

In reality the driving force toward equilibrium is never either the enthalpy H or the entropy S separately. All processes, such as chemical reactions, are governed by the combined effect of these two quantities. It is usual therefore to introduce a combined quantity, called the *free enthalpy* G and defined as $G = H - TS$. If the change in a quantity X during a process is denoted by ΔX, we have for the change in free enthalpy during a process occurring at constant temperature and pressure

$$\Delta G = \Delta H - T\Delta S. \tag{2.1.1}$$

The general rule for a process to occur spontaneously is that

$$\Delta G < 0. \tag{2.1.2}$$

If $\Delta G = 0$ we say that the process is in equilibrium, which, together with (2.1.2), means that the free enthalpy of a system in equilibrium is a minimum.

We see that the examples introduced above are limiting cases of equation (2.1.2); if T or ΔS are small the tendency towards minimum energy is predominant, if T or ΔS are large it is the tendency toward maximum randomness which prediminates.

The study of the consequences and applications of equations (2.1.1) and (2.1.2) forms the subject matter of chemical thermodynamics[1,2]. Some of the most important features of this will now be applied to corrosion reactions.

For a first reading and for those who need only a superficial knowledge of the theory the study of this chapter can be limited to section 2.9, which gives a summary of the most important points.

2.2. THERMODYNAMICS OF OXIDATION REACTION

For the reaction of nickel with oxygen:

$$Ni + \tfrac{1}{2}O_2 = NiO \qquad (2.2.1)$$

the change in free enthalpy can be written as the difference between the free enthalpy of the product NiO minus that of the reactants Ni and O_2:

$$\Delta g = -\mu_{Ni} - \tfrac{1}{2}\mu_{O_2} + \mu NiO.$$

The use of lower case g denotes that we consider one mole of NiO to be formed, i.e., the reaction occurs once as written. Furthermore μ_A denotes the free enthalpy of one mole of A and is usually called the *thermodynamic potential* of A.

From thermodynamic considerations (see Appendix 5) it is possible to derive for the free enthalpy change of reaction (2.2.1):

$$\Delta g = \Delta g^{\ominus} - \frac{RT}{2} \ln p_{O_2} \qquad (2.2.3)$$

where p_{O_2} is the (partial) pressure of the oxygen.
At a chosen temperature $\Delta g^{\ominus}$ is a constant. If there is equilibrium $\Delta g = 0$, from which we find that:

$$p_{O_2}\ (\text{equil}) = \exp\,(2\ \Delta g^{\ominus}/RT) \qquad (2.2.4)$$

If the oxygen pressure is lower than this value, which is called the dissociation pressure, we see that $\Delta g > 0$ which means that reaction (2.2.1) tends to proceed spontaneously to the left: the oxide dissociates into metal and oxygen. However, if the oxygen pressure is higher $\Delta g < 0$ and the metal will tend to be oxidized.

For NiO the dissociation pressure is 10^{-74} atm at room temperature and 10^{-10} atm at 1000°C. This means that the oxidation of nickel by air is a spontaneous process. Using the values of $\Delta g^{\ominus}$ given in Appendix 6 it is possible to calculate the dissociation pressure of other oxides and thus to determine whether under certain circumstances of temperature and oxygen pressure oxidation of the metal is a spontaneous process or not.

2.3. REACTIONS IN SOLUTION

If we put a piece of iron (e.g., a screw driver) in an aqueous solution containing copper ions we observe the formation of a deposit of solid copper on the iron. When the solution is analyzed this will be seen to contain iron ions which have been dissolved. The reaction which has taken place can be written

$$\mathrm{Fe} + \mathrm{Cu}^{2+}\,(\mathrm{aq}) = \mathrm{Fe}^{2+}\,(\mathrm{aq}) + \mathrm{Cu} \qquad (2.3.1).$$

As this occurs spontaneously we conclude that Δg for this reaction must be negative. Now we have

$$\Delta g = -\mu_{\mathrm{Fe}} - \mu_{\mathrm{Cu}^{2+}} + \mu_{\mathrm{Fe}^{2+}} + \mu_{\mathrm{Cu}} \qquad (2.3.2).$$

With the method given in Appendix 5 this can be shown to be equal to:

$$\Delta g = \Delta g^{\ominus} + RT \ln \frac{[\mathrm{Fe}^{2+}]}{[\mathrm{Cu}^{2+}]} \qquad (2.3.3).$$

The standard free enthalpy change $\Delta g^{\ominus}$ is again a function of temperature only. In equilibrium $\Delta g = 0$ which means that the equilibrium ratio of the iron and copper concentrations is a constant at a certain temperature. This is often called the *equilibrium constant* K and from (2.3.3) we find:

$$K = [\mathrm{Fe}^{2+}] \,/\, [\mathrm{Cu}^{2+}] = \exp\left(-\Delta g^{\ominus}/RT\right) \qquad (2.3.4)$$

For this particular case $\Delta g^{\ominus} = -151$ kJ. mole^{-1} which means that equilibrium will only be reached at the extremely high ratio of 10^{26}. In all practical cases this ratio will be much smaller so that reaction (2.3.1) will always proceed to the right.

It is important to note that it is only the ratio of the two concentrations which influences the driving force of this reaction and not the absolute value of the separate concentrations.

2.4. ELECTROCHEMICAL CELLS

The reaction discussed in section 2.3. can be separated into the two partial reactions

$$\mathrm{Fe} = \mathrm{Fe}^{2+} + 2e^{-}$$
$$\mathrm{Cu}^{2+} + 2e^{-} = \mathrm{Cu} \qquad (2.4.1)$$

in which the electrons produced by the first reaction are consumed by the second. When summed we come back to reaction (2.3.1). The first reaction is called an *oxidation* reaction, the second a *reduction* reaction. This is in agreement with the general definitions of oxidation as a reaction in which electrons are produced and reduction as one in which electrons are consumed.

Although this separation is purely formal when applied to this reaction as performed in section 2.3., namely by immersion of iron in a solution containing copper ions, it is possible to devise a way to perform this reaction so that oxidation and reduction are really separated. This is done by putting a piece of iron in a solution containing iron-ions and a piece of copper in a solution containing copper-ions. The solutions are then connected by a porous membrane permitting current to pass but preventing mixing of the solutions. If the pieces of iron and copper are connected by a metal wire a current starts to flow while iron dissolves and copper is deposited. We have now obtained what is called an *electrochemical cell* which is shown schematically in Fig. 2.4.1a. The two pieces of metal are called the electrodes. The electrode at which oxidation takes place, i.e., where electrons are produced is called the *anode* and the reaction taking place there an *anodic reaction*. Similarly the electrode at which electrons are consumed is called the *cathode* and the corresponding reaction a *cathodic reaction.* In the example described above the iron electrode is the anode, the copper electrode the cathode.

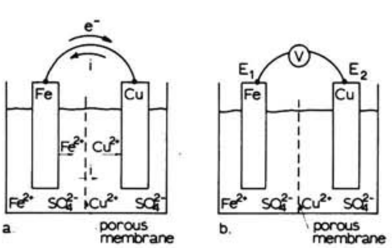

Fig. 2.4.1. Electrochemical cell consisting of an iron and a copper electrode:
a. electrodes connected by a conducting wire, i.e., with external current;
b. electrodes connected by a voltmeter with very high internal resistance, i.e., without external current.

If the electrodes are not connected by a wire but by a voltmeter (see figure 2.4.1b) an electric potential difference is measured which is called the *electromotive force* of the cell or the *cell voltage.* The origin of this can be explained as follows. If a metal, e.g., iron, is placed in a solution containing its ions it will in general not be in equilibrium. This means that either metal ions dissolve leaving the valence electrons in the metal or metal ions deposit on the metal leaving the corresponding negative ions in the solution in excess. In both cases a potential difference is set up between the metal and the solution, in the first case the metal becoming negative, in the second positive with respect to the solution. Metal ions will continue to dissolve or deposit until the tendency for dissolution or deposition is just counterbalanced by the electrical field pulling the metal ions back and equilibrium is reached.

In the case of the metals copper and iron examined above, copper has a smaller tendency to dissolve (or larger to deposit) than iron. Thus the copper electrode will become positive with respect to the iron electrode. In section 2.3. we saw that reaction (2.3.1) proceeded to the right spontaneously. This means that electrons flow from the iron to the copper electrode and the current thus in the reverse direction. This is just what we expect: current flows from the positive to the negative electrode in the external circuit.

The electrochemical cell will produce energy when the reaction takes place. It can be shown from thermodynamics that the maximum amount of work which can be produced when one mole of reaction occurs is $-\Delta g$. This is also equal to the cell voltage E times the charge transported: nF. Here n is the number of moles of electrons per unit of reaction and F the Faraday, i.e., the absolute value of the charge of one mole of electrons. We thus obtain:

$$\Delta g = -nFE \qquad (2.4.2).$$

If we define $E^{\ominus} = -\Delta g^{\ominus}/nF$ we obtain from equation (2.3.4) an equation for the cell voltage, which in this case is

$$E = E^{\ominus} - \frac{RT}{2F} \ln \frac{[Fe^{2+}]}{[Cu^{2+}]} \qquad (2.4.3).$$

This is called the Nernst equation. For practical purposes it is mostly rewritten in common logarithms and at 25°C we obtain

$$E = E^{\ominus} - \frac{0.059}{2} \log \frac{[Fe^{2+}]}{[Cu^{2+}]} \text{ (Volt)} \qquad (2.4.4).$$

This equation is extremely important because using this we can, from measurements on electrochemical cells, obtain by means of equation (2.4.2) the free-enthalpy change in the corresponding cell-reaction.

2.5. ELECTRODES AND ELECTRODE POTENTIALS

An electrochemical cell consists of two electrodes. If we consider a single electrode, which is also called a half-cell, we can try to define the *electrode potential* or electric voltage of a half-cell. Unfortunately it is impossible to measure this: we can only measure the electric voltage of a complete cell, i.e., electrode potential differences. Therefore one introduces a *standard electrode* and defines 'the' electrode potential of a single electrode as the electric voltage of the cell formed of the standard electrode and the electrode under consideration. In this way, e.g., for 100 electrodes we only need 100 electrode potentials instead of 4950 cell voltages.*

For theoretical purposes the standard reference electrode is the hydrogen electrode. This is an electrode of an inert metal (usually Pt) placed in an acid solution with hydrogen ion concentration $[H^+] = 1$ mole.l^{-1}, i.e., pH = 0 (see Appendix 7) and into which hydrogen gas is bubbled at 1 atm. The electrode reaction of the hydrogen electrode is

$$2H^+ + 2e^- = H_2 \qquad (2.5.1)$$

We can now combine this with another electrode, e.g., with the iron electrode to form the cell

$$H_2(g) \,|\, H^+(aq) \,|\, Fe^{2+}(aq) \,|\, Fe \qquad (2.5.2)$$

This notation means that the left hand electrode is the hydrogen electrode and the right hand one the iron electrode. Each vertical line denotes a phase boundary. Fig. 2.5.1. shows a schematic drawing of this cell.

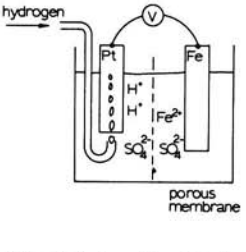

Fig. 2.5.1. Electrochemical cell consisting of a hydrogen and an iron electrode connected by a voltmeter with high internal resistance.

The cell reaction taking place in the cell (2.5.2) is

$$H_2 + Fe^{2+} = 2H^+ + Fe \qquad (2.5.3).$$

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* There are 100 x 99/2 = 4950 ways to choose distinct pairs out of 100 objects.

Using the methods of the previous sections we deduce for the change in free enthalpy for this reaction

$$\Delta g = \Delta g^{\ominus} + RT \ln \frac{[H^+]^2}{p_{H_2} \cdot [Fe^{2+}]} \qquad (2.5.4)$$

and using equation (2.4.2) we find for the cell voltage

$$E = E^{\ominus} + \frac{RT}{2F} \ln p_{H_2} - \frac{RT}{F} \ln [H^+] + \frac{RT}{2F} \ln [Fe^{2+}] \qquad (2.5.5).$$

If the normal hydrogen electrode is used $p_{H_2} = 1$ atm and $[H^+] = 1$ mole.l^{-1}. We then obtain (at 25°C)

$$E = E^{\ominus} + \frac{0.059}{2} \log [Fe^{2+}] \text{ (Volt)} \qquad (2.5.6).$$

In this equation E is by definition the equilibrium electrode potential of the iron electrode. If this is considered under standard conditions (i.e., $[Fe^{2+}] = 1$ mole.1^{-1}) $E = E^{\ominus}$ and this is called the *standard potential* of the iron electrode. Of course what was done here for the iron electrode can be done in a completely analogous way for any metal electrode.

For practical purposes other standard electrodes are in most cases used instead of the normal hydrogen electrode. Some of the most important ones in corrosion work are the saturated calomel electrode (E = +0.244 V), the silver-silver chloride electrode (E = 0.288 V in a solution containing 0.1 mole.l^{-1} Cl^--ions) and the saturated copper-copper sulphate electrode (E = +0.318 V). All these potentials are given with respect to the normal hydrogen electrode.

In order to obtain unambiguous results, in particular regarding the signs of potentials and cell voltage some international agreements have been reached which are summarized in Appendix 8.

2.6. ELECTROCHEMICAL SERIES AND THEIR APPLICATIONS

For any half-cell reaction

$$M^{n+} + ne^- = M \qquad (2.6.1)$$

the Nernst equation reads

$$E = E^{\ominus} + \frac{0.059}{n} \log [M^{n+}] \; (25^{\circ}) \qquad (2.6.2).$$

In Appendix 9 the standard potentials for a number of reactions of this type are given in the order of increasingly positive $E^{\ominus}$. This is usually called the *electrochemical series of the metals.*

As stated above these potentials are given with respect to the normal hydrogen electrode. This means that for all metals with a *negative* standard potential the reaction

$$\frac{n}{2}H_2 + M^{n+} = nH^+ + M \tag{2.6.3}$$

has a positive $\Delta g^{\ominus}$ (= $-nFE^{\ominus}$) and tends to proceed spontaneously to the left: the metal tends to corrode. These metals are therefore called *base* metals, in contrast to those with a positive $E^{\ominus}$: the *noble* metals. Because, when defined in this way, we consider a metal standing in a strongly acid solution (pH=0) and one molar in metal-ions, the series in this form is only of theoretical importance.

From the electrochemical series we also deduce that, when two metals, e.g., Zn and Cd are connected and placed in a solution containing both metal ions, the metal with the lowest standard potential will corrode, while that with the highest potential will be deposited. Similarly, when a base metal is placed in a solution containing ions of a more noble metal, the base metal will tend to corrode under deposition of the more noble one, just as was discussed above for the case of iron and copper.

Of course when the solutions are not 1 molar in the metal ions we can still determine what happens by using equation (2.6.2) for both metals and applying rule no. 5 of Appendix 8. If, for example, we put a piece of iron in a solution containing 0.1 mole.l^{-1} Cd^{2+}-ions and 10^{-6} mole.l^{-1} Fe^{2+}-ions we have the cell reaction

$$Cd + Fe^{2+} = Cd^{2+} + Fe \tag{2.6.4}$$

with

$$\begin{aligned} E &= E_{Fe} - E_{Cd} \\ &= E_{Fe}^{\ominus} + \frac{0.059}{2}\log[Fe^{2+}] - E_{Cd}^{\ominus} - \frac{0.059}{2}\log[Cd^{2+}] \\ &= -0.44 + \frac{0.059}{2}(-6) + 0.40 - \frac{0.059}{2}(-1) \\ &= -0.187 \text{ Volt} \end{aligned}$$

As this is negative, Δg for reaction (2.6.4) is positive under these conditions, which means that iron tends to corrode. However, if we take the case where $[Cd^{2+}] = 10^{-6}$ mole.l^{-1} and $[Fe^{2+}] = 0.1$ mole.l^{-1} we obtain

$$E = +0.107 \text{ Volt}$$

which means that now cadmium tends to corrode!

Except for the hydrogen electrode we considered reactions in which one component was a solid metal. It is also possible that both the reduced and oxidized forms of a substance taking part in an electrode reaction are present in solution or that one is a gas other than hydrogen. We then speak of a *redox-reaction* (or redox couple). The potential of a redox-reaction is measured by putting an inert electrode (usually platinum) in the solution. This then takes up the potential of the redox couple. In Appendix 10 the standard potentials of a number of redox-reactions are given.

Just as a metal tends to corrode with hydrogen evolution when its equilibrium potential is lower than that of the hydrogen electrode in a certain solution, it also does so when placed in a solution where a redox reaction is possible with an equilibrium potential higher than that of the metal. One of the most common and important reactions of this type is the reduction of oxygen:

$$O_2 + 2H_2O + 4e^- = 4OH^- \quad E^\ominus = 0.401\ \mathrm{V} \qquad (2.6.5)$$

with the Nernst equation

$$E = E^\ominus + \frac{RT}{4F}\ln\frac{p_{O_2}}{[OH^-]^4}$$

$$= 0.401 + \frac{0.059}{4}\log p_{O_2} - 0.059\log[OH^-].$$

Because $[OH^-] = 10^{-14}/[H^+]$ (see Appendix 7) this can also be written

$$E = 0.401 + \frac{0.059}{4}\log p_{O_2} - 0.059\,(pH - 14) \qquad (2.6.6).$$

In a neutral solution pH=7 and under atmospheric conditions $p_{O_2} = 0.2$ atm giving

$$E = 0.804\ (\mathrm{Volt}).$$

Comparing this with the electrochemical series we see that many metals which do not tend to corrode even in a strongly acidic solution, such as copper and silver, do tend to corrode in a neutral solution if oxygen is present, as it usually is.

Up to now we considered the metal to dissolve in the form of ions. However, often components may be present in the solution which cause precipitation of insoluble compounds. For example many oxides, hydroxides, sulphides etc. are only sparingly soluble in water. The solubility is expressed as the equilibrium constant for the dissolution reaction. For example for silver sulphide this is

$$Ag_2S = 2Ag^+ + S^{2-} \tag{2.6.7}$$

with

$$K_{sol} = [Ag^+]^2 [S^{2-}] \tag{2.6.8}$$

which is called the *solubility product.*

Writing the Nernst equation for the silver-electrode in a solution containing sulphide ions we obtain

$$E = E^{\ominus} + 0.059 \log [Ag^+] = E^{\ominus} + \frac{0.059}{2} \log \frac{K_{sol}}{[S^{2-}]} \tag{2.6.9}$$

The solubility product for Ag_2S is 1.6×10^{-49} and in a solution containing 1 ppm S^{2-}-ions, i.e., $[S^{2-}] = 3 \times 10^{-5}$ mole.l^{-1} the equilibrium potential of the silver electrode is found to be $E = -0.55$ Volt. In a neutral solution the equilibrium potential of the hydrogen electrode is $E = -0.42$ Volt. We see that with such a small amount of sulphide present silver tends to corrode under hydrogen evolution even in neutral solutions. This explains the well-known tarnishing of silver, which is the formation of black silver sulphide in foodstuffs (such as eggs) or an atmosphere containing sulphides, mentioned in section 2.1.

A similar lowering of the equilibrium potential is found when the solution contains compounds which form stable, soluble complexes with the metal. This occurs for example with copper ions in solutions containing ammonia. Then also we may expect corrosion reactions to be spontaneous, which in the absence of the complexing reagent would not be so.

These examples again show that the electrochemical series of the metals, although very important as such, has to be used with caution in practical cases.

2.7. POTENTIAL-pH DIAGRAMS

The above considerations can conveniently be summarized in graphical form, as was shown for example by Pourbaix in 1945, in what we call *potential-pH* or *Pourbaix* diagrams. A slightly simplified form of the E-pH diagram of water (leaving out of consideration species such as H_2O_2, O_3, HO_2^-, H^-, etc.), is shown in Fig. 2.7.1.

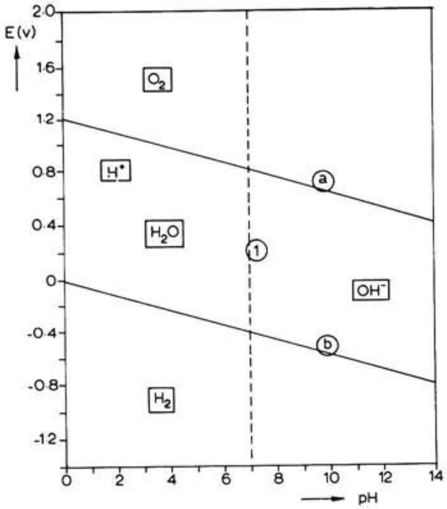

Fig. 2.7.1. Simplified Pourbaix diagram for water at 25°C.

Line a in the diagram represents the equilibrium of the reaction

$$O_2 + 4H^+ + 4e^- = 2H_2O \tag{2.7.1}$$

with the Nernst equation

$$E_a = E_a^{\ominus} + \frac{0.059}{4} \log p_{O_2} \cdot [H^+]^4 \tag{2.7.2}$$

or at $p_{O_2} = 1$ atm

$$E_a = 1.228 - 0.059\ \mathrm{pH} \qquad (2.7.2a).$$

Similarly line b represents the equilibrium of the reaction

$$2H^+ + 2e^- = H_2 \tag{2.7.3}$$

with, at $p_{H_2} = 1$ atm

$$E_b = 0.000 - 0.059\ \mathrm{pH} \qquad (2.7.4).$$

In the region marked H_2O between the lines a and b water is stable with respect to hydrogen and oxygen at 1 atm. In other words: in that region the reaction $2H_2 + O_2 = 2H_2O$ has a $\Delta g < 0$ and tends to proceed spontaneously to the right. If water is brought into the region marked O_2

the reaction (2.7.1) will proceed spontaneously to the left with oxygen evolution. In a closed system this means that the pH will decrease and the oxygen pressure increase, i.e., the system will tend to approach line a. Similarly in the region marked H_2 reaction (2.7.3) proceeds spontaneously to the right with hydrogen evolution and increasing pH.

The line 1 represents the equilibrium

$$H_2O = H^+ + OH^- \qquad (2.7.5).$$

In this reaction electrons do not play a part. This means that it is not influenced by the potential and thus runs vertically.

In Fig. 2.7.2 the E-pH diagram of zinc [3] in contact with water is given.

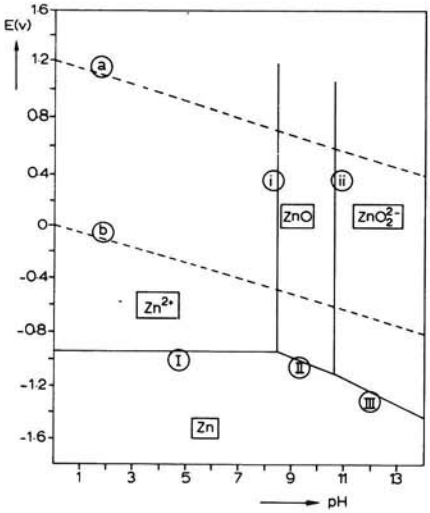

Fig. 2.7.2. Simplified Pourbaix diagram for zinc in water at 25°C.

The heavy lines represent the different equilibria in which zinc is involved. These are:

I $\quad Zn^{2+} + 2e^- = Zn$

with $\quad E_I = -0.76 + \dfrac{0.059}{2} \log [Zn^{2+}]$

II $\quad ZnO + 2H^+ + 2e^- = Zn + H_2O$

with $\quad E_{II} = -0.44 - 0.059\ pH$

III $ZnO_2^{2-} + 4H^+ + 2e^- = Zn + 2H_2O$

with $E_{III} = 0.44 - 0.118\ pH + 0.0295 \log [ZnO_2^{2-}]$

i $Zn^{2+} + H_2O = ZnO + 2H^+$

with $K_i = \dfrac{[H^+]^2}{[Zn^{2+}]} = 1.1 \times 10^{-11}$

ii $ZnO + H_2O = ZnO_2^{2-} + 2H^+$

with $K_{ii} = [ZnO_2^{2-}]\,[H^+]^2 = 1.6 \times 10^{-30}$.

All lines for the zinc equilibria are drawn for $[Zn^{2+}] = 10^{-6}$ mole.l^{-1}. This concentration is often chosen in corrosion work as being so low that this corresponds to 'natural' conditions.

We will now discuss the application of this type of diagram to the corrosion of zinc. To start with we see that in acid solutions the line I is below line b of the hydrogen evolution reaction. This means that reaction I cannot be in equilibrium in water because the total reaction

$Zn + 2H^+ = Zn^{2+} + H_2$

will proceed spontaneously to the right and zinc corrodes. Only when, with the help of an external voltage source, zinc is brought to a potential below line I will the dissolution of zinc stop. In this region the zinc is said to be *immune.* The hydrogen evolution will of course continue.

If the pH of the solution is raised we come to line II. Again this is below the hydrogen evolution line and the total reaction:

$Zn + H_2O = ZnO + H_2$

will tend to proceed spontaneously to the right. However, it now depends on the form in which the solid zinc oxide is produced whether this reaction continues or not. If the oxide forms a closed, adherent layer the reaction, although remaining spontaneous, will nevertheless stop because the direct contact between metal and solution is broken. When this occurs we say that zinc has become *passive.* If the oxide is porous or non-adherent no passivity occurs and the dissolution reaction continues. The E-pH diagram shows the regions in which passivity may be expected to occur, but not if it will indeed do so, because that depends upon the form in which the oxide is produced. The subject of passivity will be treated more extensively in the next chapter.

At still higher pH the zinc starts to corrode again but now according to the reaction

$$Zn + 2OH^{-} = ZnO_2^{2-} + H_2.$$

Of course all zinc-dissolution reactions also lie under the oxygen reduction line a. In oxygen containing solution we will thus simultaneously have reactions such as

$$2Zn + O_2 + 4H^{+} = 2Zn^{2+} + 2H_2O, \text{etc.}$$

proceeding spontaneously to the right.

The E-pH diagram of copper [3] is somewhat similar to that of zinc and is shown in Fig. 2.7.3. Two solid phases are possible here: Cu_2O and CuO. We see that corrosion with hydrogen evolution is not possible because all copper equilibria lie above the hydrogen evolution equilibrium. Only in oxygen containing solutions will corrosion, with oxygen reduction as cathodic reaction, be possible.

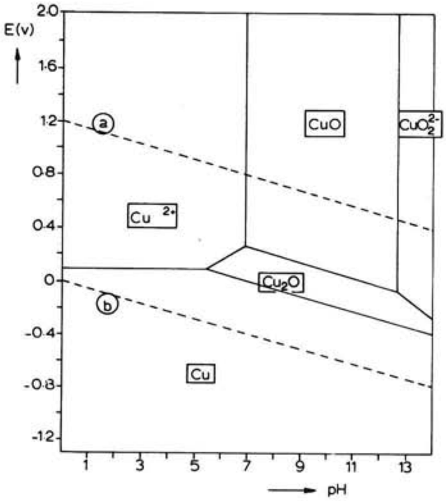

Fig. 2.7.3. Simplified Pourbaix diagram for copper in water at 25°C.

The E-pH diagram of iron in water [3] is shown in Fig. 2.7.4. This is somewhat more involved than the previous diagrams because iron has two important valencies: Fe^{2+} and Fe^{3+} both in solution and in solid compounds. We can still discern, however, the regions where corrosion is expected to occur, where passivity may be found if the solid compounds form a closed and adherent layer and where iron is exp form a closed and adherent layer and where iron is expected to be immune.

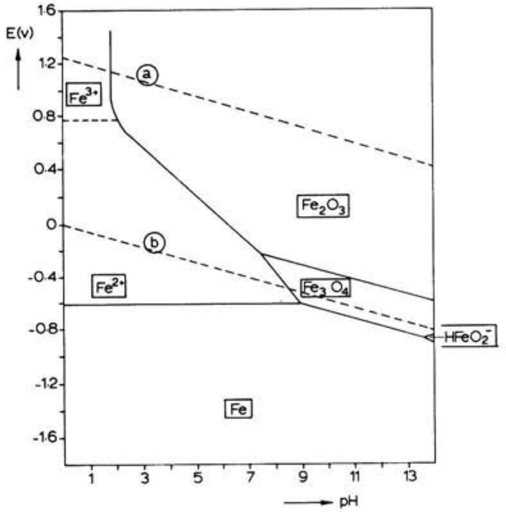

Fig. 2.7.4. Simplified Pourbaix diagram for iron in water at 25°C.

2.8. LIMITATIONS OF THERMODYNAMIC CONDIDERATION

The thermodynamics of corrosion reactions, as discussed in this chapter, are an important guide in determining which reactions are theoretically possible under given circumstances. Summarizing we can say that a metal tends to corrode when it is in contact with a solution where a cathodic reaction is possible with an equilibrium potential higher than that of the metal dissolution reaction in that solution.

However, there are also some serious limitations making it impossible to rely on thermodynamics alone. For example, in Appendix 11 is given a so called 'practical galvanic series' showing the potentials of a number of metals and alloys under practical conditions. Although there certainly is a certain resemblance to the electrochemical series of the metals, as given in Appendix 9, there are also large discrepancies in the case of several metals. In some cases this can be ascribed to passivity, e.g., stainless steel, in others, as we shall see in the next chapter, these differences are caused by the fact that the metal-dissolution reaction is not in equilibrium, but occurs at a finite rate. For alloys, moreover, it is hardly to be expected that the dissolution reactions for the several components all have the same equilibrium potential.

By definition it is impossible to obtain from thermodynamics insight into the rates of the reactions considered. Even if a reaction is thermodynamically possible it may well be that its rate is so low that for all practical purposes it can be said not to occur at all. A well known example is a mixture of hydrogen and oxygen at room temperature. When undisturbed it can be kept indefinitely even though the driving force to form water is rather high ($\Delta g^{\ominus} = -237$ kJ.mole^{-1}). Only upon ignition with a flame or spark or in the presence of a catalyst does it proceed spontaneously.

Finally, as was seen in the discussion of passivity, the form of the reaction products may have a large influence on further reaction. This again is not so much a matter of thermodynamics as of kinetics.

2.9. SUMMARY

The central point in this chapter is that if a metal M is placed in a solution containing its own ions M^{n+} the dynamical equilibrium

$$M^{n+} + ne^- \rightleftarrows M$$

will be established. This causes an electrical potential difference between the metal and the solution. When equilibrium has been reached this potential is given by the Nernst-equation:

$$E = E^{\ominus} + \frac{RT}{nF} \ln [M^{n+}]$$

or at 25°C

$$E = E^{\ominus} + \frac{0.059}{n} \log [M^{n+}] \quad \text{Volt.}$$

$E^{\ominus}$ is called the *standard potential* and when the metals are placed in the order of increasing $E^{\ominus}$ we obtain the electrochemical series of metals given in Appendix 9. The zero point of this series is chosen as the standard potential of the hydrogen electrode. When two electrodes with different equilibrium potentials are connected with a conducting wire (as in Fig. 2.4.1a) a current will start to flow in such a direction that the potential difference tends to decrease. At one of the electrodes reduction takes place and that is called the cathode, at the other oxidation and that is called the anode.

The above is applicable to all redox reactions of the general type

$$aA + bB + ne^- \rightleftarrows pP + qQ$$

with the corresponding Nernst equation

$$E = E^{\ominus} + \frac{RT}{nF} \ln \frac{[A]^a\,[B]^b}{[P]^p\,[Q]^q} \ .$$

For a number of reactions of this type the standard potentials are given in Appendix 10.

Two important examples, which are often met in practical cases of corrosion, are the hydrogen evolution reaction:

$$2H^+ + 2e^- \rightleftarrows H_2$$

with $E = 0.0 + \frac{RT}{2F} \ln \frac{[H^+]^2}{p_{H_2}}$

and the oxygen reduction reaction

$$O_2 + 2H_2O + 4e^- \rightleftarrows 4OH^-$$

with $E = 0.401 + \frac{RT}{4F} \ln \frac{p_{O_2}}{[OH^-]^4}$

A metal will tend to corrode if it is placed in an environment in which the oxidized form of a redox couple (A, B in the general example) with an equilibrium potential higher than that of the metal is present. For example any metal with an equilibrium potential below 0 V will tend to dissolve in strong acid.

In many electrode reactions H^+ or OH^- ions take part. In that case the potential is influenced by pH (see Appendix 7). The behaviour of a system can then conveniently be represented in an E-pH or Pourbaix diagram. Figs. 2.7.1 to 2.7.4 present some examples. When solid compounds can be formed instead of dissolved metal ions it may happen that the metal will then be completely covered with such a compound so that further reaction is stifled. This is called passivity.

Thermodynamic arguments only lead to conclusions about the direction of possible reactions and not about the rates with which they take place. Therefore the rates of reactions will be considered separately in the next chapters.

2.10. REFERENCES

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2. O. Kubaschewski, E.Ll. Evans and C.B. Alcock, *Metallurgical Thermochemistry*, 4th ed. Oxford, Pergamon Press (1967).

3. M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, Oxford, Pergamon Press, 1966.

2.11. PROBLEMS

1. For reactions at constant pressure the proper quantity to use is the enthalpy $H = U + pV$ where U is the internal energy. The change in enthalpy due to a process at constant pressure is:

   $$\Delta H = \Delta U + p\Delta V$$

   Calculate the term $p\Delta V$ for a reaction in which one mole of gas (22.4 l at 1 atm and 25°C) is consumed. Compare the value obtained with some enthalpies of formation ($h^\ominus$) as given in Appendix 6.
   Comment!

2. a. Derive an equation for Δg for the formation of some metal oxides (e.g. Fe_3O_4, Cu_2O, Al_2O_3, etc.). From this equation find an expression for their dissociation pressures.
   b. Using the data in Appendix 6 calculate the dissociation pressure of some oxides, with the help of the expression found under a. at room temperature, 500°C and 1000°C.

3. Calculate the temperature at which Ag_2O is in equilibrium with silver and air ($p_{O_2} = 0.2$ atm). What happens if Ag_2O is heated above this temperature?

4. Calculate the change in $\mu_A{}^\ominus$ in the equation

   $$\mu_A = \mu_A{}^\ominus + RT \ln [A]$$

   if [A] is expressed in grams per litre and in weight % instead of in mole.l^{-1}.

5. Derive equation 2.5.4.

6. A piece of silver is put into a solution containing Ag^+, Fe^{3+} and Fe^{2+} ions. Write the reaction which may be expected to occur. If $[Ag^+] = 10^{-6}$ mole.l^{-1} when will you expect that this reaction is just in equilibrium? What will happen in this case if $[Fe^{3+}] = [Fe^{2+}] = 0.1$ mole.l^{-1}? And what if they are 10^{-7} mole.l^{-1}? What do you expect to happen if $[Ag^+] = 1$ mole.l^{-1} without change in the concentrations of the Fe^{3+} and Fe^{2+} ions?

7. Which of the metals in Appendix 9 do you expect to corrode with hydrogen evolution at pH = 7 and at pH = 12?

8. Which of the metals in appendix 9 do you expect to corrode with oxygen reduction if $p_{O_2} = 0.2$ atm. at pH = 0, 7 and 14?

9. A discussion similar to that given in section 2.2 is also applicable to oxidation by steam, e.g.,

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

Derive an expression for Δg for this reaction and show that the tendency of iron to be oxidized is now determined by the ratio of the partial pressures of steam and hydrogen. Use the values given in Appendix 6 to calculate the equilibrium ratio of H_2O and H_2 pressures in contact with iron at 350°C. Comment!

10. Gold ions form very stable complexes with cyanide-ions according to the equation

$$Au^+ + 2CN^- = Au(CN)_2{}^-$$

and the equilibrium constant of this reaction is:

$$K = \frac{[Au\,(CN)_2{}^-]}{[Au^+]\,[CN^-]^2} = 3 \times 10^{38}.$$

Calculate the equilibrium potential of gold in a solution containing 0.1 mole.l^{-1} CN^--ions. Comment!

11. The solubility product of copper sulphide is:

$$K_{sol} = [Cu^{2+}]\,[S^{2-}] = 10^{-44}.$$

Calculate the equilibrium potential of copper standing in a solution containing 1 mg per litre sulphide ions. Comment!

3. The rates of electrochemical reactions

3.1. INTRODUCTION

As stated at the end of Chapter 2 it is not sufficient to know whether a certain metal can corrode under given conditions. *It is necessary to know the rate of a possible reaction.* There are many well known examples of metals, such as aluminium and zinc, which are very unstable according to equilibrium calculations, but which often corrode much more slowly than a relatively more stable metal, e.g. steel.

We limit ourselves in this chapter to electrochemical corrosion, which means that we are primarily interested in the rates of electrode reactions. For a copper electrode the electrode reaction is:

$$Cu^{2+} + 2e^- \underset{I_a}{\overset{I_c}{\rightleftarrows}} Cu \qquad (3.1.1).$$

In equilibrium the forward and reverse rates of this reaction, expressed as the cathodic current I_c and the anodic current I_a are equal and opposite. This means that no net current flows and:

$$I_a + I_c = 0 \qquad (3.1.2).$$

The anodic current is counted positive, the cathodic current negative. If there is no equilibrium a net current I flows to or from the electrode, because then the partial currents are not longer equal and we have:

$$I = I_a + I_c \qquad (3.1.3).$$

If $|I_a| > |I_c|$ the current is positive and copper dissolves, if $|I_a| < |I_c|$ the current is negative and copper is deposited. This is in agreement with the usual sign convention of a current: namely the direction of flow of positive charges.

The external current represents a net chemical reaction. According to

Faraday's law the current is proportional to the reaction rate which is expressed by the equation:

$$\frac{\Delta W}{\Delta t} = eI \qquad (3.1.4).$$

Here ΔW is the mass of a substance produced or consumed by the reaction in the time Δt and e is called the *electrochemical equivalent* of this substance. For metals this is given by:

$$e_X = M_X / n_X F \qquad (3.1.5)$$

where M_X is the atomic mass and n_X the valency of metal X. A table of electrochemical equivalents is given in Appendix 12.

When there is no external current an electrode is not necessarily in equilibrium: two or more different reactions may occur simultaneously at its surface. We then speak of a *polyelectrode.* The anodic reactions together produce on such an electrode the same number of electrons as are consumed by the cathodic reactions together. An electrode at which only one reaction occurs, as in the case discussed above, is called a *single electrode.* In the case of a polyelectrode equation 3.1.2. remains valid but now the anodic and cathodic currents represent different reactions. An example is the case of an iron electrode in a solution containing copper ions, which was already discussed in Chapter 2. The two reactions occurring simultaneously are:

$$\left.\begin{array}{lcl} Fe^{2+} + 2e^- & \leftarrow & Fe \\ Cu^{2+} + 2e^- & \rightarrow & Cu \end{array}\right\} \qquad (3.1.6)$$

with as the total electrode reaction

$$Cu^{2+} + Fe \rightarrow Cu + Fe^{2+} \qquad (3.1.7)$$

From equation (3.1.4) and (3.1.5) we find that the dissolution of 1 gram of iron in one hour corresponds with a current of about 1A.

The corrosion rate of a metal can thus be expressed as the equivalent current. In general it is preferable to use the *current density,* i.e., the current per unit area because this is directly related to the penetration (see also Appendix 3).

When a single electrode is not in equilibrium its potential differs from the value expected from the Nernst equation in the given solution. This is called *polarisation* and the change in potential is the *overvoltage* η. The direction of this potential change is such that the product of overvoltage and current is positive:

$$\eta \times I > 0 \qquad (3.1.8).$$

For a net anodic reaction we thus have a positive overvoltage, for a net cathodic reaction a negative overvoltage (for a proof of this equation see Appendix 13).

In this chapter we discuss the kinetics of electrochemical reactions occurring at single electrodes. The behaviour of polyelectrodes is the subject of Chapter 4.

For a first reading and for those who need only a superficial knowledge of the theory the study of this chapter can be limited to section 3.5 which gives a summary of the most important points.

3.2. POLARISATION DIAGRAMS

We consider an electrochemical cell, as shown in Fig. 3.2.1, consisting of a zinc electrode in a solution with $[Zn^{2+}] = 1$ mole. l^{-1} and a standard

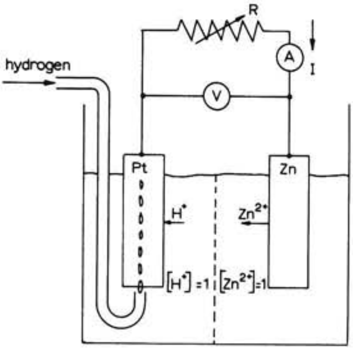


Fig. 3.2.1. Electrochemical cell consisting of a zinc- and a hydrogen electrode delivering current to an external resistance R.

hydrogen electrode. The electrodes are connected by a variable resistance R in series with an ammeter A. Simultaneously the cell voltage is measured with a voltmeter V with a high internal resistance. As follows from the electrochemical series the cell tension is -0.76 V when $R = \infty$. When R has a finite value a current flows and the cell voltage decreases until at short circuit ($R=0$) it becomes zero, if it is possible to neglect the internal resistance of the cell. By using separate standard electrodes we can also measure the potentials of the two electrodes separately. This makes it possible to construct a potential-current diagram, or as it is often called a *polarisation diagram* for the reactions in this cell. A very schematic drawing for this is shown in Fig. 3.2.2. In Fig. 3.2.2.a the current is plotted with the corresponding sign: a cathodic current to the left, an anodic current to the right. However, in many cases it is more convenient to plot both currents to

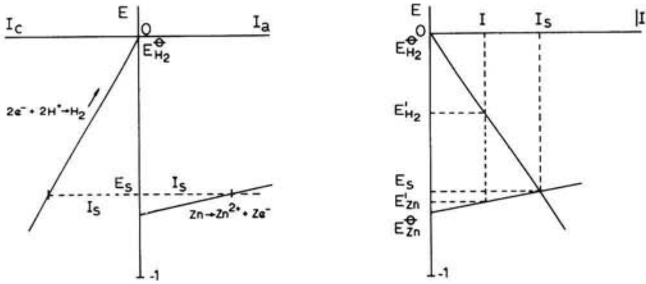


Fig. 3.2.2. Schematic potential-current diagrams of two types:
a. current plotted with corresponding sign;
b. anodic and cathodic currents both plotted to the right (Evans diagram).

the right as shown in Fig. 3.2.2b. This is called an *Evans-diagram.* From this we see directly that for a current I the cell voltage is $E' = E'_{Zn} - E'_{H_2}$. This corresponds with the overvoltages: $\eta_{H_2} = E'_{H_2} - E_{H_2}^{\ominus} < 0$ and $\eta_{Zn} = E'_{Zn} - E_{Zn}^{\ominus} > 0$.

On short circuit we reach the potential E_s with the corresponding current I_s while the cell voltage is zero.

3.3. POLARISATION OF SINGLE ELECTRODES

When considering an electrode reaction in general this can be written:

$$Ox + ne^- \underset{i_a}{\overset{i_c}{\rightleftarrows}} Red \tag{3.3.1}$$

which simply means that some substance Ox can take up electrons and be reduced to another substance Red and vice versa. In the total process several steps can be distinguished: the species Ox, for example, has to be transported through the solution to the surface of the electrode, it then has to take up the requisite number of electrons and finally has to move away again or has to be built in the lattice. Depending upon which step is rate-determining different types of polarisation behaviour are observed. If the taking-up or giving-off of electrons is rate determining we speak of *activation* or more correctly of *charge-transfer polarisation.* When the transport of a substance through the electrolyte to or from the electrode is the rate determining step we speak of *diffusion polarisation.* These two cases will now be discussed separately.

3.3.1. *Charge-transfer polarisation*

The rates of all chemical reactions obey the well-known Arrhenius equation:

$$k = Ae^{-Q/RT} \tag{3.3.2}$$

where k is the rate constant, A is a pre-exponential factor and Q is the activation energy representing an energy barrier the molecules have to pass before they are able to react. When charged species take part in the reaction, as in the case of electrode reactions, this barrier is influenced by an electric field. It can be shown that due to this effect the partial current densities for the two directions of a reaction such as (3.3.1.) become:

$$\text{anodic } i_a = i_o \exp\left\{\frac{\alpha nF}{RT}\eta\right\} \tag{3.3.3a}$$

$$\text{cathodic: } i_c = -\,i_o \exp\left\{-\frac{(1-\alpha)nF}{RT}\eta\right\} \tag{3.3.3b}$$

In these equations i_o is the *exchange current density*, i.e., the current density with which the reaction occurs simultaneously in both directions in equilibrium, i.e., when the net current density $i = i_a + i_c = 0$. The constant α is called the *transfer coefficient* which always lies between 0 and 1 and often does not differ much from 0.5.

When there is no equilibrium the net current is given by:

$$i = i_o\left[\exp\left\{\frac{\alpha nF}{RT}\eta\right\} - \exp\left\{-\frac{(1-\alpha)nF}{RT}\eta\right\}\right] \tag{3.3.4}$$

The resulting polarisation curve is sketched in Fig. 3.3.1a together with the polarisation curves for the two partial reactions.

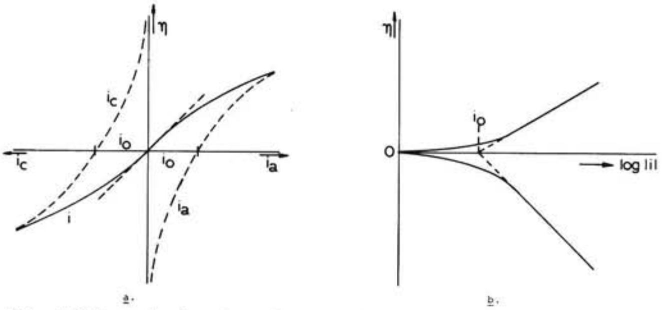


Fig. 3.3.1. Polarisation diagram for a single electrode showing charge-transfer polarisation:

a. overpotential versus current;

b. overpotential versus ℓog|current| (Tafel diagram).

For small overvoltages ($|\eta| < 0.01\,\text{V}$) a simplified equation results:

$$i = i_o \frac{nF}{RT} \eta \text{ or } \eta = \frac{RT}{nFi_o} \cdot i \qquad (3.3.5)$$

This is true close to the origin in Fig. 3.3.1a. The factor RT/nFi_o has the dimensions of a resistance and is called the *polarisation resistance.*

At large overvoltages ($|\eta| > 0.1$ V) one of the two terms in equation (3.3.4) may be neglected and the equation can be written as:

$$\eta = \beta \log |i/i_o| \qquad (3.3.6)$$

with $\beta = 2.3\ RT/\alpha nF$ for an anodic and $\beta = -2.3\ RT/(1-\alpha)nF$ for a cathodic reaction. This form is known as the *Tafel-equation.*

In those cases where the overvoltage is relatively large it is customary to plot the overvoltage against log $|i|$ as shown in Fig. 3.3.1b. This gives straight lines, which, when extrapolated back to $\eta = 0$, cross at $i = i_o$.

The exchange current density is an important characteristic for an electrode reaction and its influence on the polarisation curve is shown schematically in Fig. 3.3.2. For reactions with a large exchange current density, which also corresponds with a small polarisation resistance, the necessary overvoltage to reach a certain external current is smaller than for reactions with a small exchange current density. In a plot of η against i this leads to a less steep curve for larger i_o, in a plot of η against log $|i|$ to a shift to the right.

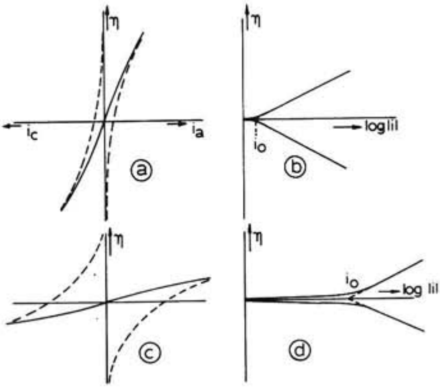


Fig. 3.3.2. Polarisation diagrams for single electrodes with charge transfer polarisation:
a,b small exchange current density;
c,d large exchange current density.

3.2.2. *Diffusion polarisation*

When the rate of the charge transfer process is very large, i.e., at large i_o and/or $|\eta|$, it is possible for the transport of ions or molecules to or from the electrode to become rate-determining. There are three main mechanisms by which the transport can take place:

i. migration in an electric field;
ii. convection due to movement of the liquid;
iii. diffusion caused by concentration differences.

Migration can nearly always be neglected in our case because there usually is an excess of 'neutral electrolyte', i.e., ions not taking part in the electrode reaction. Convection causes homogenization of the solution but, depending on velocity and geometrical factors, concentration differences still exist in a thin boundary layer of 0.01 to 0.5 mm thickness. There diffusion will take place.

Nernst introduced a simple model to calculate the effect of this diffusion. In this model the concentration is assumed to be constant at c_o in the bulk of the solution. In a boundary layer of thickness δ next to the electrode Nernst assumed a linear concentration gradient from the value c_o in the bulk of the solution to c at the surface. This is shown in Fig. 3.3.3.

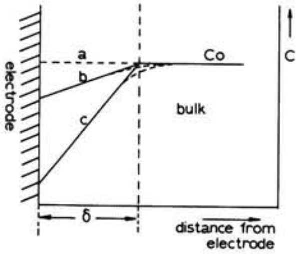


Fig. 3.3.3. Concentration profile in diffusion layer according to the model of Nernst:
a. no current;
b. small diffusion polarisation;
c. large diffusion polarisation.

According to Fick's first law the flux of the substance to the electrode is proportional to the concentration gradient with the diffusion coefficient D as the proportionality constant. Combined with Faraday's law (equation 3.1.4.) this gives for the current density:

$$i = -nFD \frac{c_o - c}{\delta} \qquad (3.3.7)$$

Because c can of course never become negative the maximum possible current, usually called the *limiting current* i_ℓ, is equal to:

$$i_\ell = -\,nFD\,\frac{c_o}{\delta} \qquad (3.3.8)$$

for c = 0. Combining this with the Nernst-equation we find:

$$\eta = E(c) - E(c_o) = \frac{0.059}{n}\,\log\frac{c}{c_o}\quad (25°C) \qquad (3.3.9)$$

Combining this with equations (3.3.7) and (3.3.8) gives:

$$\eta = \frac{0.059}{n}\log\left(1 - \frac{i}{i_\ell}\right) \qquad (3.310).$$

In Fig. 3.3.4 the resulting polarisation curve is shown schematically for a cathodic reaction. From the derivation of i_ℓ we see that this will increase with increasing concentration c_o.

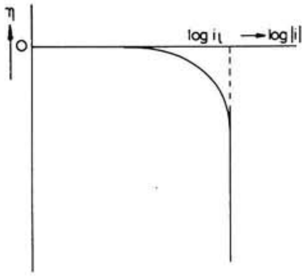


Fig. 3.3.4. Polarisation curve for cathodic reaction showing diffusion polarisation.

Also increasing velocity of the liquid will lead to a decrease in δ and thus to an increase in i_ℓ. Because the diffusion coefficient increases strongly with increasing temperature this will also be the case with i_ℓ.

3.4. PASSIVITY AND POLARISATION

When an anodic reaction is the metal dissolution reaction the treatment of section 3.3. is applicable. However, as we have seen in Chapter 2 it is also possible that insoluble solid compounds are formed as the result of an anodic reaction, e.g.,

$$2Al + 3H_2O \rightarrow Al_2O_3(s) + 6H^+ + 6e^- \qquad (3.4.1)$$

The regions of potential and pH where such reactions can take place can be found from the corresponding Pourbaix diagrams. When the solid reaction product forms as an impermeable, adherent layer on the metal surface, this leads to the phenomenon of passivity as discussed in Chapter 2.

Under circumstances where a metal can be passivated its anodic polarisation curve is drastically changed from the forms we saw in the previous section. In Fig. 3.4.1. the polarisation curve is given in a schematic form for this case.

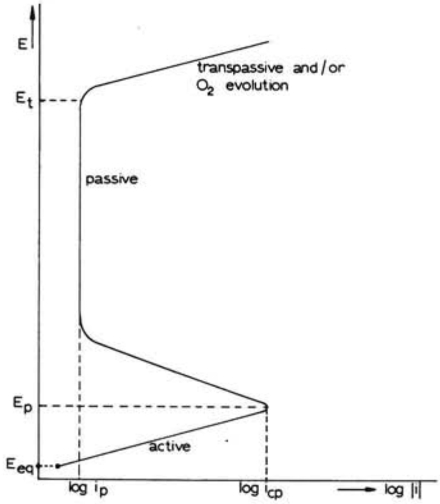


Fig. 3.4.1. Schematic anodic polarisation curve for a metal which can be passivated.

At potentials not too far above the equilibrium-potential $E_{eq,a}$ the metal dissolves as metal ions according to reaction (3.1.1.) and this reaction usually shows only charge-transfer polarisation (Tafel behaviour). When the potential is raised sufficiently the current density reaches a maximum: the *critical passivation current density* i_{cp} at the *passivation potential* E_p. When this potential is exceeded the current-density sharply drops to a very low value: the *passive current density* i_p. As an example we have for iron in a neutral aqueous solution an i_{cp} of approximately 10^{-3} A.cm^{-2} at the passivation potential E_p of about + 0.1 V. The i_p in contrast is approximately 10^{-8} A.cm^{-2}.

Above the passivation potential the metal is covered with an impermeable, adherent layer of reaction products, in most cases an oxide or hydroxide which causes the passivity.

At much higher potentials the current density sometimes increases again as indicated in Fig. 3.4.1 at potentials above E_t: the transpassive potential. This is due to a secondary anodic reaction starting to occur. In some cases this is not connected with the metal as such, e.g., it may be the oxygen evolution reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, \; E^{\ominus} = 1.23 \text{ V} \qquad (3.4.2)$$

However, it may also be that a new corrosion reaction sets in, as is for example the case for chromium or chromium alloys, where above E ~ 0.8 to 1 V chromate ions may be formed according to the equation

$$Cr + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 6e^-, \; E^{\ominus} = 0.71 \text{ V} \qquad (3.4.3)$$

In general it can be stated that if we wish to be certain that a metal is passive, its potential must be kept above E_p and below E_t.

3.5. SUMMARY

In section 3.1 we have seen that there is a direct correspondence between the rate of an electrochemical reaction and the current or current density at the electrode. Whenever a current flows the potential of the electrodes differs from the equilibrium potential; this is called polarisation. The behavior of an electrode is then described by the relation between the potential change or overvoltage and the current density, the polarisation curve. For anodic reactions overvoltage and current are positive, for cathodic reactions negative.

The shape of the polarisation curve is determined by that step of the total process at the electrode which is rate determining. If the charge-transfer step at the surface is rate determining we speak of *charge-transfer polarisation* and the polarisation curve has the form given in Fig. 3.3.1 and 3.3.2. An important parameter characterising the reaction in this case is the exchange current density which is equal to the rate with which the reaction occurs simultaneously in opposite directions in equilibrium. If this is small a large overvoltage is necessary to produce a certain current density, if the exchange current density is large a small overvoltage is sufficient.

In particular when the charge transfer reaction is fast (high current density) the transport of reacting or product species to or from the electrode surface may become rate determining and we then speak of *diffusion polarisation.* The polarisation curve for this situation is shown in Fig. 3.3.4. In this case there is a limiting current density representing the maximum rate with which the reaction can occur. Increasing the concentration of the reacting species leads to an increase of the limiting current density and vice versa.

Finally we have the case where a metal may become *passive* due to the formation of a impermeable, adherent layer of insoluble reaction products of the anodic reaction. Then the polarisation curve has the form shown schematically in Fig. 3.4.1. The metal behaves passively in this case when its potential lies between the potentials E_p and E_t.

In Chapter 4 we will apply these concepts to the corrosion of metals where the metal behaves as a polyelectrode, i.e., two different electrochemical reactions take place simultaneously at its surface: an anodic reaction in which the metal is oxidized and a cathodic reaction in which some component of the environment is reduced.

3.6. PROBLEMS

1. Calculate the amount of iron (in gram) which dissolves as Fe^{2+}-ions when an anodic current of 1 mA flows for 24 hours.
2. Calculate the amount of zinc (in gram) which is deposited when a cathodic current of 10 mA flows for 5 hours. What is the thickness of the deposit when the surface area of the electrode is 15 cm^2?
3. Calculate the amount of hydrogen (in ml) at S.T.P. evolved at an electrode when a cathodic current of 5 mA flows for 15 hours.
4. Calculate the amount of oxygen (in ml) at S.T.P. consumed at an electrode when a cathodic current of 2 mA flows for 48 hours.
5. Draw the polarisation diagram for an electrode reaction which shows only charge-transfer polisation and for which the exchange current density is 10^{-5} $A.cm^{-2}$ and the transfer coefficient $\alpha = 0.45$.
6. Calculate the overvoltage η in Volt for an electrode reaction showing only charge-transfer polarisation with an exchange current density $i_o = 5 \times 10^{-7}$ $A.cm^{-2}$ and $\alpha = 0.5$ at a net current density of a $mA.cm^{-2}$.
7. Calculate the limiting current density for oxygen reduction at an electrode standing in a solution containing 8 $mg.l^{-1}$ oxygen. The diffusion coefficient of oxygen is 10^{-5} $cm^2.s^{-1}$ and the thickness of the diffusion layer 0.5 mm.

4. Rates of electrochemical corrosion reactions

4.1. INTRODUCTION

The rate of corrosion of iron as a function of pH as observed in practice is shown in Fig. 4.1.1. Below pH $\simeq 4$, i.e., in strongly acid solutions the corrosion rate is seen to increase strongly with decreasing pH. However, between pH $\simeq 4$ and pH $\simeq 10.5$ the corrosion rate is practically independent of pH. Above pH $\simeq 10.5$ there is a sharp drop in corrosion rate with increasing pH.

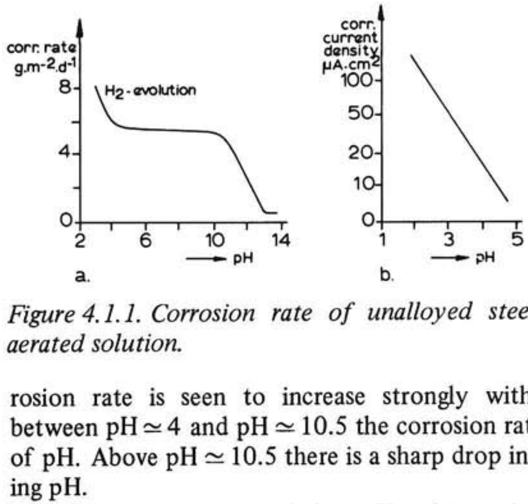


Figure 4.1.1. Corrosion rate of unalloyed steel as a function of pH in aerated solution.

In the acid region, i.e., below pH $\simeq 4$ impurities in the iron and its microstructure, as determined by heat treatment, have a large influence on the corrosion rate as shown in Fig. 4.1.2 and 4.1.3 and in Table 4.1.1. In approximately neutral solutions, on the other hand, there is hardly any difference between corrosion rates of steels with different microstructures or compositions.

In this case both the oxygen content and the velocity of the corrosive medium do have a large influence on corrosion rate as shown in Fig. 4.1.4 and 4.1.5. In acid solution these parameters have only a negligible influence.

Similar phenomena, of course differing in detail, are observed for other metals. In all these cases the corrosion reactions can be expected to be

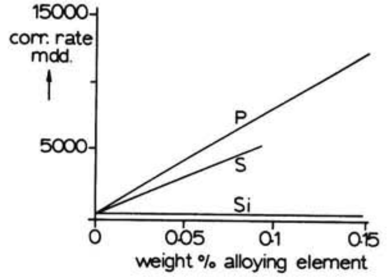


Figure 4.1.2. Effect of P-, S- and Si-content of iron on the corrosion rate in deaerated 0.1 N HCl at 25°C.

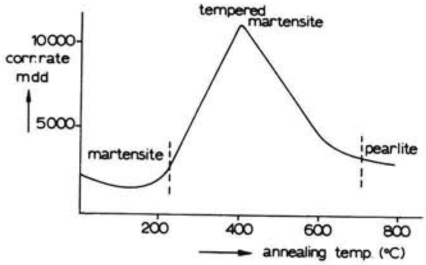


Figure 4.1.3. Influence of heat treatment of 0.95% carbon steel on the corrosion rate in 1% H_2SO_4.

Table 4.1.1. Corrosion rates of iron alloys in deaerated citric acid and in sodium chloride + hydrochloric acid at 15°C.

Alloy composition	Corrosion rate (in mdd) in	
	0.1 M citric acid pH = 2.06	4% NaCl + HCl pH = 1
Pure iron (0.05% C)	29	30
+ 0.02% P	165	1000
+ 0.015% S	706	2830
+ 0.11% Cu	41	390
+ 0.1% Cu + 0.03% P	376	606
+ 0.08% Cu + 0.02% S	32	186

electrochemical in character. This means that the considerations relating to the kinetics of electrochemical reactions, as discussed in the previous chapter, should be applicable to these cases and should furnish an explanation for these observations. As stated already in section 3.1 a corroding metal constitutes a polyelectrode and we shall therefore start in section 4.2 with a consideration of polarisation diagrams of polyelectrodes. We will

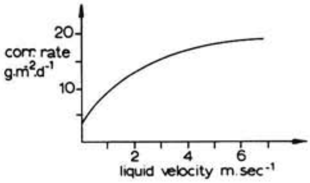


Figure 4.1.4. Corrosion rate of steel tubes in sea water as a function of the velocity of the solution.

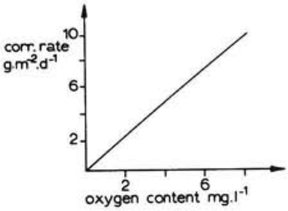


Figure 4.1.5. Weight loss of unalloyed steel after 48 hours exposure to a moving solution containing 165 mg.l^{-1} CaCl$_2$ as a function of the dissolved oxygen concentration.

then in turn consider corrosion in acid and in neutral solutions, the influence of the electrical resistivity of the solution, the effects of coupling dissimilar metals together and the conditions under which passivity will occur.

4.2. POLARISATION DIAGRAMS FOR POLYELECTRODES

A corroding metal constitutes a polyelectrode because at its surface at least two different electrode reactions occur simultaneously. These are the anodic reaction of metal dissolution, e.g.,

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^- \tag{4.2.1}$$

and some cathodic reaction, e.g.,

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2 \tag{4.2.2}$$

Both reactions are written in the direction in which they actually occur during corrosion. They can of course occur as equilibrium reactions (although not simultaneously) at the appropriate equilibrium potentials $E_{eq,a}$ and $E_{eq,c}$ with exchange current densities i_{oa} and i_{oc}. As was shown in Chapter 2, corrosion will only be possible if $E_{eq,a} < E_{eq,c}$.

In principle the polarisation of both reactions, if we limit ourselves in the first instance to charge-transfer polarisation, is given by an equation of the form (3.3.4) as was shown in Fig. 3.3.1. The nett current density, according to equation (3.1.3) is then given by

$$i = i_a + i_c \tag{4.2.3},$$

where it is assumed that the anodic and cathodic reaction both take place on the complete electrode surface.

The complete polarisation diagram is now given by a combination of two diagrams of the type given in Fig. 3.3.1a and is shown in Fig. 4.2.1. It is seen that if the difference between the equilibrium potentials, i.e., $E_{eq,c} - E_{eq,a}$, is large enough only the cathodic curve of the cathodic reaction and only the anodic curve of the anodic reaction need to be taken into consideration. Plotting potential against log |i| gives the simplified diagram shown in Fig. 4.2.2. This simplified form will be used in the remainder of

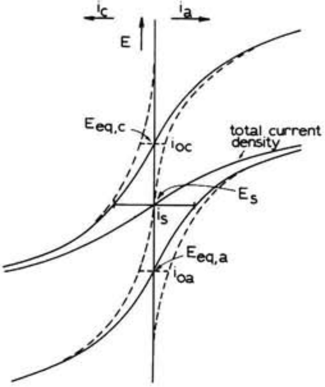


Figure 4.2.1. Polarisation diagram for binary electrode with both reactions showing charge-transfer polarisation only.

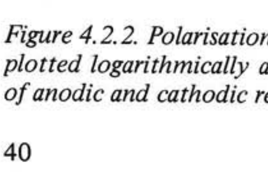


Figure 4.2.2. Polarisation diagram for binary electrode with current density plotted logarithmically and large difference between equilibrium potentials of anodic and cathodic reactions.

this book in all cases where only charge transfer polarisation occurs.

From Fig. 4.2.1 and 4.2.2 we see directly that when the anode and cathode are short circuited a stationary state is reached with a *stationary current density* i_s given by

$$i_s = i_a (E_s) = |i_c (E_s)| \tag{4.2.4}$$

at the *stationary* or *mixed potential* E_s. For a corroding metal these are usually called the *corrosion current density* $i_{corr} = i_s$ and the *corrosion potential* $E_{corr} = E_s$.

Under the circumstances prevailing in corrosion reactions the metal dissolution reaction always shows charge-transfer polarisation. However, there are several important examples of cathodic reactions showing diffusion polarisation. In Fig. 4.2.3 we show the corresponding polarisation diagram. In

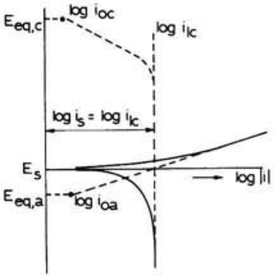


Figure 4.2.3. Polarisation diagram for binary electrode with charge-transfer polarisation of anodic reaction and diffusion polarisation of cathodic reaction.

this case $|i_s| = i_{lc}$ at the stationary or corrosion potential $E_s = E_{corr}$ and thus we have also

$$i_s = i_{\ell c} = i_{corr} \tag{4.2.5}$$

4.3 CORROSION IN ACID SOLUTION

As shown in section 2.6 base metals corrode when put in an acid solution. The cathodic reaction then is hydrogen evolution

$$2H^+ + 2e^- \rightarrow H_2 \tag{4.3.1}$$

However, there are several curious phenomena, some of which were already mentioned in section 4.1. For example pure iron corrodes much more slowly than iron containing impurities which do not significantly change the equilibrium potential. Pure zinc with a much lower equilibrium potential than iron shows a corrosion rate which is only a little larger than that of iron.

An indicator to the explanation of these observations is furnished by the following experiment. Pure zinc standing in acid corrodes only slowly, but if it is connected to a piece of platinum standing in the same solution vigorous hydrogen evolution is observed *on the surface of the platinum* and simultaneously the zinc starts to dissolve quickly. Apparently it is the ease with which the hydrogen evolution reaction occurs which determines the corrosion rate.

Reaction (4.3.1) always shows charge-transfer polarisation at sufficiently low pH ($\leqslant 4$). Moreover the exchange current density has been found to be very sensitive to the type and surface condition of the metal on which the reaction occurs. This is clearly shown by the data given in Table 4.3.1.

For the anodic dissolution of iron and zinc, which also show charge-transfer polarisation the corresponding parameters are:

$$Fe \rightarrow Fe^{2+} + 2e^-, \quad \beta_a = 0.12\ V, \quad i_{oa} = 10^{-8}\ A.cm^{-2}$$
$$Zn \rightarrow Zn^{2+} + 2e^-, \quad \beta_a = 0.12\ V, \quad i_{oa} = 10^{-5}\ A.cm^{-2}$$

Using these data we can construct the polarisation diagram of Fig. 4.3.1 which shows that zinc is indeed expected to show nearly the same corrosion rate as iron notwithstanding its much lower equilibrium potential.

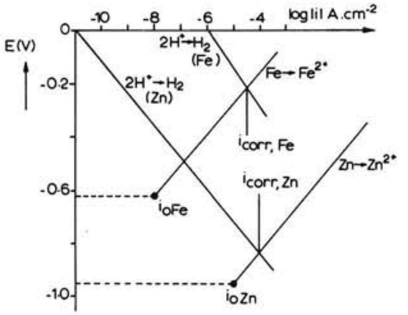


Figure 4.3.1. Polarisation diagram for iron and zinc in acid solution.

Similarly Fig. 4.3.2. shows the reason for the acceleration of the corrosion of zinc when it is coupled to platinum. It is important to note that the reason for the accelerated corrosion of zinc coupled to platinum is different from that for the corrosion of a base metal coupled to a noble metal discussed in chapter 2. There the coupling with a more noble metal furnished a cathodic reaction. Here the noble metal only furnishes a surface on which a cathodic reaction already taking place slowly on the zinc can take place at a much higher rate.

Table 4.3.1. Parameters of charge-transfer polarisation for hydrogen evolution at different metals (From: H.H. Uhlig, Corrosion and Corrosion Control, New York, Wiley, 2nd ed. 1971).

Metal	Solution	β(V)	i_o (A.cm^{-2})	η (V) for i = 1 mA.cm^{-2}
Pt	1 N HCl	0.03	10^{-3}	0.00
Au	1 N HCl	0.05	10^{-6}	0.15
Ag	0.1N HCl	0.09	5×10^{-7}	0.30
Ni	0.1N HCl	0.10	8×10^{-7}	0.31
Fe	1N HCl	0.15	10^{-6}	0.45
	4% NaCl pH 1–4	0.10	10^{-7}	0.40
Cu	0.1N HCl	0.12	2×10^{-7}	0.44
Al	2N H_2SO_4	0.10	10^{-10}	0.70
Sn	1N HCl	0.15	10^{-8}	0.75
Cd	1N HCl	0.20	10^{-7}	0.80
Zn	1N H_2SO_4	0.12	10^{-11}	0.94
Mg	0.1N HCl	0.12	7×10^{-13}	1.10
Pb	0.01–8N HCl	0.12	2×10^{-13}	1.16

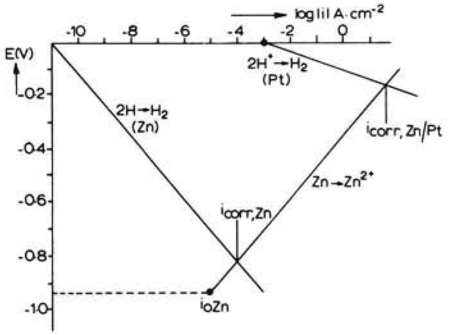


Figure 4.3.2. Polarisation diagram for the corrosion of zinc in acid solution coupled to a platinum electrode of the same surface area.

The acceleration of the corrosion by impurities is explained in the same way as that caused by coupling with platinum. The hydrogen evolution reaction occurs much more readily at these impurities, i.e., has a much larger exchange current density at their surface than at the metal surface itself. If this increase is large enough even small amounts of impurities cause greatly increased corrosion rates (see problem 4.1).

On this basis it is also possible to understand the influence of pH on the corrosion rate as indicated schematically in Fig. 4.3.3. When the pH is increased the equilibrium potential of the hydrogen evolution reaction is lowered by 0.059 V for every pH unit as follows from equation (2.7.4). If the influence of pH on i_{oa} and i_{oc} is not too large this means that the

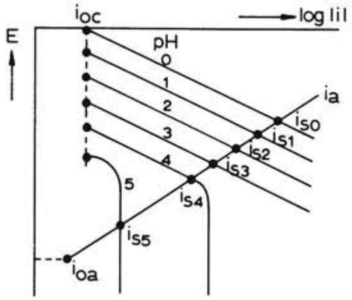


Figure 4.3.3. Schematic polarisation diagram for a metal corroding with hydrogen evolution in acid solutions of different pH.

anodic and cathodic polarisation curves will cross at smaller current densities with increasing pH. Of course at a sufficiently high pH ($\gtrsim 4$) the transport of H^+-ions to the electrode may become rate determining and diffusion polarisation sets in.

As stated above the charge-transfer polarisation is very sensitive to the surface condition of the electrode. This means that it will in general be strongly influenced by substances present in the electrolyte when these are adsorbed on the surface. Substances which in this way lead to a decrease in corrosion rate are commonly called *inhibitors.*

Sometimes this leads only to a decrease of the rate of the hydrogen evolution reaction. We then speak of an inhibitor showing cathodic control and examples are certain compounds of arsenic and of antimony. A large class of organic substances, usually containing active nitrogen or sulphur groups by which they are attached to the metal surface, influence both the cathodic and the anodic reaction and we speak of mixed control. Schematically the action of these types of inhibitors is shown in Fig. 4.3.4.

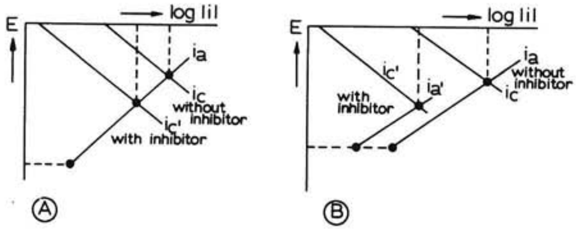


Figure 4.3.4. Schematic polarisation diagrams showing the effect of inhibitors: A. showing cathodic control; B. showing mixed control.

In Fig. 4.3.5. we show the efficiency η of a number of inhibitors, where the efficiency is defined as:

$$\eta\,(\%) = \frac{\text{corr.rate without inhibitor} - \text{corr.rate with inhibitor}}{\text{corr. rate without inhibitor}} \times 100 \qquad (4.3.2).$$

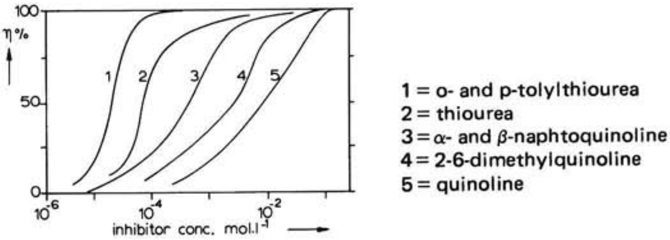


Figure 4.3.5. Efficiencies of some inhibitors in 5% H_2SO_4 *as a function of inhibitor concentration (adapted from T.P. Hoar and R. Holliday, J. Appl. Chem.* **3** *(1953)p. 502)*

An important application of inhibitors of this type is in pickling baths used to remove oxides from metal surfaces. The use of inhibitors has three important consequences:

a. it decreases metal losses;
b. it saves acid;
c. it reduces the formation of acid fumes caused by hydrogen evolution.

4.4. CORROSION IN NEUTRAL SOLUTION: 'OXYGEN CORROSION'

When the pH of a solution, in which iron is immersed, is increased above about 4 we would expect, according to Fig. 4.3.3, a very sharp drop in corrosion rate. However, as shown in Fig. 4.1.1a, this is contrary to observation. In fact the corrosion rate levels off and becomes nearly independent of pH over a wide pH range. This is only possible if a new cathodic reaction consumes the electrons produced in the anodic reaction. This has been shown to be the oxygen reduction reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4.4.1).$$

This reaction shows diffusion polarisation in nearly all practical cases: the transport of oxygen to the metal is rate determining. Under these circumstances we have to use the polarisation diagram of Fig. 4.2.3.

On this basis the behaviour of steel, and of several other metals which behave similarly, shown in Fig. 4.1.4. and 4.1.5. is easily explained. When the velocity of the liquid in a tube is increased the thickness of the diffusion layer (see Fig. 3.3.3) will decrease. This leads to a larger concentration gradient and thus to a larger limiting current for oxygen reduction which is equal to the corrosion current density according to equation (4.2.5). At very high velocities charge-transfer polarisation may become rate-determining which leads to a levelling off of the corrosion rate as seen in Fig. 4.1.4. Similarly an increase in oxygen content leads to a proportional increase in limiting current density and thus also in the corrosion rate in agreement with the observations shown in Fig. 4.1.5.

The rate determining step in this case takes place *in the solution.* This automatically explains why impurities and the microstructure of the metal do not have a direct influence on the corrosion rate in neutral solutions.

An increase in temperature increases the diffusion coefficient of oxygen and is thus expected to lead to an increased corrosion rate. In closed systems or in open systems at not too high temperatures this is indeed observed. However, in open systems at higher temperatures the corrosion rate decreases again as shown in Fig. 4.4.1a. This is simply due to the decrease in solubility of oxygen in water with increasing temperature shown in Fig. 4.4.1b.

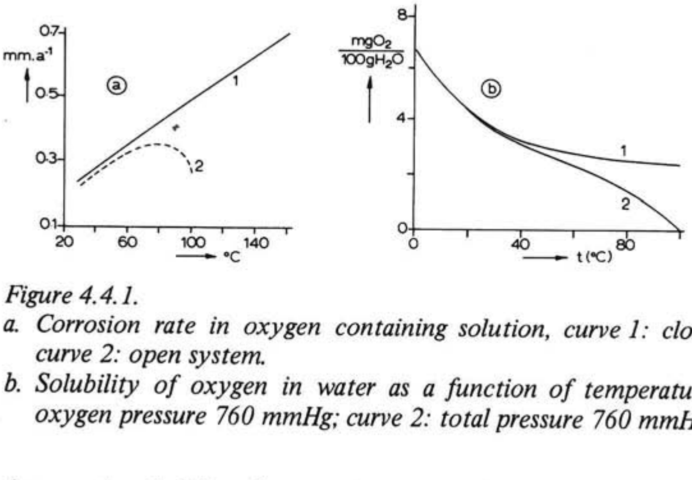


Figure 4.4.1.

- *a. Corrosion rate in oxygen containing solution, curve 1: closed system, curve 2: open system.*
- *b. Solubility of oxygen in water as a function of temperature, curve 1: oxygen pressure 760 mmHg; curve 2: total pressure 760 mmHg.*

This at once suggests a way to control this type of corrosion: the removal of oxygen. This can be done chemically by adding substances which react with oxygen (sometimes called *scavengers*). Examples are hydrazine (N_2H_4) and sulphites (containing the SO_3^{2-}-ion), which react as follows:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$
$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$

In modern practice it is more usual to remove oxygen by deaeration. This can be done by vacuum treatment or inert gas sparging, nearly always combined with heating, e.g., by steam.

The fact that central heating systems usually show surprisingly little corrosion is due to the fact that in these practically closed systems the oxygen content becomes very low after a short time. This is due both to the heating and gas removal and to reaction with the iron. However, if such a system shows leaks and fresh water is added regularly serious corrosion may result due to the supply of oxygen and insufficient time for complete removal.

4.5. INFLUENCE OF ELECTROLYTE RESISTIVITY ON CORROSION RATE

Corrosion usually takes place in solutions containing so called 'neutral' electrolytes which neither influence the pH nor take part in the electrode reactions. However, they make it possible that charge is transported through the solution from anode to cathode. If the liquid has a finite electrical resistivity a finite potential difference ΔE between the anodic and cathodic parts of the surface is needed to force the current through the solution. This has a direct influence on the corrosion rate as illustrated schematically in Fig. 4.5.1. When the total resistance is zero the corrosion current density has the maximum possible value i_{corr} and the metal surface has the same potential E_{corr} everywhere. At a finite resistance R a potential difference $\Delta E = i'_{corr} \cdot R$ exists and $i'_{corr} < i_{corr}$. With increasing electrolyte resistivity, i.e., with decreasing salt content the corrosion rate decreases. In Table 4.5.1 the specific resistance ρ of the NaCl-solutions of different concentration is given together with the potential drop which develops over 1 cm of the solution at a current density of 1 mA.cm^{-2}. In practice the distance between the local cathodes and anodes will be much smaller than 1 cm. However, from the data in section 4.3 it can be calculated that, in the case of charge-

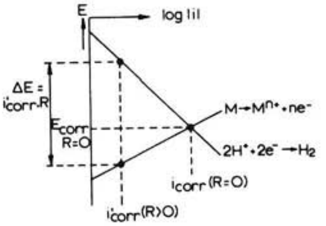


Figure 4.5.1. Polarisation diagram of a corroding metal with and without a finite resistance in the system.

Table 4.5.1. Specific resistance ρ and potential drop in NaCl solutions (sea-water $\simeq 0.5$ mol.l^{-1}).

Concentration mol.l^{-1}	ρ Ω.cm	ΔE (Volt) at $i = 1$ mA. cm^{-2}, electrode distance = 1 cm
0.001	8100	8.1
0.005	1660	1.66
0.01	843	0.84
0.05	173	0.173
0.1	93	0.093
0.5	21.4	0.021
1.0	11.7	0.012
5.0	4.05	0.004

transfer polarisation, a potential drop of 0.02 V approximately halves the corrosion rate.

Fig. 4.5.2 shows the influence of NaCl concentration on the corrosion rate of iron in solutions saturated with oxygen.

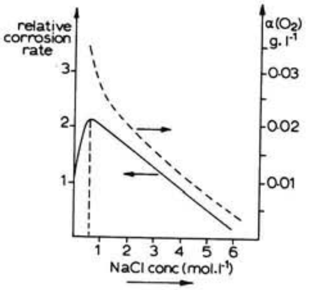


Figure 4.5.2. Influence of NaCl concentration on corrosion rate of iron in aerated solution at 25°C (——) and on solubility (α) of oxygen in these solutions (– – –)

At low NaCl concentration the corrosion rate indeed increases rapidly with increasing concentration. Above about 0.5 mol.l^{-1} NaCl, which is approximately the total salt content of sea water, the corrosion decreases with a further increase in NaCl concentration. This is explained by the fact that the solubility of oxygen then decreases as is also shown in Fig. 4.5.2. As discussed in the previous section this leads directly to a corresponding decrease in corrosion rate.

Removal of dissolved salts is used widely to control corrosion in practice. For example ship's diesel engines are usually cooled with fresh water in modern practice instead of with sea water as was done previously. Similarly boiler feed water is usually desalted by ion exchange or destillation.

4.6. BIMETALLIC CORROSION

It has been mentioned several times that the coupling of two different metals standing in the same solution causes (accelerated) corrosion of the base metal. This is called *bimetallic* or *galvanic corrosion.* A special form of this phenomenon was discussed in section 4.3., i.e., the case where the hydrogen evolution reaction occurs faster at the surface of the noble metal than at that of the base metal. In this case it is not the equilibrium potential of the noble metal itself but that of the hydrogen evolution reaction which, together with its kinetic parameters, determines the acceleration of the corrosion.

The ratio of the surface areas of the two metals is also of great importance. In Fig. 4.6.1 this is shown for a cathodic reaction which shows charge-transfer polarisation. If the surface areas of the anode (A_a) and cathode (A_c) are equal the corrosion current density is given by the crossing point of the polarisation curves, when the very slight hydrogen evolution occurring at the anodic metal is neglected. We also neglect in these considerations the resistance of the electrolyte. If the surface area of the cathode is ten times that of the anode the cathodic current density must be one tenth that of the anodic current density (conservation of charge). We see in Fig. 4.6.1 that this occurs at a higher potential and thus at an increased corrosion rate.

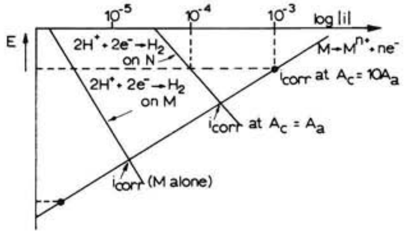


Figure 4.6.1. Polarisation diagram for bimetallic corrosion of base metal M with hydrogen evolution at noble metal N.

In neutral solutions, with oxygen reduction as the cathodic reaction, something quite analogous happens as shown in Fig. 4.6.2. In this figure we have plotted the total cathodic current (on both metals) instead of the current density. It is seen that the reason for the accelerated corrosion is the increase in surface area available for the cathodic reaction: the total oxygen transport is increased.

An important practical consequence is that when different metals are connected the danger for inadmissible corrosion losses is greatest when the anode is small with respect to the cathode. Thus aluminium sheets can be fastened with steel or cadmium plated bolts, but aluminium bolts must not

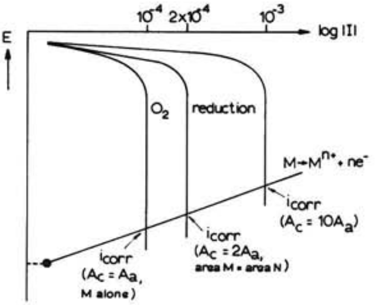


Figure 4.6.2. Polarisation diagram for bimetallic corrosion with oxygen reduction as cathodic reaction as a function of increasing surface area of noble metal (N).

be used for fastening steel sheets. Brass fittings can be used in central heating systems because their surface area is so much smaller than the steel pipes and radiators with which they are connected.

We now consider the case where two corroding metals M and N are coupled together. Fig. 4.6.3. shows the corresponding polarisation diagram

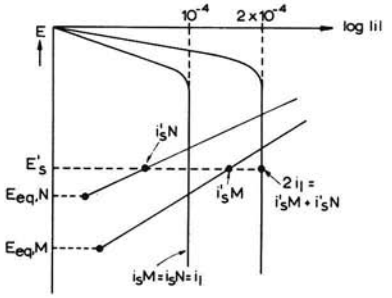


Figure 4.6.3. Polarisation diagram of corroding metals connected together with oxygen reduction as cathodic reaction.

with oxygen reduction as the cathodic reaction. Separately they show the same corrosion rate: $i_{sM} = i_{sN}$ = limiting current density i_ℓ of oxygen reduction. When the metals are connected the total rate of reduction becomes $I = 2i_\ell$ if their surface areas are equal. This leads to a stationary state with the two metals at the potential E'_s if the influence of resistance is again neglected. In this stationary state the sum of the two anodic current densities $i'_{sM} + i'_{sN}$ is equal to $2i_\ell$. Fig. 4.6.3 shows again increased corrosion of the less noble metal but simultaneously decreased corrosion of the more noble one. This is in fact the principle of *cathodic protection* which is discussed in the next section.

4.7. CATHODIC PROTECTION

If the potential of a metal is lowered beneath its equilibrium potential all corrosion stops: it has become immune. This was discussed in relation with the Pourbaix diagrams in section 2.7. As shown above connecting a metal with another one which is less noble leads to a decrease in potential. By proper choice of surface area ratio of the two metals and of an anode material with a sufficiently negative potential complete protection can be obtained. This is called *cathodic protection.* Of course the less noble metal is consumed in protecting the other metal and is usually called a *sacrificial anode.*

For the protection of iron and steel the commonly used anode materials are zinc, magnesium and aluminium. Some of their properties are given in Table 4.7.1. For copper and copper alloys iron can be used as material for sacrificial anodes.

Table 4.7.1. Properties of materials for sacrificial anodes.

Material	Potential with respect to Cu/Cu_2SO_4 (Volt)	Theoretical consumption kg/A.year	Efficiency %	Effective capacity Ah/kg
zinc	– 1.05 to – 1.15	10.7	90–96	~ 700
aluminium	– 1.05 to – 1.35	2.9	45–55	~ 2400
magnesium	– 1.25 to – 1.75	3.9	65–90	~ 100

It is also possible to obtain cathodic protection by impressing an external current. In that case it is usual to use *inert anodes* which are consumed only very slowly or not at all. Some properties of materials commonly used for anodes in cathodic protection with an impressed current are given in Table 4.7.2. Of course scrap steel is not an inert material: it is consumed by anodic dissolution. However, its low price may make its use economical in particular when the total protective current is not too high.

The total protective current and thus also the consumption of the anode material or of external current is directly proportional to the surface area of the metal to be protected. This usually makes it uneconomical to protect bare metal and cathodic protection is very often combined with a surface coating on the protected metal. In this way only the metal under pores or damaged spots of the coating has to be protected. Table 4.7.3. gives the necessary current density for protection of steel under different circumstances. Another important point is the resistivity of the environment. If this is high a large voltage drop results at a given current, again making it advisable to limit the necessary current by using good coatings.

In practice cathodic protection is used very extensively. Examples of objects protected in this way are: underground pipelines and tanks, cooling

Table 4.7.2. Properties of anode materials for cathodic protection with impressed current.

Material	Permissible current density $A.m^{-2}$.	Maximum voltage V	Anode consumption kg/A.year
scrap steel	–	–	9.1
graphite	2.5 – 10	–	0.1 – 2
silicon iron (about 15% Si)	10 – 20	40	0.1 – 0.5
lead	100 – 2000	–	0.05 – 0.1
platinized titanium*	500 – 1000	12	negligible

*Cannot be used in hot, chloride containing solutions.

Table 4.7.3. Current densities (calculated on the basis of total surface area) necessary for protection of steel in different environments.

Object	Environment	Coating	Age	Typical current density $(mA.m^{-2})$
steel	fresh water	none	–	40–70
steel	fresh water	good	–	0.1–1
steel	sea water (stagnant)	none	before natural deposit has formed	500–1000
steel	sea water (stagnant)	none	after formation of deposit	50–100
steel	sea water (streaming)	none	after formation of deposit	200–300
steel	sea water	good	–	1–10
pipeline	soil	asphalt	~ 10 year	1–3
pipeline	soil	plastic	–	0.001–0.1
central heating	soil	cork shells	–	10–50

systems, waterboxes of condensors, evaporators, ships, harbour and offshore installations, etc. Fig. 4.7.1. gives a schematic drawing of two practical cases of cathodic protection. In Figure 4.7.2. we show a part of an offshore drilling platform with aluminium sacrificial anodes welded to the structure. A platinized titanium anode as used in the protection of a harbour installation is shown in Fig. 4.7.3.

The choice between the two methods is governed principally by economic considerations such as investment, maintenance costs, production loss due to replacement of sacrificial anodes, etc. Of course the possibility of external regulation and control in using an impressed current may also be an important factor.

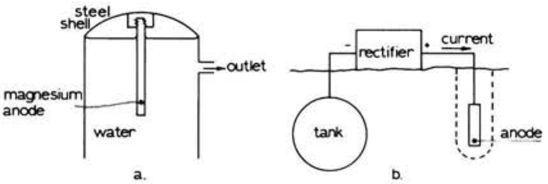


Figure 4.7.1. Practical examples of cathodic protection.
a. Internal protection of boiler with sacrificial anode;
b. External protection of underground tank with impressed current.

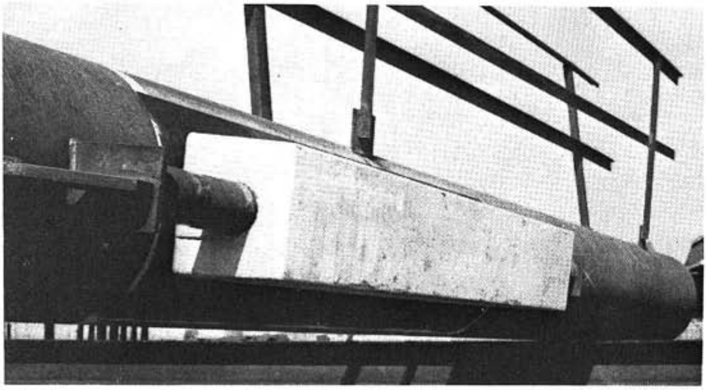


Figure 4.7.2. Part of off-shore drilling platform with aluminium sacrificial anode (Vandervelde Protection, The Hague, Netherlands).

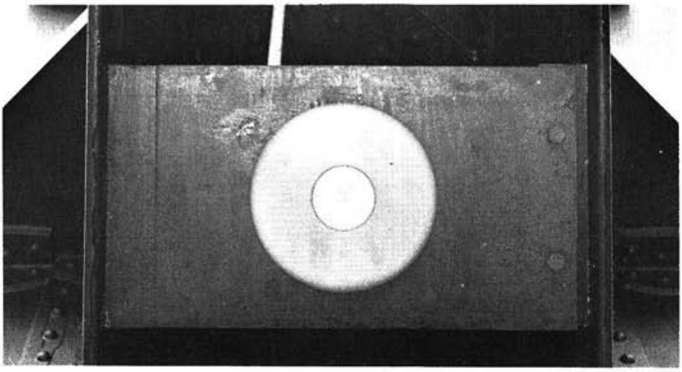


Figure 4.7.3. Platinized titanium anode (Vandervelde Protection, The Hague, Netherlands).

4.8. PASSIVITY

In discussing the corrosion of iron as a function of pH (see Fig. 4.1.1a) we have not yet explained why the corrosion rate suddenly drops above pH $\simeq$ 10. Obviously there is no reason for the rate of oxygen transport to the surface, which gives a corrosion rate of about 5 $g.m^{-2}.d^{-1}$ for iron, to be dependent on pH. A similar behaviour is shown, in different pH-regions, by other metals as shown in Fig. 4.8.1 for zinc and aluminium. This is in agreement with our daily experience: zinc and aluminium hardly corrode under normal conditions in neutral solution whereas iron is covered with rust after a short time.

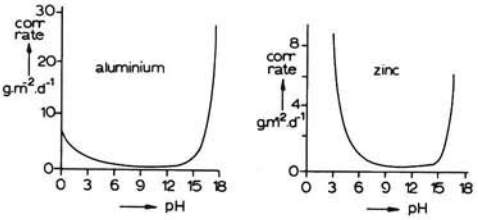


Figure 4.8.1. Corrosion rate of aluminium (a) and zinc (b) as a function of pH in aqueous solution.

Comparison of the pH-regions where these low corrosion rates are observed with the Pourbaix-diagrams shows that they coïncide with the regions where passivity is possible (see Figs. 2.7.2, 2.7.4).

Evidently the explanation of the low corrosion rate is that the metal has become passive.

In section 3.4 the anodic polarisation curve for a metal which can be passivated was discussed (see also Fig. 3.4.1). In order to know how the metal will behave in practice this has to be combined with the polarisation curve of the cathodic reaction. We can then distinguish a number of possibilities, the most important of which are shown in Fig. 4.8.2. Spontaneous

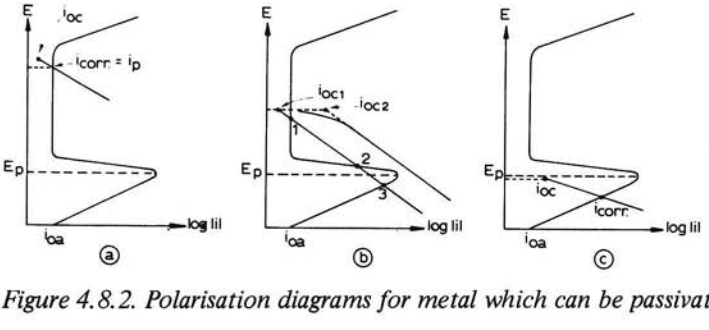


Figure 4.8.2. Polarisation diagrams for metal which can be passivated.

and stable passivity is obtained in the case shown in Fig. 4.8.2a. Here the cathodic reaction has a sufficiently high equilibrium potential that the curves cross only in the passive region so that the corrosion rate is $i_{corr} = i_p$. At a lower equilibrium potential for the cathodic reaction we have the two possibilities of Fig. 4.8.2b. A cathodic reaction with a large exchange current density still makes it possible to obtain spontaneous and stable passivity. For a cathodic reaction with a small exchange current density it may happen that there are three crossing points of the polarisation curves. For practical purposes the middle one (2 in Fig. 4.8.2b) is not important because it is electrically unstable (comparable to a cone standing on its apex) so that the system goes spontaneously to 1 or 3. If the metal is passive to begin with it starts in point 1 and if undisturbed remains passive. But if the passive layer is locally damaged, the resulting active spot can not be repassivated and corrodes with a rate corresponding to point 3. We then have what is called an *active-passive element* with a small anode and a large cathode. Because the cathodic reaction is unable to 'lift' the active metal over its critical passivation current density this situation usually leads to serious, localized corrosion.

Finally, as shown in Fig. 4.8.2c, for a cathodic reaction with a still lower equilibrium potential, passivation is no longer possible, in fact this represents the case of corrosion of an active metal discussed above.

The critical passivation current density i_{cp} and sometimes also the passivation potential E_p, can be influenced by external circumstances. Examples are temperature, velocity of liquid, composition of the electrolyte and of the metal. In Fig. 4.8.3 we see the i_{cp} of iron-chromium alloys as a function of chromium content. This is typical for the behavior of these alloys in many environments although the exact value of i_{cp} still depends on temperature, stirring and specific ions present. These data are combined with the cathodic polarisation curve for oxygen reduction in figure 4.8.4. It is seen that alloys containing more than about 12% chromium will be spontaneously passivated and remain so. These alloys form one example of the so-called *stainless steels.* Most of these also contain other alloying elements such as the common 18% chromium 8% nickel steel (type 304). Some of

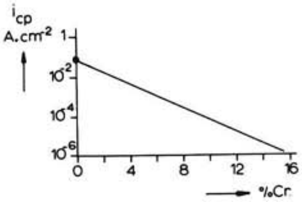


Figure 4.8.3. Critical passivation current density of iron-chromium alloys as a function of chromium content in a 3% sodium sulphate solution at 25°C.

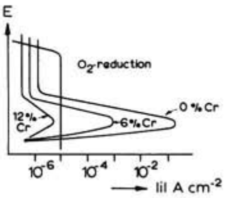


Figure 4.8.4. Polarisation behaviour of iron-chromium alloys in an oxygen-saturated 3% sodium sulphate solution.

these alloying elements are added to improve the corrosion resistance in specific environments, e.g., molybdenum in stainless steels used in chloride-containing solutions.

A second important variable influencing i_{cp} is the pH of the solution. In Table 4.8.1 some data for iron are collected. This makes it possible to understand the sharp drop in corrosion rate of iron above pH ~ 10 (Fig. 4.1.1a). The critical passivation current density then becomes lower than the limiting current density for oxygen reduction and spontaneous passivation results (Fig. 4.8.2a).

Table 4.8.1. Passivation parameters for iron as a function of pH.

pH	i_{cp} A.cm^{-2}	E_p Volt	i_p A.cm^{-2}
0.3	2×10^{-1}	0.40	8×10^{-6}
3	6×10^{-2}	0.40	3×10^{-6}
4	8×10^{-3}	0.35	1.5×10^{-6}
5	3×10^{-3}	0.30	6×10^{-7}
6	1.5×10^{-3}	0.25	2×10^{-7}
8.4	10^{-5}	− 0.40	–
9.3	10^{-7}	− 0.50	7×10^{-9}

Another possible method of obtaining passivity is by adding *passivators* to the environment. These are usually inorganic oxidizing compounds with a high equilibrium potential and a large exchange current density thus giving the polarisation diagram of Fig. 4.8.2a. Two of those most commonly used are sodium chromate and sodium nitrite. In neutral solution a concentration of about 10^{-3} mol.l^{-1} is generally sufficient to passivate mild steel. At lower pH and/or high chloride content a higher concentration is necessary. For this reason an alkaline substance such as sodium borate or sodium carbonate is often added together with the passivator.

With decreasing concentration the situation of Fig. 4.8.2b with three crossing points may result due to the general downward shift of the cathodic polarisation curve and to the possibility that diffusion polarisation sets in. Because passivators are consumed due to their protective action regular additions are necessary to maintain a high enough concentration and to avoid the danger of localized corrosion.

Some compounds such as sodium benzoate and sodium polyphosphate are not able to passivate the surface directly. However, they do lead to greatly decreased corrosion because they react with the iron surface leading to a much smaller i_{cp} so that the oxygen reduction reaction already is sufficient to passivate the steel.

Chromate is often used in closed cooling systems such as internal combustion engines and chemical process industry installations etc. Usually 0.04 to 0.1 weight % sodium chromate is used and the pH is brought to 7.5 to 9.5. A practical disadvantage is that chromate is poisonous and that some people are allergic to it. Furthermore many organic compounds, such as glycol, which is used as an anti-freeze additive, are oxidized to acids. This leads to decreased pH and increased chromate consumption together with the destruction of the anti-freeze.

These disadvantages have led to an increasing use of sodium nitrite, in particular in cooling systems where anti-freeze additives are present. Inhibitors are also used extensively in oil-water emulsions which are employed in the machining of metals. Another important application is in pipelines for petroleum products. Although these products are not corrosive themselves they usually contain water which may separate at lower temperatures. Due to the high solubility of oxygen in the petroleum (about 6 times as high as that in water) this causes heavy rusting. To prevent this a concentrated (5–30%) aqueous solution of sodium nitrite is continuously injected together with an alkaline substance because nitrite is ineffective at a $pH < 6$.

Finally we may mention another possible way of using the property of a metal to become passive: *anodic protection.* In a sense this is the reverse of cathodic protection: the metal to be protected is connected to an auxiliary electrode via an external current source and so brought in the passive region by raising its potential.

4.9 PROBLEMS

1. Iron is placed in an acid solution ($pH = 2$) and $[Fe^{2+}] = 10^{-5}$ mole.l^{-1}.
   a. What are the anodic and cathodic reactions which are occurring at the iron surface?
      Both reactions may be assumed to show charge-transfer polarisation with the parameters:
      anodic reaction: $\beta_a = 0.12$ V; $io_a = 10^{-8}$ A.cm^{-2}
      cathodic reaction: $\beta_c = 0.10$ V; $io_c = 10^{-7}$ A.cm^{-2}.
   b. Construct the complete polarisation diagram and determine from this

the corrosion rate of iron when the electrolyte resistance is 0.1 Ω. What will the corrosion rate be if the electrolyte resistance is 10000 Ω?

We now suppose the iron to contain an impurity in such a way that 1% of its surface consists of a component at which the cathodic reaction is much faster and shows the parameters:

cathodic reaction at impurity: $\beta_c = 0.10\text{V}, i'_{oc} = 10^{-3}\ \text{A.cm}^{-2}$.

c. Draw the corresponding polarisation curve in the diagram of b taking into account the surface area of the impurity. The change in surface area of the iron may be neglected. What does the corrosion rate become when the electrolyte resistance is 0.1 Ω?

2. Derive an equation for the corrosion current density of a metal when both the anodic and cathodic reaction show charge-transfer polarisation only (Hint: use eq. (3.3.6) remembering that for the cathodic reaction $\eta_c = E - E_{eq,c}$, for the anodic reaction $\eta_a = E - E_{eq,a}$ and in the stationary state $E = E_s$).
3. A number of iron specimens of the same surface area have different fractions of their surface covered with a noble metal. When these are put into a neutral aerated electrolyte solution they all show the same weight loss after a certain time, independent of the fraction of the surface covered with the noble metal. Explain!
4. For off-shore constructions standing in deep water cathodic protection using sacrificial anodes is often the only possible way of corrosion prevention. These anodes have to be large enough to give protection during the whole expected lifetime of the construction because maintenace or replacement is often impossible.

   If the protective current for bare steel is 0.1 A.m^{-2} under the prevailing conditions calculate the amount of zinc or aluminium necessary to protect a surface area of 100 m^2 during 20 years. Which of these metals is preferable?
5. Iron is immersed in the aqueous solution specified in problem 7 of section 3.6. At what pH will the iron become spontaneously passive?
6. In a number of figures used as illustrations in this chapter of the practical behavior of metals under different circumstances different units are given for the corrosion rate. Recalculate these to a common unit, e.g., to mm.a^{-1}.

5. Characteristic forms of electrochemical corrosion

5.1. INTRODUCTION

Corrosion manifests itself in a number of characteristic forms. The basic distinction is that between *uniform* attack and *localized attack*. As the name implies uniform attack takes place (practically) evenly over the whole metal surface. This is found with active metals and with metals in the passive state but in the latter case the attack is very slow. This type of corrosion, as a rule, is not a great problem from the *technical* point of view; its rate can usually be determined with a reasonable accuracy. Prediction of the expected lifetime is usually not difficult and if necessary a corrosion allowance can be applied. Most methods of preventing corrosion presented in Chapter 4 are also applicable, together with others, such as painting, to be discussed in Chapter 6. A special type of uniform corrosion is the *atmospheric rusting* of iron and steel which is discussed in more detail in section 5.2.

Much more insidious and unpredictable are the different types of localized corrosion to be treated in the further sections of this chapter. These are: pitting corrosion, crevice corrosion and deposit attack, selective dissolution, intercrystalline corrosion, stress corrosion cracking and corrosion fatigue, erosion corrosion, cavitation corrosion and impingement attack and finally fretting corrosion. These forms usually cause unexpected, local failures, some of which are not of a purely electrochemical nature but are strongly influenced or partly caused by mechanical or metallurgical factors.

Fig. 5.1.1. schematically shows the difference in the amount of corrosion before failure of a metal, which has to support a mechanical load, with uniform and with localized corrosion, in this case in the form of cracks.

5.2. RUSTING AND ATMOSPHERIC CORROSION OF IRON AND STEEL

In approximately neutral solutions and upon exposure to the atmosphere, corrosion of iron and steels takes place with formation of rust. This is a

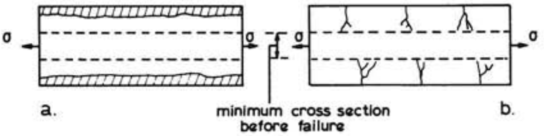


Figure 5.1.1. Schematic representation of: a. uniform and b. localized corrosion. The total metal loss leading to failure is much greater with a. than with b. Usually this corresponds with a much longer life.

collective noun for a number of hydrated iron oxides and hydroxides with the general composition $FeO(OH).nH_2O$, containing trivalent iron.

In the anodic reaction iron dissolves as Fe^{2+}-ions, while simultaneously hydroxyl-ions are formed at the cathode. In the solution where these ions meet, the solubility product of $Fe(OH)_2$ will be exceeded so that this compound precipitates. Subsequently it is rapidly oxidized by the oxygen present in the solution to the brown oxy-hydroxides mentioned above. They form a porous layer because they are formed in the solution at some distance from the metal surface. Fig. 5.2.1 shows schematically the formation of rust in a drop of water.

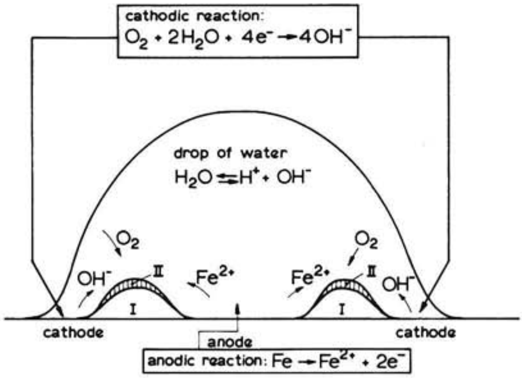


Figure 5.2.1. Schematic representation of the formation of rust in a drop of water on a steel surface.

The cathodic and anodic areas move over the surface with time causing reasonably uniform corrosion. When the iron is continuously submerged the rust layer slows down the oxygen supply and thus the corrosion rate, as shown in Fig. 5.2.2. In atmospheric corrosion the rate determining factor in

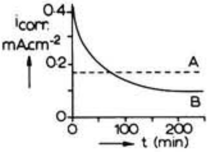


Figure 5.2.2. Change in corrosion rate of steel with time. A = average, B = instantaneous rate. (Steel in oxygen saturated sea water).

the corrosion process is still the oxygen supply. However, the attack as a whole is then determined by the time of wetting.

The main components of the atmosphere responsible for atmospheric corrosion are oxygen (20%), water (at 20°C maximum 2.3%) and carbon dioxide (0.03%). Other active components are often added to these due to natural processes or human activities, e.g., sulphur dioxide, soot, hydrogen sulphide, sodium chloride, nitrogen oxides, etc. The total composition of the atmosphere strongly influences corrosion behavior. Therefore a number of types of atmosphere are distinguished and related to typical corrosion rates of unprotected steel. In countries like Great Britain or those of Western Europe these are: rural (0.5–2 mil.year^{-1}), urban (1–3 mil. year^{-1}), marine (2–4 mil.year^{-1}) and industrial (4–10 mil.year^{-1}). Factors like direction of prevailing wind, temperature, rainfall and suspended solids also play an important role. However, the influence of these factors is not always clear-cut. Rain, for example, causes on the one hand wetting and thus corrosion but on the other hand it may wash off aggressive substances thus diminishing the attack.

As shown schematically in Fig. 5.2.3. the relative humidity exerts a strong

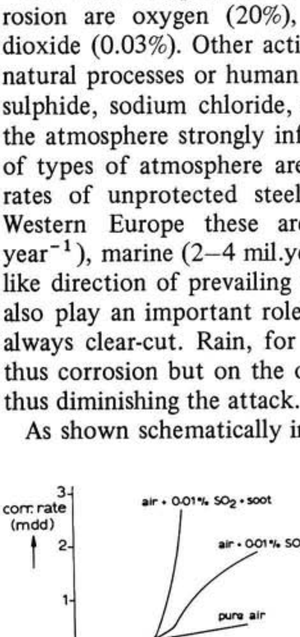


Figure 5.2.3. Influence of relative humidity on the atmospheric corrosion of iron under different circumstances.

influence on corrosion. However, we see from this figure that humidity alone does not lead to serious corrosion, which occurs only if an aggressive component, such as SO_2, is present. In the presence of solid particles, such as soot, the corrosion is even more severe because solid particles lying on a metal hold moisture and may act as condensation nuclei.

In 'closed' spaces, such as the inside of automobile doors, box girders and petrol tanks, heavy corrosion may occur on cooling as this leads to increased relative humidity or even condensation on the inside surfaces. An unpleasant aspect of this type of corrosion is that it is usually discovered too late, namely when perforation occurs. Such imperfectly closed spaces should either be sealed completely or adequate ventilation must be provided. Sometimes protective coatings (see Chapter 6) or temporary corrosion preventives can successfully be applied.

The composition of the steel may also have a large influence on the rate of atmospheric corrosion. In particular the presence of relatively small amounts of alloying elements such as Cu, Cr and Ni leads to improved behaviour as shown in Fig. 5.2.4.

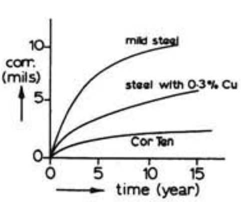


Figure 5.2.4. Atmospheric corrosion of different types of steel. See Table 5.2.1 for composition of CorTen.

As these steels are also stronger than mild steel, which was the original reason for their introduction, they are sometimes called HSLA = high strength low alloy steels. At present they are increasingly used, under the name *weathering steels*, without additional corrosion protection. This is possible because they become covered with a dense rust layer with good adhesion to the steel surface. This has led to their application in architecture, for bridges, steel constructions in industry, etc. Even when these are painted their use shows advantages. In damaged spots of the paint less rust is formed and there is less penetration of corrosion under the paint. This means that repainting can be less frequent and derusting is easier and less costly.

Maintenance costs are thus decreased which, together with the smaller weight needed as a consequence of their higher strength, compensate for the higher price of these steels. Schmitt and Mathay (*Materials Protection* **6** (sept. 1967), p. 37) have calculated for a certain installation used in a very aggressive industrial atmosphere that the yearly costs of CorTen, (purchase price at the time $ 167 per ton) were $ 52.257 against $ 68.647 for mild steel (purchase price $ 117 per ton). In Table 5.2.1 the names and compositions of some representative steels of this type are given.

Table 5.2.1 Composition of some types of steel.

Steel	C	Mn	P	S	Si	Cu	Ni	Cr
mild steel	0.16	0.6	0.01	0.03	0.01	0.01	0.01	0.03
Cor Ten A*	0.09	0.5	0.07	0.03	0.52	0.31	0.40	0.74
Cor Ten B*	0.15	1.3	0.01	0.03	0.26	0.31	–	0.44
Mayari R**	0.10	0.7	0.10	0.03	0.28	0.35	0.65	0.55

* U.S. Steel

** Bethlehem Steel

Finally it should be remarked that these steels in general only show this improved behavior under atmospheric conditions. In fully submerged condition the differences between weathering steels and mild steels are as a rule, much smaller or absent. In marine atmosphere, containing chlorides, these steels also do not show a great advantage over mild steel.

5.3. PITTING CORROSION

As the name indicates this is a strongly localized type of attack which manifests itself in the form of deep and narrow pits. Active metals show this type of corrosion only as a consequence of particular external circumstances such as local wetting or damaged spots in mill scale or a protective coating. Porous corrosion products, which accumulate moisture and aggressive substances, can then cause accelerated attack. The mechanism of this is the same as that of uniform corrosion.

A much more important type of pitting corrosion occurs with passive metals, such as stainless steel and aluminium, in specific environments, e.g., chloride containing solutions. A typical example of pitting corrosion of this type is shown in Fig. 5.3.1.

In this case we must distinguish *pit initiation* and *pit growth.*

Suppose that the metal originally is covered with a passive layer. This must break down locally before growth of a pit is possible. Pit initiation may have many different causes such as: mechanical damage, heterogeneities, local cold-working of the metal, deposits of dirt (see also section 5.4.), differences in composition of the environment. Once the passive layer has broken down an *active-passive-element* is formed. This has a very high potential difference of 0.5 to 1 Volt between the small active anode and the large, passive cathode. It then depends on the local circumstances whether the active spot will be repassivated or not. Fig. 5.3.2a shows the polarisation curves if the conditions remain unchanged. However, the composition of the solution in the pit may change drastically as shown schematically in Fig. 5.3.3.

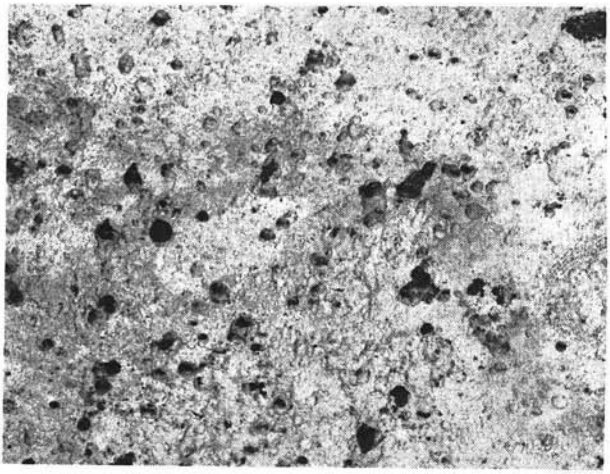


Figure 5.3.1. Pitting corrosion of stainless steel in hot seawater.

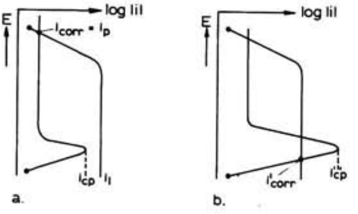


Figure 5.3.2. Schematic polarization curves during pitting corrosion
a. original situation;
b. after pit initiation with increased critical passivation current density i_{cp}' and corrosion current density i_{corr}' in the pit.

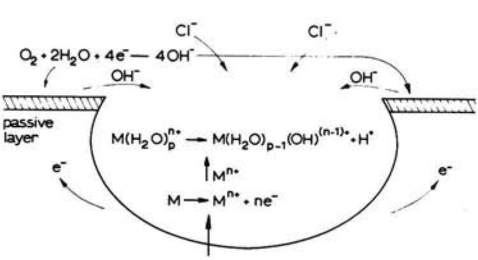


Figure 5.3.3. Schematic representation of corrosion pit with the different reactions.

One of these changes is an increased chloride ion concentration as a consequence of its contribution to the charge transport in the solution. Furthermore the pH in the pit in general decreases due to the hydrolysis of the dissolved metal ions, according to a reaction like:

$$Cr(H_2O)_6{}^{3+} \rightarrow [Cr\,(H_2O)_5(OH)]^{2+} + H^+$$

where trivalent chromium is taken as a specific example. These changes lead to the situation depicted in Fig. 5.3.2b. Both changes in the composition lead to a greatly increased passivation current density i_{cp}' making spontaneous repassivation impossible. In the pit the metal corrodes with the very large local current density i_{corr}'.

In practice it is of course the maximum pit depth which determines the useful life of a piece of equipment. Experimentally it has been found that pit depths show an approximately Gaussian distribution about the average. This means that the expected lifetime, at a given average pit depth, will be smaller when we have more pits or, under otherwise constant conditions, a larger total surface area. Another important consequence is that it is very dangerous to draw conclusions about the practical pitting behaviour of a metal from experiments on test pieces because these have a much smaller total surface area than the equipment itself.

Some methods which can be used to combat pitting corrosion are:

1. Increase of pH. This allows a larger contribution from the hydroxyl ions to the current resulting in both a higher pH ànd a lower chloride ion concentration in the pit. For metals such as aluminium which show amphoteric character, i.e., corroding in both acid and alkaline solutions (see Fig. 4.8.1) this method of course is only of limited applicability.
2. Cathodic protection. In the case of passive metals, such as aluminium, the potential in this case is not brought down into the region of immunity but only so far that stable passivity is obtained.
3. The use of alloys with special additions. For example molybdenum improves the pitting resistance of stainless steel. The critical passivation current density increases less with increasing chloride concentration and decreasing pH in molybdenum containing stainless steel.
4. Addition of passivators. It is important that sufficient passivator be added, otherwise the rate of pit growth may even be increased (see section 4.8).
5. Increasing the velocity of flow of the solution. This lessens the danger of pit initiation due to deposits, but more importantly the solution in the pit is mixed more completely with the rest of the solution so that the local concentration changes are smaller.
6. Lowering the temperature. For most metals there is a critical temperature, depending on the composition of the environment and the alloy, below which pitting corrosion does not occur. For stainless steels this critical temperature is raised with increasing molybdenum content.

5.4. CREVICE CORROSION AND DEPOSIT ATTACK

Local differences in composition of a solution cause potential differences on an immersed metal and thus accelerate corrosion. Of particular importance in this respect are differences in oxygen content commonly known as *differential aeration.*

In practice this occurs especially in narrow crevices and under deposits. When in the crevice the oxygen is consumed we obtain a situation for which the polarisation diagram of Fig. 5.4.1 applies. As such this does not lead to increased corrosion. As long as no other changes take place the current density i_{crev} in the crevice becomes at most equal to that outside the crevice i_ℓ. However, the conditions in the crevice do change in a way similar to that discussed in section 5.3 in pits. The pH in the crevice will decrease due to hydrolysis of the dissolved metal ions and the chloride ion concentration increases due to their contribution to the current flow. Furthermore the decreased oxygen content may make repassivation more difficult. Thus in particular for passive metals crevice corrosion can become very severe.

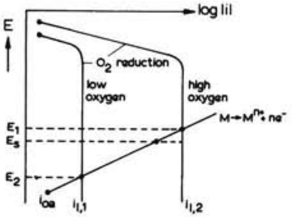


Figure 5.4.1. Polarization diagram for differential aeration.

A practical example of crevice corrosion is given in Fig. 5.4.2. This shows a stainless steel shaft running in a rubber bearing in which seawater, acting as 'lubricant', is supplied through triangular grooves running along the length of the bearing (see Fig. 5.4.2b). When the shaft is idle the oxygen concentration in the crevices between the rubber and the stainless steel will rapidly decrease below that in the seawater in the grooves. The differential aeration element formed in this way causes the crevice corrosion beside the grooves. Note that this attack occurs when the plant is idle, not when it is running. Moral!

Of course the most important method to combat this type of corrosion is to avoid crevices altogether either by closing them completely or by widening them so much that replenishment of the solution becomes possible. For some examples of this type of change of design see section 6.4. If narrow crevices are unavoidable increase of pH and decrease of the concentration of aggressive ions will decrease the severity of the attack.

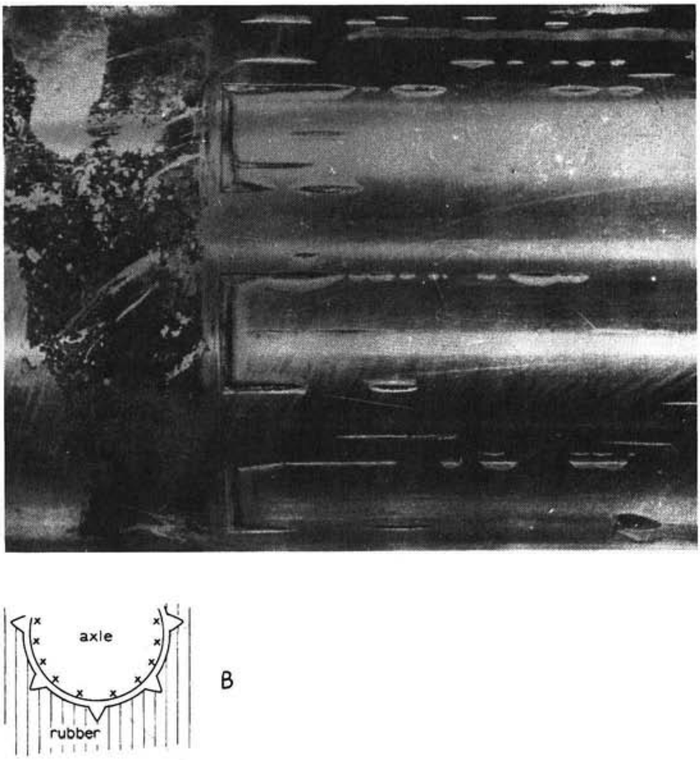


Figure 5.4.2. Crevice corrosion of stainless steel shaft in rubber bearing.
a. photograph of corroded shaft;
b. cross section of shaft in bearing (at the points marked x the attack occurs. The width of the crevice is exaggerated for greater clarity).

Another possibility is to use materials less susceptible to crevice corrosion. In marine environments and other chloride containing solutions monel and special stainless steels alloyed with molybdenum and with an increased nitrogen content are very resistant to crevice corrosion. When deposits are the cause of crevice corrosion increased flow of the liquid or cleaning by filtration or centrifuging can be effective ways to prevent it.

5.5. SELECTIVE DISSOLUTION

The corrosion of certain alloys occurs by selective dissolution of the least noble component of the alloy, leaving the more noble component as a porous residue. The most common example is the *dezincification* of brass which can occur in two forms. *Layer type* dezincification is uniform over the whole surface, *plug type* dezincification occurs in the form of conical pits filled with a porous copper residue as shown in Fig. 5.5.1. A cross section of a brass part with layer type dezincification is shown in Fig. 5.5.2.

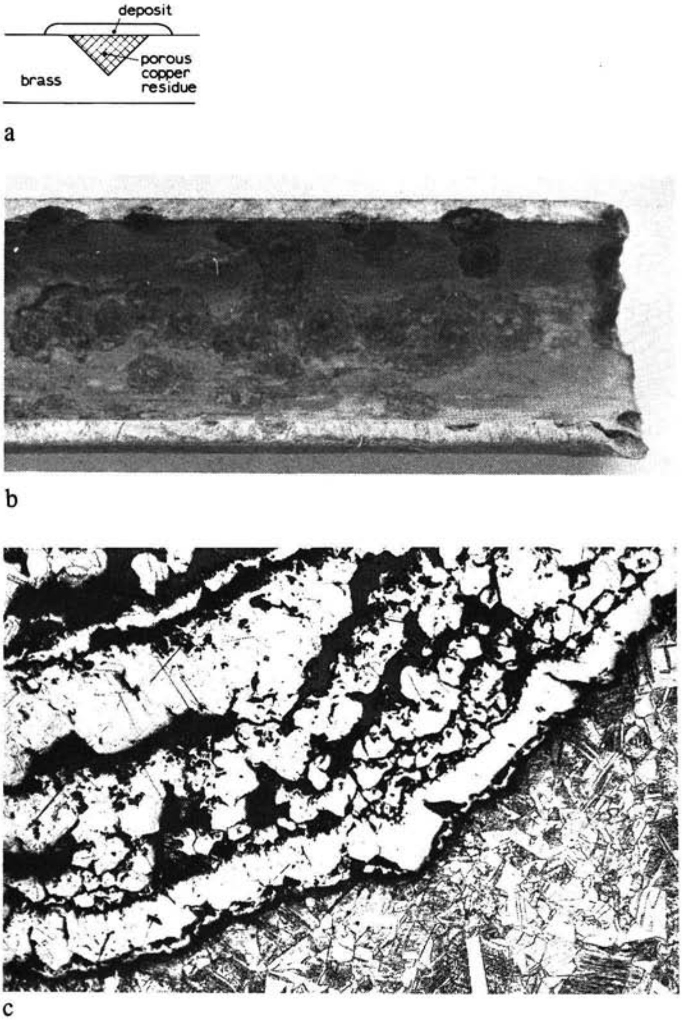


Figure 5.5.1. Plug type dezincification. a. schematic cross section; b. photograph of tube with plug type dezincification; c. photomicrograph of boundary between porous copper residue (upper left) and unattacked brass.

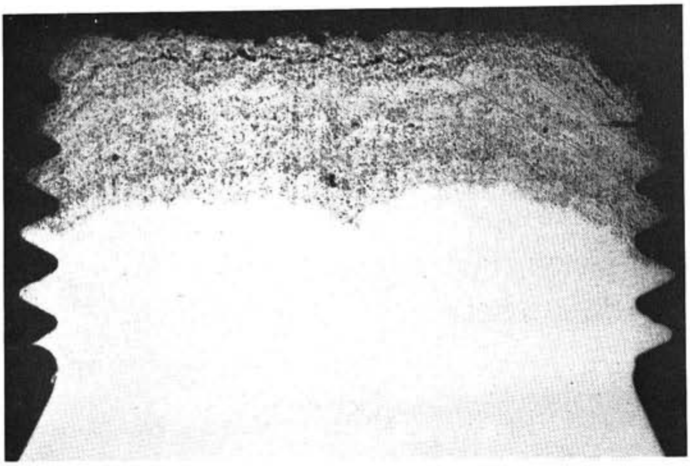


Figure 5.5.2. Layer type dezincification.

Two models have been proposed for this type of corrosion. In the first the less noble component dissolves out of the alloy, leaving the more noble one. In the second the alloy dissolves as a whole whereupon the more noble component is deposited upon the alloy which has a potential more negative than the reversible potential for the pure noble component (compare section 2.3).

The second explanation is supported by the observation that this type of corrosion nearly always occurs under deposits: there is then less renewal of the solution making redeposition of the more noble component more probable. These deposits may be dirt, scale formed from hard water, porous corrosion products, etc. Once the more noble component has been redeposited the whole process is accelerated because of the potential difference between deposit and unattacked alloy.

One possibility to control dezincification is to make the solution less aggressive by changing the pH and the chloride concentration. Addition of small amounts of tin or, even better, of arsenic to brass greatly improves the resistance to dezincification. Increase of liquid velocity can also be effective but is not always possible (central heating and water distribution systems). Finally softening of the water can also exert a favorable influence by preventing scale formation.

5.6. INTERCRYSTALLINE CORROSION

All metals as used in practice are *polycrystalline.* This means that they consist of a large number of small, usually randomly oriented, crystalline regions: the *crystallites* (or grains). In *intercrystalline* (or *intergranular*) corrosion only the narrow boundaries between these crystallites are attacked. The total weight loss is usually small but the crystallites lose their adhesion and the material desintegrates. The most important practical example of intercrystalline corrosion is that of the austenitic stainless steels. For a typical example see Fig. 5.6.1. Fig. 5.6.2. is a micrograph showing a cross-section of this type of corrosion.

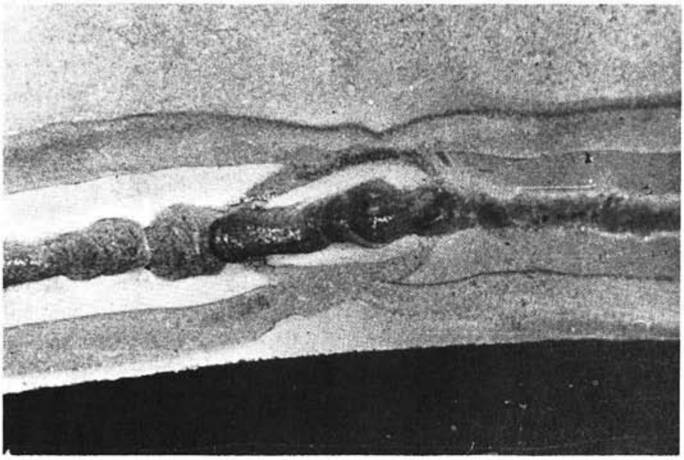


Figure 5.6.1. Intercrystalline corrosion alongside a weld in stainless steel.

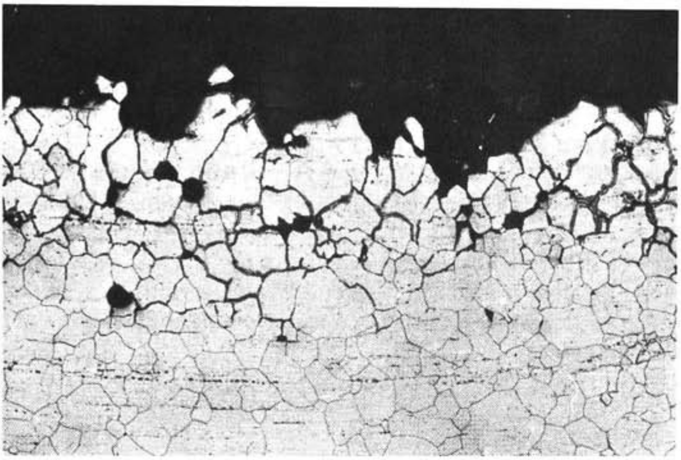


Figure 5.6.2. Microstructure of intercrystalline corrosion in stainless steel.

The cause of the intercrystalline corrosion of the austenitic stainless steels has been shown to be the precipitation of chromium carbides during heat treatment or welding on the grain boundaries according to the equation:

$$23Cr + 6C \rightarrow Cr_{23}C_6$$

This reaction occurs at an appreciable rate between about 600 and 750°C. The precipitation is preferentially on the grain boundaries because nucleation of a new phase is much easier at an interface than in the interior of a crystal. Fig. 5.6.3 shows two typical microstructures. The first is that of a purely austenitic structure obtained by heating to about 1050°C followed

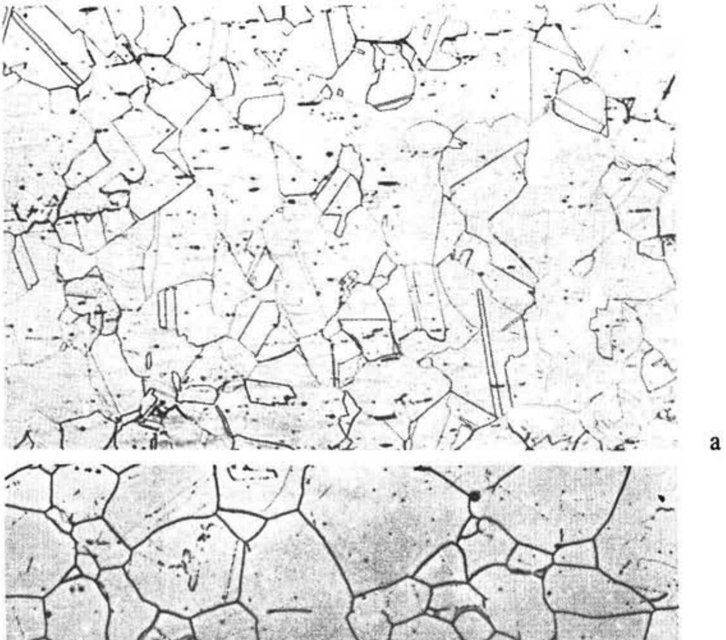


Figure 5.6.3. Microstructures of austenitic stainless steel: a. purely austenitic (step structure), b. with grain boundary precipitate (ditch structure).

by rapid quenching. Here only the grain surfaces are etched (step structure). The second is that of a specimen in which a grain boundary precipitate is present, due to heating for some time at 650°C, sometimes called *sensitizing*. Here only the grain boundaries are etched (ditch structure).

During the precipitation of the carbides both chromium and carbon have to be supplied from the bulk of the crystallites. Chromium in stainless steel has a very much lower diffusion coefficient then carbon. This causes a much larger concentration gradient of chromium and thus chromium depletion occurs in a narrow zone along the grain boundary as shown schematically in Fig. 5.6.4a. Thus as discussed in section 4.8., the critical passivation current density is much larger close to the grain boundary. As shown in the polarisation diagram of Fig. 5.6.4b this causes loss of passivity and fast corrosion along the grain boundaries in the case where the cathodic polarisation curve is given by the continuous line. From this figure it is also clear that not all environments give rise to intercrystalline corrosion. If the cathodic curve runs higher, such as the broken line in Fig. 5.6.4b, the material remains passive everywhere without any intercrystalline corrosion.

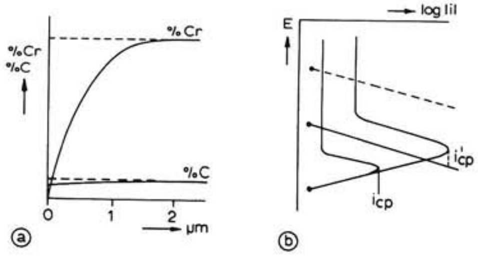


Figure 5.6.4.

- a. *Concentrations of chromium and carbon as a function of distance from the grain boundary;*
- b. *polarization diagram for sensitized stainless steel.*

This corrosion is often found (see Fig. 5.6.1) in the form of narrow regions at some distance from a weld and is thus sometimes also called *weld decay* (even though it is nòt the weld itself which is attacked). That region is attacked where the material spent a long enough time in the dangerous temperature range.

One way to combat this corrosion would be to reheat the material after welding to a temperature of about 1050°C (where all chromium carbides dissolve) followed by rapid quenching. This is obviously only possible for relatively small and not too complicated parts.

The two most important methods applied to prevent this type of corrosion are the use of *low-carbon* stainless steels with less than about 0.03% carbon and the use of *stabilized* stainless steels, i.e. with additions of titanium or niobium. In the first case the formation of carbides is slowed down so much that they are not formed during normal welding. In the second case very stable titanium or niobium carbides are formed so that the carbon is no longer available to form chromium carbides. Even in environments where intercrystalline corrosion as such is not a problem, for example seawater, the use of these steels may be necessary as pit initiation (see section 5.3) is sometimes much more rapid in the sensitized regions.

Some other materials such as nickel-chromium alloys of the type known as Hastelloy and certain aluminium-copper alloys may also show a similar type of corrosion. Here also precipitates formed on the grain boundaries have been shown to be responsible for the localized attack.

5.7. STRESS CORROSION CRACKING AND CORROSION FATIGUE

As the name implies stress corrosion cracking manifests itself in the form of cracks which are due to the combined action of tensile stresses and corrosion. These cracks can either be *transcrystalline*, see Fig. 5.7.1a, or *intercrystalline*, see Fig. 5.7.1b. In both cases the direction of the cracks is

Figure 5.7.1. Stress corrosion cracks; a. transcrystalline .

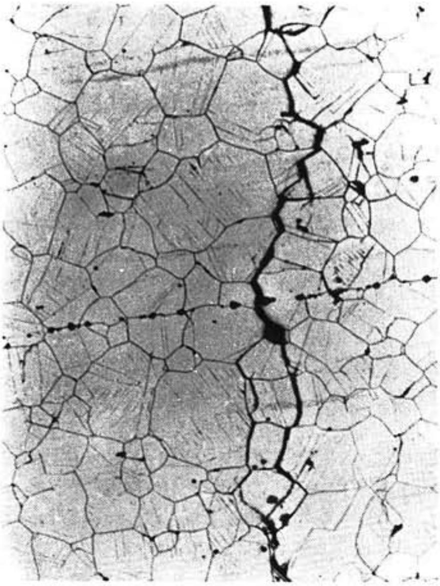


Figure 5.7.1. Stress corrosion cracks; b. intercrystalline.

approximately perpendicular to the tensile stress. Intercrystalline stress corrosion cracking is clearly different from ordinary intercrystalline corrosion described in section 5.6 (compare Fig. 5.6.2 and 5.7.1b).

Nearly all alloys are sensitive to stress corrosion cracking in a limited number of very specific environments. Some examples are: copper alloys in humid atmospheres containing ammonia or sulfur dioxide (intercrystalline), mild and low alloy steels in nitrates and concentrated alkalies (intercrystalline), austenitic stainless steels in hot chloride solutions (transcrystalline) and in steam contaminated with chlorides (trans- and intercrystalline), aluminium alloys in sea water (intercrystalline). For a more complete survey see Logan [1].

Corrosion fatigue is in a certain sense a special case of stress corrosion cracking. Here also it is the simultaneous action of stress, which is now cyclic as in ordinary fatigue, and corrosion which leads to failure. However, it occurs in a wider range of environments than stress corrosion cracking and it is nearly always transcrystalline.

In practice the transcrystalline stress corrosion cracking of austenitic stainless steel is of particular importance because nearly all natural waters contain chlorides. In general the sensitivity to cracking increases with increasing chloride concentration, tensile stress and temperature. Stress corrosion cracking in these steels is usually not observed at temperatures below 70°C.

In 42% magnesium chloride (a solution often used for testing purposes) complete cracking of 2 mm thick specimens of stainless steel type 304 occurs within half an hour to one hour at the boiling point, 154°C, at stresses of 20 to $30\text{x}10^7$ N.m^{-2}. In the same solution at 130°C, however, it takes 20 to 40 hours. The composition of the steel also has an important influence on time to failure as shown in Fig. 5.7.2 for the nickel content.

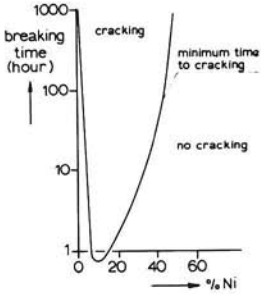


Figure 5.7.2. Sensitivity to stress corrosion cracking of stainless steel with 18 to 20% chromium in boiling 42% $MgCl_2$ as a function of nickel content.

In all cases of stress corrosion cracking, just as with pitting, most of the total time to failure is an initiation time during which no cracks are visible. The same type of variables, with of course the tensile stress added, which influence the initiation time of pits are of importance here. The cracking speed, once visible cracks have developed, is of the order of millimeters per hour. This is much slower than the rate of crack propagation in ordinary brittle fracture: usually from some hundreds to some thousands of meters per second. A similarity to brittle fracture is that the total deformation at failure is usually small. There is as yet no generally accepted theory for stress corrosion cracking, although it is certain that both mechanical failure and electrochemical dissolution are essential and that these two reinforce each other [2, 3].

The stresses responsible for this type of failure can be service stresses due to internal or external pressure or to the weight of the equipment and its contents, to unequal expansion upon heating etc. Residual stresses due to fabrication, either alone or in combination with service stresses, are an important cause of stress corrosion cracking.

A typical example of stress corrosion cracking of stainless steel type AISI 316 is shown in Fig. 5.7.3. This shows part of a tube from an evaporator in which a citric acid solution is evaporated in vacuum by heating the tubes on the outside with steam at 120°C. The temperature of the solution is limited to about 60–65°C in order to prevent decomposition of the citric acid. The final chloride concentration is 200 to 250 mg per liter. Contrary

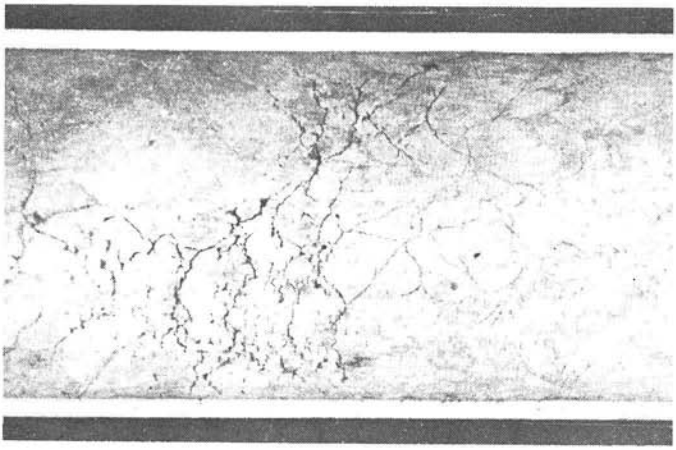


Figure 5.7.3. Stress corrosion cracking of a tube from a citric acid evaporator. Material: stainless steel type AISI 316.

to what is observed these circumstances would not be expected to lead to stress corrosion.

Upon removal of the tubes from the evaporator the inside surface was found to be covered with a thick porous scale (removed in Fig. 5.7.3). This consisted mainly of calcium sulphate with which the citric acid solution was saturated. This deposit furnished heat insulation so that the inside surface of the tube became much hotter than 70°C as shown by the presence of carbonaceous matter, due to citric acid decomposition, in the scale. The higher temperature made evaporation in the scale much faster while renewal of the solution was much less. This led to a greatly increased local chloride concentration, which was estimated from the chloride content of the deposit to be 100 to 200 grams per liter. Both the higher temperature and chloride concentration contributed to the occurrence of stress corrosion cracking. Preventing scale deposition by a higher velocity of the solution together with slight changes in the design of the evaporator provided a complete remedy.

There have been several cases of intercrystalline stress corrosion cracking of the lower ends of cables of suspension bridges. The cause of this was shown to be the presence of nitrates in rain, especially after thunderstorms. The rain collects at the lower ends of the cables and if drainage is incomplete evaporation leads to high local nitrate concentrations while tensile stresses are obviously present. Complete drainage of the rain water is necessary to prevent the stress corrosion.

Another case of intercrystalline stress corrosion is the so called 'season cracking' of brass. This was observed already at the end of the previous century in brass shells. This was shown to be due to a humid atmosphere containing ammonia (horse stables!) together with the high residual stresses caused by deep drawing. A stress relief heat treatment prevents this type of cracking.

Fig. 5.7.4 shows a wrongly laid weld where the high local stresses have caused highly accelerated stress corrosion cracking. Sometimes a stress relief heat treatment may be applied but is has to be noted that unequal cooling can again give rise to high internal stresses. With stainless steels stress relieving heat treatments may make the material susceptible to intercrystalline corrosion, depending on the temperature and time used.

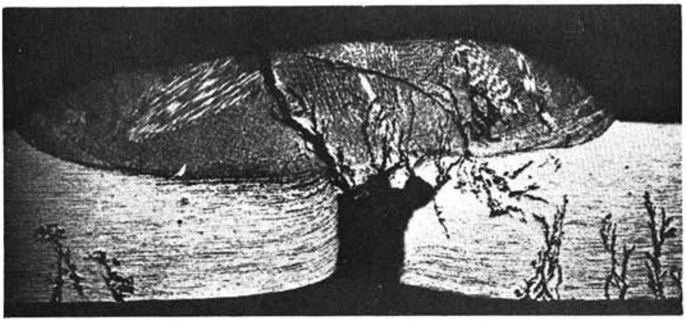


Figure 5.7.4. Stress corrosion cracking in and near wrongly laid weld in stainless steel after 600 hours in a hot chloride solution.

The main methods to control or prevent stress corrosion cracking and corrosion fatigue are:

1. Preventing high tensile stresses and in particular stress concentrations.
2. Removing aggressive components from the environment.
3. In some cases using cathodic protection, inhibitors or protective coatings.

If none of these methods can be used the only solution is the choice of a different material which is resistant against the given environment. For example copper alloys such as cupronickel can be chosen instead of stainless steels in hot seawater.

5.8. EROSION AND CAVITATION CORROSION; IMPINGEMENT ATTACK

When the simultaneous action of corrosion and erosion by a fast streaming liquid causes an unexpectedly heavy attack, which is much larger than that of the separate phenomena, we speak of *erosion-corrosion.* This is observed in particular at places where strong turbulence occurs such as at sharp bends, constrictions, inlets of narrow tubes, pump impellers, etc. The generally accepted explanation is that the erosive action destroys a protective layer causing direct contact between active metal and liquid. Two typical examples of erosion-corrosion are shown in Fig. 5.8.1 and 5.8.2.

Figure 5.8.1. Erosion corrosion in a bend.

Cavitation corrosion is caused by cavitation in the liquid close to the metal surface. This may be due to fast movement of the metal in a direction perpendicular to its surface or to the formation of a local vacuum in the liquid. In most cases it takes the form of closely spaced, sharply bordered pits. It is found in practice on ship's propellors, pump impellers and sometimes, as shown in Fig. 5.8.3, on the cooling water side of diesel engine cylinder liners.

Impingement attack is a form of pitting corrosion which is due to local destruction of a protective layer by air bubbles moving at high speed in a liquid, e.g., in condensor tubes. A similar type of attack is caused by a liquid jet impinging on a metal.

Some possible ways to prevent these types of corrosion are:

1. Changes in design to obtain lower liquid velocities or more 'streamlined' flow, e.g., by increasing the radius of bends (see also section 6.4).
2. Application of cathodic protection or inhibitors.
3. Filtering or centrifugating the solution to remove solid particles or air bubbles if these are the cause of the erosive effects.
4. Application of protective coatings. A particular example of this is the use of plastic inserts as shown in Fig. 5.8.4. These are frequently used in condensors and heat exchangers where erosion corrosion is often noted in the first few centimeters of the tubes due to the heavy turbulence close to the inlet. The insert must be so long that the liquid comes into contact with the metal after a laminar boundary layer has been established.

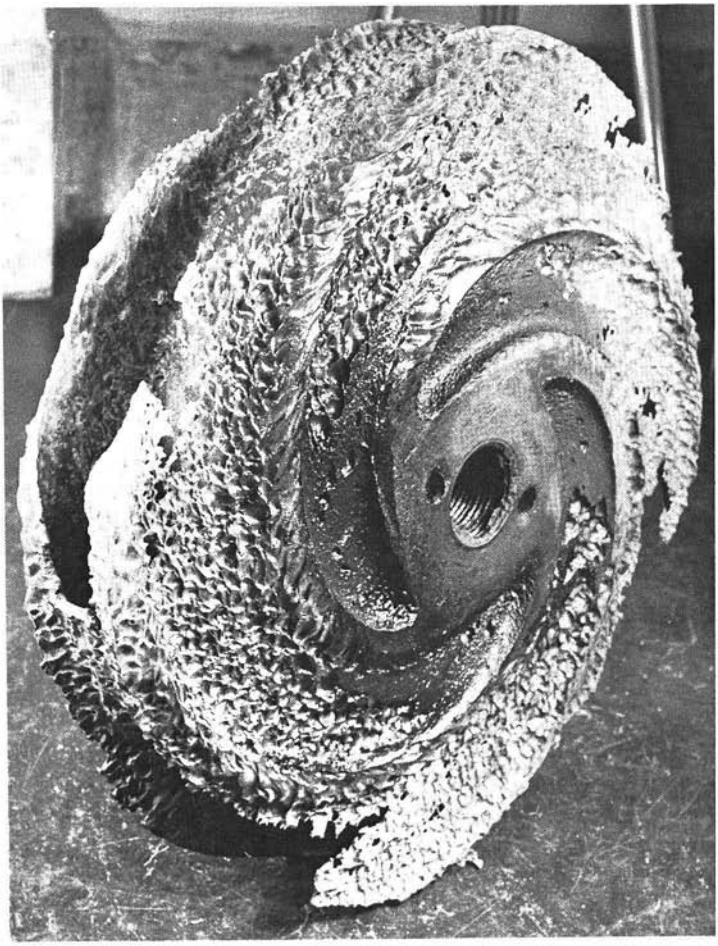


Figure 5.8.2. Erosion corrosion of grey cast iron pump impeller after a service life of less than a year in an alkaline permanganate solution containing solid manganese dioxide.

Figure 5.8.3. Cavitation corrosion in diesel engine cylinder liner.

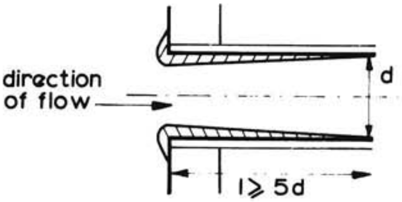


Figure 5.8.4. Plastic insert (hatched in the figure) at inlet end of tube.

5. Use of alternative materials with stronger protective films. In the example shown in Fig. 5.8.2 the grey cast iron was replaced by Ni-resist which gave a service life of more than 7 years under the same circumstances. Another example is the use of cupro-nickel instead of brass in condensors and seawater evaporators.

5.9.FRETTING CORROSION [4]

This type of attack is caused by the combined action of vibration and slip of metal surfaces and corrosion. A necessary requirement for fretting corrosion is repeated relative motion; it does not occur under continuous motion such as that of an axle in a bearing. Fretting corrosion, by causing destruction of metallic components and the formation of oxide debris, often leads to seizing and galling. Furthermore it may also cause fatigue failures due to excessive strains caused by the loosening of components and stress concentrations due to the sharp pits which are often formed.

It is thought to be caused by destruction of protective oxide layers on the interacting surfaces leading to fast oxidation of the bare spots and of the rubbed off metal particles. As a practical example Fig. 5.9.1 shows fretting corrosion of thrust rings mounted between the crank shaft of a diesel engine and the propeller shaft driven by it. An important cause of fretting corrosion in practice is the vibration of parts during shipment and it has been observed for example with axles in bearings, in ball and roller bearings, etc., which in normal service show continuous motion and thus no fretting corrosion.

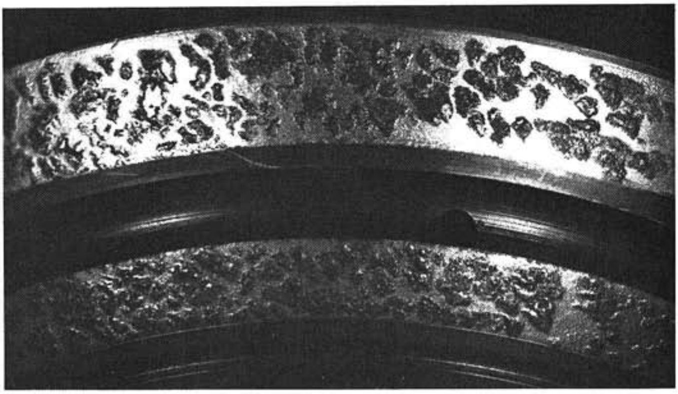


Figure 5.9.1. Fretting corrosion of thrust rings.

Some important ways to combat fretting corrosion are:

1. Lubrication with special oils having low viscosity and high tenacity and if possible containing inhibitors. This both reduces friction and excludes aggressive substances such as oxygen and moisture.
2. Phosphating the parts ('Parkerizing') and impregnating the porous phosphate layer with oil.
3. Using materials of different hardness for the two parts.
4. Using rubber or plastic gaskets. This reduces vibration and may exclude aggressive substances.

5.10. CONCLUDING REMARKS

In this chapter some of the most important forms of corrosion are discussed together with typical circumstances under which they are expected to occur and with the most common methods to prevent them. It will be clear that this review must be far from complete. For those who want to enquire more deeply into these and related topics more extensive treatments, where further references can be found, are listed in section 5.11.

5.11. REFERENCES

1. H.L. Logan, *The stress corrosion of metals*, New York, John Wiley (1966).
2. M.G. Fontana and N.D. Greene, *Corrosion Engineering,* New York, McGraw Hill (1967).
3. H.H. Uhlig, *Corrosion and Corrosion Control*, New York, John Wiley (1972).
4. R.B. Waterhouse, *Fretting Corrosion*, Oxford, Pergamon Press (1972).

6. Prevention and control of electrochemical corrosion

6.1. INTRODUCTION

The previous chapters have been primarily concerned with how electrochemical corrosion takes place. Both the visible manifestation and the more fundamental mechanism were discussed. Attention was also given to methods to prevent or control the different forms of corrosion. However, before one needs to apply this knowledge in a particular case, it is necessary to know whether corrosion will occur and to what extent. Therefore we will discuss in section 6.2 how to obtain and use corrosion data.

When looking back at the methods presented so far to prevent or control corrosion we note that these were nearly all of one of two types: *either the environment or the metal has to be changed.* Examples of the former are: change of pH, removal of oxygen or aggressive ions, addition of passivators, etc. Examples of the latter are: alloying to obtain spontaneous passivity, the use of a different metal, changing the potential of a metal in cathodic or anodic protection, etc.

A third general group of methods to combat corrosion, which was already mentioned above, is to *cover the metal surface with a protective coating,* thus separating the metal from the environment. These coatings can be of different types: metallic, inorganic or organic and they may be applied in different ways such as dipping, spraying, electrolytic deposition, etc. This subject will be discussed more fully in section 6.3.

Another important point, which was already mentioned, *is the need to give attention to proper design.* Some principles of design in relation to corrosion control will therefore be treated in section 6.4.

Both the corrosion itself and the methods used to combat it lead to increased costs. *It is of course desirable to find that solution of a corrosion problem which leads to the lowest overall costs.* Therefore some aspects of the economics of corrosion control are discussed in section 6.5.

6.2. OBTAINING AND USING CORROSION DATA

In order to judge whether corrosion is to be expected in a particular case and to apply the principles in the previous chapters numerical data are needed. Many experimental data obtained from laboratory experiments or practical experience have been published in tabulated form [1, 2, 3, 4, 5]. Nearly all these tables give the corrosion environments in alphabetical order and for each of these the known behaviour of a number of materials. Sometimes the dependences on temperature and concentration are also given.

It is necessary to be very careful in using these tables as many of the data have been obtained from laboratory experiments under conditions which may not be representative of the practical situation. For example small amounts of impurities may have a large influence on the corrosion rate. In laboratory experiments most solutions are prepared using distilled water. Natural waters, however, may have chloride concentrations of 500 to 2000 mg per liter or even higher. For metals which show pitting corrosion or stress corrosion cracking in chloride solutions, such as stainless steel and aluminium, this may lead to very unpleasant surprises.

Furthermore the tables usually only give data about uniform corrosion, often in very general terms such as: resistant (< 0.1 mm. year^{-1}), fairly resistant (0.1 to 0.5 mm.year^{-1}), not resistant (> 0.5 mm.year^{-1}). Secondary factors are not mentioned, only the influence on lifetime of the attack being considered. Thus, even though from this point of view an attack of 0.5 mm.year^{-1} would be perfeclty admissible in certain cases, this might at the same time cause an unacceptable contamination of the product in contact with this material (see problems 2 and 3 of section 1.6).

In most cases the only *reliable* conclusion which can be drawn from this type of table is that certain materials cannot be used if additional protection is not applied. About the applicability of the different methods of corrosion protection the tables do not as a rule give any indication.

This means that the data from these tables must nearly always be supplemented with other data, either from previous experience or from special experiments. The latter are preferably performed under the actual conditions envisaged. A great problem is that, due to the limited sensitivity of most direct methods such as weight loss or change in thickness, these experiments take a very long time. Indirect methods, either accelerated tests or electrochemical measurements, give results faster but the uncertainties due to the long extrapolation times increase. Moreover accelerated tests often give misleading results because of the artificial circumstances. In this respect electrochemical measurements are certainly preferable.

Corrosion testing is an activity with many dangers and pit-falls and all results have to be examined extremely critically before they are applied. We will therefore not go deeper into this somewhat specialized subject. For those who need more detail several books [6, 7, 8, 9] can be recommended for further study.

6.3. PROTECTIVE COATINGS

There are several different types of coating which are used to protect metals against corrosion. We distinguish metallic, inorganic non-metallic and organic coatings. These can of course be further divided in a number of subtypes and also according to their method of application.

With all coatings and methods of application an essential point, which is unfortunately often neglected, is the *surface preparation.* The state of the surface before coating determines to a high degree the adhesion and impermeability of the layer. Moreover, if moisture is trapped under a coating when it is applied, corrosion can continue. The voluminous corrosion products then cause premature failure of the coating by pushing it off.

There exist many different methods of surface preparation. The choice thereof of course depends on the metal, on the coating and on the type of surface contamination. To remove rust or mill scale from steel, for example, it is possible to use abrasive blasting, wire brushing, grinding, scraping and pickling in strong acid. For large surfaces, such as ship's hulls, flame cleaning is often used: the surface is heated with a blowtorch so that organic substances burn off and rust and mill scale are loosened by different expansion from that of the metal. In nearly all cases this has to be combined with scraping or wire brushing.

Oil and grease can be removed by cleaning with organic solvents, either in liquid form or as a vapour. In some cases alkaline cleaning solutions are also used. Usually different forms of surface preparation must be combined, e.g., degreasing followed by pickling.

After cleaning it is important that the coating is applied as soon as possible. Any protective layers are usually also removed by cleaning so that a highly active surface remains which is very sensitive to (atmospheric) corrosion. Touching cleaned surfaces with bare hands may be very dangerous as aggressive substances present on the skin can initiate an attack which completely undermines the coating.

Some idea of the importance of coatings as a method of preventing corrosion can be obtained from the data in appendix 14. Some of the most important aspects of the different types of coating and their application will now be discussed separately.

6.3.1. Metallic coatings

The use of metallic coatings is in effect equivalent to choosing another metal for the surface of a part to be protected. Coatings are applied in those cases where it would be either too expensive or impossible, e.g., for mechanical reasons, to use the protecting metal in massive form. It is essential to distinguish the case of the underlying metal being more noble or less noble than the coating. In the latter case pores or damaged spots in the coating cause accelerated attack of the underlying metal: there are then small anodic areas in contact with a very large cathode. The reverse does not lead to excessive corrosion: there the underlying metal is cathodically protected and the attack is spread over the large anodic area.

A possible way to classify metallic coatings is by the method of application. The first of these is *cladding* which consists of hot rolling a thin sheet of a corrosion resistant metal onto a thick plate of a less resistant metal. In the chemical and petrochemical industries, for example, much use is made of mild steel clad with stainless steel or monel. Another example is the cladding of aluminium alloys, such as duralumin, which contain copper, with a layer of pure aluminium to prevent pitting or stress corrosion cracking in chloride containing environments. This method is only useful if the total thickness of the combined sheet is above a certain minimum, which for stainless steel on mild steel is about 6–8 mm. Otherwise the extra costs of fabrication are greater than the saving from using the cheaper backing metal instead of a complete thickness of the more corrosion resistant material.

Somewhat similar are *duplex tubes,* which consist of two thin walled tubes rolled together. These are used mainly in heat exchangers where no single metal can be found to resist both media. Examples are brass-mild steel, copper-stainless steel, etc. Against their obvious advantages stands their high price.

A second method of application is *hot dipping* which is mainly limited to low melting metals such as zinc, tin and aluminium on mild steel. As the name implies the coating is applied by immersing the steel in the molten metal with which it is to be covered.

Yet another method is *electroplating,* i.e., the metal coating is deposited electrolytically upon the substrate. Nearly all metals can be electrodeposited, for example, Cu, Ni, Zn, Cr, Cd, Ag, Au, Pb, Sn, etc. Tinplate is now usually made by electroplating instead of hot dipping, mainly because a thinner, smoother and more uniform coating is obtained in this way. After electroplating it is then heat treated to improve the bond between the tin and the steel.

Finally we may mention *metallizing* or *flame spraying.* This is performed by feeding metal wire or powder through a flame where it is dispersed as molten droplets and blown onto the surface to be coated. It is as a rule limited to relatively low melting metals such as zinc and aluminium. By using a plasma jet high melting metals can also be sprayed. An important use of this method is in applying coatings locally on already assembled constructions. These coatings are always porous so that they are usually combined with an organic coating sealing the pores. Another application is flame spraying platinum on titanium sheet for making anodes.

The major use of metallic coatings is in protecting mild steel. Those most extensively applied are tin, zinc, cadmium, copper and nickel. Tinplate, for example is used mainly for cans for foodstuffs and beverages, although for the latter aluminium cans are increasingly being used.

Zinc and cadmium are used in particular as protection against atmospheric corrosion. Cadmium is more expensive than zinc but stays bright longer and is mainly used for small parts such as nuts and bolts. Zinc, in the form of hot-dip galvanized coatings, is used very extensively to protect small and large constructions such as cranes, parts for automobiles, pylons, bridge railings, reinforcing bars, steel joists and columns for buildings, traffic signs, etc. One characteristic example is shown in Fig. 6.3.1. Some typical values for the corrosion rates to be expected under different circumstances in comparison with mild steel are given in Table 6.3.1.

Figure 6.3.1. Typical example of application of hot-dip galvanizing: nearly 10.000 tons of hot-dip galvanized steel have been used for the enormous halls of the Aalsmeer flower market.

Table 6.3.1. Typical corrosion rates (in μm per year) of mild steel and hot-dip galvanized steel in different atmospheres.

atmosphere	mild steel	hot-dip galvanized
rural	10–50	1–1.5
urban	15–60	1–5
marine	15–100	1.5–10
industrial town	50–100	5–8
industrial	100–200	6–20

Nickel is used extensively in industry to protect essential parts. Often the part is first copper plated then the nickel is plated on top of the copper. The main reason for this is that nickel is very expensive. Common thickness ratios are from 1:1 to 3:1 of Cu:Ni. Nickel turns yellow to brown in many atmospheres and is therefore often covered with a thin layer (0.1 to 0.3 μm) of chromium for decorative purposes. The quality of these coatings is determined mainly by the number of pores per unit area because both nickel and copper are noble with respect to mild steel. Under otherwise constant conditions the number of pores decreases with increasing thickness so that the latter is often used as the quality criterion. Typical requirements are: for interior use (steel furniture) a total thickness of at least 10 μm, for outside use (parts of motorcars, etc.) 40 to 60 μm, for aggressive industrial circumstances 100–300 μm.

6.3.2. Inorganic non-metallic coatings

The main types of these are *glass* and *enamel* and *conversion coatings.* Glass and enamel are usually silicates and are applied by firing at high temperatures. The principal advantages of these are their high resistance to nearly all chemicals (excluding fluorides), their smoothness and non porosity making them easy to clean, their hardness and their ability to withstand high temperatures (sterilizing!). These properties explain their widespread use in the food and drug industries, in medical applications and in the household. Their most important disadvantage is their brittleness while repair, once they are damaged, is in most cases impossible.

Conversion coatings are formed by (electro)chemical reaction of the metal to form of insoluble compounds with good adhesion. An example is the phosphating of steel which is performed by immersion in or spraying with phosphoric acid. Sometimes compounds such as manganese, iron or zinc phosphate are added to the acid, and these are built into the phosphate layer formed. This coating, due to its low solubility, gives temporary protection against atmospheric corrosion and provides a good basis for painting. It can also be impregnated with oil and may then help to prevent fretting corrosion and wear.

Anodizing, in particular of aluminium, is also widely used. An oxide layer is then formed on the metal by making it sufficiently anodic, usually in acid solutions. The layer as formed is porous and can be impregnated with dyes. Afterwards it has to be *sealed* by treatment with hot water or steam. This layer is in principle identical to the normal passive layer so that the main advantage is longer life, primarily due to the greater abrasion resistance. In environments where aluminium shows heavy corrosion anodizing does not present a real solution.

6.3.3. Organic coatings

The most widely used organic coating is *paint.* This consists of a solid, the *pigment,* which is suspended in an organic liquid, the *binder.* The paint is applied in liquid form on the metal by spraying, brushing or immersion. A modern development is *electrophoretic paint application.* The paint is then present as charged droplets forming an emulsion in a conducting solution. By applying an electric potential to the object to be painted the droplets are attracted to it and form a continuous film.

After application the paint film must harden for which there are three mechanisms. The first is a reaction of the binder, in this case usually linseed oil, with oxygen from the air. This means that the paint must be sufficiently permeable for air. The second is the evaporation of a solvent, which again necessitates a certain permeability of the paint. The third is a modern development in which the hardening is obtained by a polymerization reaction, usually under the influence of a catalyst added shortly before application ('two component paint').

There are so many different types of paint, all with their specific properties and fields of application, that it is not possible to go into any detail here. We shall therefore only discuss some general aspects.

Table 6.3.2. Effect of surface preparation upon durability of paint (Sheffield, England).

Surface treatment	2 coats red lead paint + 2 coats iron oxide paint	2 coats red lead paint
undamaged mill scale	8.2 years	3.0 years
weathered and wire brushed	2.3	1.2
pickled	9.5	4.6
sand blasted	10.4	6.3

In Table 6.3.2 some data are collected showing the importance of the surface preparation. From this it is clear that it is better to use a cheaper paint system on a well prepared surface than the reverse. The surface preparation and paint application together in most cases determine the total costs. Derusting, for example, contributes in general 30 to 50% to the total. The application of the paint is usually three to five times as expensive as the paint itself. Using a cheap paint is therefore as a rule false economy (see also Appendix 14). Important cost saving aspects of better paints are the longer time before repainting is necessary and the smaller amount of derusting.

The same reasons often lead to the application of so-called *duplex systems,* in particular the combination of hot-dip galvanizing and painting.

Even though the initial investment is higher the greatly decreased maintenance costs may make this cheaper in the long run. The savings are greater in more aggressive atmospheres and with longer desired lifetime (see also section 6.5).

Painting is probably, on a tonnage basis of protected metal, the most used method of protection iron against atmospheric corrosion. In most cases one does not use a single paint coat but several, sometimes of different compositions. The use of several coats lessens the probability for pinholes to penetrate down to the metal and usually makes drying more rapid and complete. For the first coat, the so-called *primer,* paints are used with good wettability and adhesion. Moreover they contain as a rule special pigments such as red lead (or lead plumbate, $Pb_3O_4 = Pb(II)_2Pb(IV)O_4$), zinc chromate ($ZnCrO_4$) or metallic zinc. If the paint is damaged the first two dissolve in any moisture present and act as passivators, zinc provides cathodic protection. This means that less rust is formed in the damaged spots reducing maintenance costs.

Sometimes the primer is already applied to sheets directly after rolling and one then speaks of a *shop-primer.* In building outdoor structures such as ship's hulls, large tanks, etc. this greatly reduces rusting during the building period. Consequently less derusting is necessary before application of the top coat and costs are reduced. The pigments in top coats are often chosen on the basis of colour although other factors, such as abrasion resistance, may also be of importance.

For continuously submerged structures, such as harbour installations and ships special paints are used, often together with cathodic protection. Because the electrolyte becomes more alkaline in the neighbourhood of a cathode this means that the paint then has to be alkali-resistant. An extra point is that often a top coat has to be an *anti-fouling paint,* to prevent or at least diminish the deposition and growth of marine organisms on the surface.

For underground pipelines and tanks much thicker coatings of asphalts or bituminous paints, often together with a cloth wrapping for reinforcement, are applied. There also cathodic protection is often used too, in order to protect any bare spots or pinholes.

Paints can not be used when the environment is such that it rapidly attacks the uncoated metal. A tank for hydrochloric acid, for example, will not be made from steel and painted because any small damaged spot or pinhole will lead to extremely rapid, local penetration. In such cases a plastic lining is sometimes used made from materials like rubber, neoprene, polyvinylidenechloride (Saran), polytetrafluorethylene (Teflon), etc. The cost of these materials and of their application, however, is usually so high that they are only used when no other alternative is available.

6.3.4. Temporary corrosion preventives

Very often fabricated parts or complete constructions such as engines have to be transported or stored before they are put into use. In particular machined surfaces which are essential for proper operation, such as axles, bearings, screwthreads, must not corrode during transport or storage.

One requirement is that the temporary corrosion preventive must be easy to remove when the part is put into use. All temporary corrosion preventives are organic compounds and they are often removed by washing with a suitable solvent. In some cases no special action is necessary because certain of the temporary corrosion preventives dissolve in lubricating oil. These can for example be used in internal combustion engines which can then be put into use without any special measures after storage or transport.

Temporary corrosion preventives show a wide range of consistencies. On one hand there are relatively thin oils which are brushed or sprayed on the part to be protected. Greaselike corrosion preventives are also sometimes applied directly, but are more often sprayed or brushed on in dissolved form after which the solvent evaporates. Finally there are relatively hard, waxy solid corrosion preventives which are usually applied by immersion in the molten compound.

Several of these compounds are used for protection of cars, for example, the underside and the interior of doors and box girders of the frame. These can give a very efficient protection against corrosion but it is essential that the treatment is repeated periodically as these compounds do not furnish permanent protection.

In the application of temporary corrosion preventives the surface preparation is usually not as critical as in the application of permanent coatings. One reason is that usually only machined surfaces are protected in this way, so that rust or mill scale will not be present. However, cleaning and drying the surface usually gives a better and longer lasting protection.

In many cases parts which are protected by temporary corrosion preventives are also packaged. An important function of the packaging is to prevent damage to the preventive and to exclude moisture. But care should be taken that porous packaging materials, such as paper, do not become saturated with water because this can lead to serious corrosion.

A special group of temporary corrosion preventives, which are usually combined with the packaging material, are the *vapour phase inhibitors.* These are volatile compounds, with which paper can be impregnated and which protect the packaged metal parts. Because of their slow rate of evaporation and low vapour pressure these compounds should only be used in small closed spaces.

A more detailed description of properties and uses of these temporary corrosion preventives is given in British Standard 1133. This also discusses the requirements for different applications and the testing of these compounds.

6.4. DESIGNING AGAINST CORROSION

Protection of equipment should begin at the drawing-board [10]. In chapter 5 several cases were cited where corrosion could be controlled or prevented by changing the design of the equipment considered. In nearly all cases where, according to the Hoar report (Chapter 1, ref. [2]), considerable savings are possible a recurring recommendation is that more attention should be paid to proper design (see Appendix 1). Without exaggeration it may be stated that many corrosion costs can be eliminated at the design stage.

One way to reach this objective is for the design engineer to have a reasonable knowledge of corrosion, which is one of the main reasons for writing this book! Another way is closer cooperation between design engineer, materials engineer *and* corrosion engineer *at the design stage.* All too often the corrosion engineer or the engineer in charge of surface treatment is called in after the design has been settled to give advice about proper paint, surface treatment, etc. Very often it is then too late to choose optimum solutions which would have been possible if they had been consulted earlier. In this section some practical examples and general rules are given to show the importance of proper design in corrosion prevention and control.

One of the most important general rules is that all crevices, where dirt and moisture can accumulate and which are not accessible for maintenance, such as (re)painting, must be avoided. In this respect the construction of Fig. 6.4.1a is very poor. In the upper space dirt and water can accumulate and drainage is impossible. Moreover painting of this and of the lower space is rather difficult. It is much better to use a single inverted T-section as shown in Fig. 6.4.1b. It would be even more favourable if the horizontal faces could be made sloping in order to make complete drainage easier.

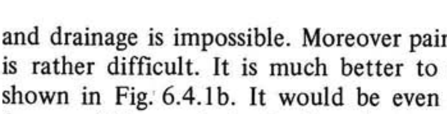
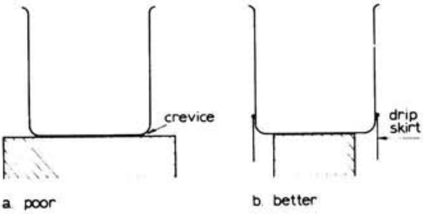


Figure 6.4.1. Avoiding crevices.

Frequently tanks have to be supported for example on a concrete foundation or steel supporting beams. Examples are storage tanks, pickling- or electroplating baths, etc. The design of Fig. 6.4.2a is very poor because

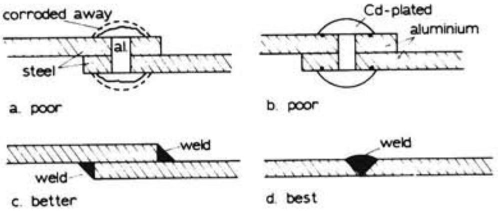


a. poor b. better

Figure 6.4.2. Support of tanks.

spilled liquid can seep into the crevice between tank bottom and support where cleaning is difficult and heavy corrosion of the tank bottom or the support may result. Much better is the design of Fig. 6.4.2b where the drip skirt prevents the penetration of spilled liquid and also of condensation and rain between support and tank.

Connections often present corrosion problems of which some examples are shown in Fig. 6.4.3. In case a., where the rivet is less noble than the metals which it connects, heavy corrosion of the rivets occurs due to the extremely unfavourable anode to cathode surface area ratio. In Fig. 6.4.3b this mistake has been avoided but insufficient tightening has resulted in crevice corrosion. A welded construction, as shown in Fig. 6.4.3c, is better provided the crevice is completely closed at both ends and no corrosive agents have been trapped in the crevice during welding. Therefore the best solution is butt welding as shown in Fig. 6.4.3d.



a. poor b. poor c. better d. best

Figure 6.4.3. Different types of connection.

An important general principle is that the design of tanks, reaction vessels and constructions which are intermittently wetted (rain), etc. should always allow complete drainage of liquids. This not only shortens the time of exposure to the corrosive medium, but it also prevents evaporation causing concentrated solutions which usually lead to increased attack. Deposits under which crevice corrosion may occur, can in this way be avoided or more easily removed. Some examples of poor and good designs are shown in Fig. 6.4.4.

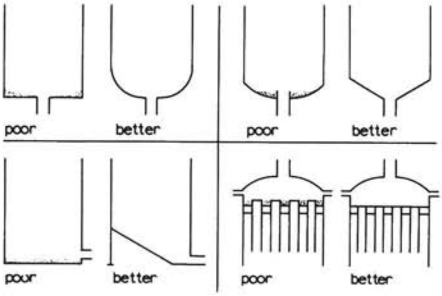


Figure 6.4.4. Drainage of liquids for corrosion prevention.

Similarly in those cases where coatings are applied by or during immersion in a liquid (electroplating, hot dip galvanizing, electrophoretic painting, etc.) the design should allow complete wetting, i.e., no air pockets, and complete drainage. This is illustrated in Fig. 6.4.5 and of course also applies to pickling, degreasing, etc.

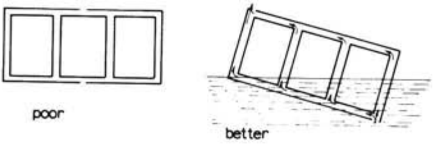


Figure 6.4.5. Location of holes in constructions which have to be immersed in a liquid for surface preparation or coating.

It is of great importance to avoid local differences in concentration or temperature. For example the addition of concentrated acid to a reaction mixture should be done in such a way, by suitable positioning of the inlet, that there is no direct contact with the wall before thorough mixing has taken place. This is shown schematically in Fig. 6.4.6.

Similarly heaters should be situated well away from vessel walls in order to avoid overheating, or even local boiling leading to increased concentrations by evaporation. This is shown schematically in Fig. 6.4.7.

The importance of the relative positioning of parts also applies to complete installations or factories. For example a line of stacks emitting possibly corrosive gases should preferably be set perpendicular and not parallel to the prevailing wind direction.

Corrosion may also be caused by local cooling of hot gases leading to

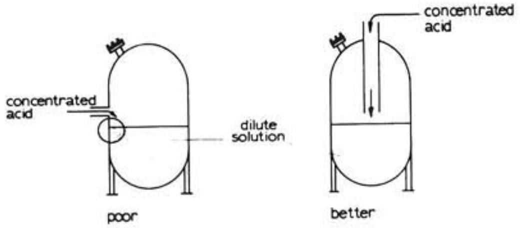


Figure 6.4.6. Positioning of acid inlet.

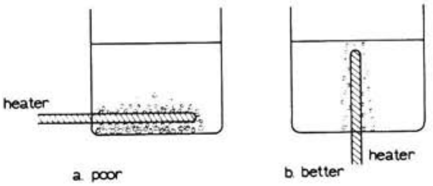


Figure 6.4.7. Positioning of heater.

condensation of corrosive substances. In the construction shown on the left in Fig. 6.4.8 the support acts as a cooling fin and leads to local corrosion due to this phenomenon. Insulating the support, as shown on the right in Fig. 6.4.8 makes it possible to avoid this sort of failure by diminishing the temperature difference.

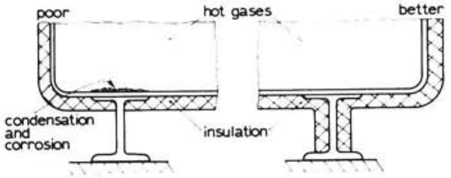


Figure 6.4.8. Prevention of condensate corrosion by proper insulation.

Unneccessarily high and in particular local stresses should be avoided in order to minimize the risk for stress corrosion cracking. Often overlooked in this respect are the stresses around the supports of vessels or tanks. These should be distributed over as large an area as possible. One way to do this is to weld these supports to a wide ring completely surrounding the vessel instead of directly to the vessel wall.

As already mentioned in section 5.8 places were excessive turbulence occurs should be avoided in order to decrease the risk of erosion- and cavitation corrosion and impingement attack. For example bends should not be too sharp and constrictions not too sudden (see Fig. 6.4.9a). Unexpected failures due to erosion corrosion may also be caused near flange connections

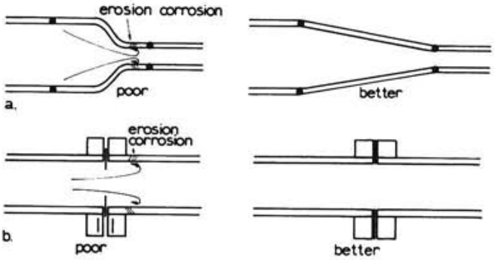


Figure 6.4.9. Prevention of erosion corrosion by avoiding local excessive turbulence: a. constriction in tube; b. packing ring between flanges.

by jointing rings of the wrong size as shown in Fig. 6.4.9b. The hole in the ring should be as close as possible in size to that of the tubes. If it is too small, as shown here, there is the risk of erosion corrosion, if it is too large there is a danger for crevice corrosion. Attention should also be given to liquid flow velocities. If these are too low settling of dirt can lead to corrosion by differential aeration. Too high velocities of course increase the risk for erosion corrosion.

It is of extreme importance in fabrication that the design is really followed. There have been many examples where the design was correct but mistakes, mostly through lack of insight into the 'why' of the design, were made in fabrication. One example is given in Fig. 6.4.10 where the design was correct but the protuding weld bead around the outlet tube prevented complete drainage.

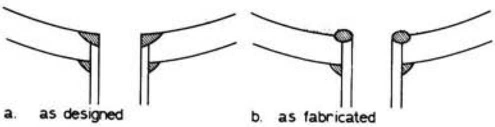


Figure 6.4.10. Correct design and incorrect fabrication.

Summarizing it can be said that the most essential rules to be followed in design when corrosion risks are to be minimized are:

1. avoid all heterogeneities such as local differences in concentration or temperature, local stresses or turbulence, crevices where aggressive substances can accumulate, etc.
2. all parts needing maintenance or replacement (if corrosion cannot be avoided completely) must be easily accessible.

3. all parts which must be coated must be easily accessible for coating application.
4. fabrication must conform to the design.

6.5. THE ECONOMICS OF CORROSION CONTROL

Corrosion unfortunately practically always leads to increased costs. This is either due to the cost of maintenance, repair or replacement of corroded parts or to the cost of measures to prevent or control corrosion. No magical way can be found making it possible to use mild steel or cast iron, which are often the cheapest available materials, while at the same time preventing their corrosion at no extra cost. This means that it is important to find a way to minimize these costs by comparing the economic merit of different methods of preventing or controlling corrosion, such as using more corrosion resistant material, applying protective coatings, adding a passivator to the environment, etc.

There are different ways to perform this type of economic comparison. We limit ourselves here to the method based upon the calculation of the *net present value.* For a more extensive treatment and a comparison with other methods we have to refer to the literature [12, 13]. The basic principle of this method is that £1 received (or paid) n years from now represents a present value $P_{n,r}$ given by

$$P_{n,r} = \pounds(1+r)^{-n} \qquad (6.5.1).$$

Here r is the 'cost of capital', i.e., the rate of interest corrected for the effect of inflation. A second measure of present value needed for our purpose is the present value $A_{n,r}$ of £1 received or paid each year for a period of n years and this is given by

$$A_{n,r} = (1+r)^{-1} + (1+r)^{-2} + \ldots\ldots + (1+r)^{-n} =$$

$$= \frac{1-(1+r)^{-n}}{r} \qquad (6.5.2).$$

Tables of $P_{n,r}$ and $A_{n,r}$ have been published [12, 13] and a short abstract is given in Appendix 16.

In comparing investments I_i with different service lives n_i the equivalent cost $C_{eq,i}$ per year is then calculated to be

$$C_{eq,i} = I_i/A_{n_i,r} \qquad (6.5.3)$$

where it is assumed that the equipment will be replaced after n_i years.

In many cases there will also be operating costs $C_{op,i}$ per year which have to be added to the equivalent cost. Furthermore there often are maintenance costs M_i arising every m_i years. These give rise to equivalent costs $M_{eq,i}$ given by

$$M_{eq,i} = M_i/A_{m_i,r} \tag{6.5.4}$$

The total cost per year $C_{tot,i}$ will thus be given by the equation:

$$C_{tot,i} = C_{eq,i} + C_{op,i} + M_{eq,i} \tag{6.5.5}$$

In cases where maintenance costs do not recur at regular intervals it is easier to calculate their net present values and add these to the initial cost for the different alternatives and we then obtain:

$$(NPV)_i = I_i + \sum_{j=1}^{n} P_{m_j,r} \cdot M_j \tag{6.5.6}$$

We will not go deeper into refinements of these equations involving investment grants, different taxation of investments and operating costs, scrap value at end of service life, etc.

Evidently thàt investment will be preferable which gives the lowest total yearly cost C_{tot} or the lowest present value NPV. We shall now discuss the application of these principles to some typical cases of corrosion control.

The first example is concerned with the choice of material for a tube and shell heat exchanger in a case where experience has shown that a mild steel heat exchanger failed after about 3 years, while its purchase price was £ 2.000. As alternative materials the stainless steels 304 (18%Cr, 8% Ni) and 316 (18% Cr, 10% Ni, 1.5% Mo) were proposed. These were expected to have lives of about 10 years while the purchase prices were £ 6.500 for 304 and £ 7.500 for 316. The transport and installation costs were £ 750 and did not depend on the material of the heat exchanger. In Table 6.5.1 the data relevant to this case have been collected.

It is seen that for low cost capital the 304 heat exchanger gives the lowest costs, at high cost capital the mild steel one. It is also clear that the relative merits should be calculated on the basis of purchase price and transport and installation costs and not on the former alone. Finally we see that type 316 will only be chosen if its life is longer than 10 years. Calculation shows that at $r = 6\%$ this has to be at least 12.5 years and at $r = 12\%$ at least 17 years before 316 becomes the cheapest alternative.

As the second example we consider an oil cooler used in a power generating station. A brackish cooling water is available which, as experience has shown, causes heavy corrosion of mild and of stainless steel within 2 to 3 years. However, aluminium bronze and cupronickel are sufficiently resistant against this type of water. It is only necessary to remove deposits by regular cleaning at a cost of about £ 40 per year. Fresh water, against which mild and stainless steel are sufficiently resistant, is also available. In the quantities needed in this cooler this leads to extra costs amounting to £ 450 per year. In Table 6.5.2. the costs of the different alternatives are shown.

It is seen that the much lower operating costs make the copper alloy cooler more economical under all conditions given here even though its purchase price is highest. We also see that this advantage decreases with increasing cost of capital. For the case considered here mild steel becomes preferable, even using fresh water for cooling, if r is larger than about 13%.

Table 6.5.1. Equivalent yearly cost of tube and shell heat exchangers made of different materials

Material	1 Initial cost (£)	2 Transport & Install. cost (£)	n (year)	Equivalent cost (£/year)			
				r=6% based on		r=12% based on	
				1	1+2	1	1+2
mild steel	2000	750	3	750	1030	830	1145
304	6500	750	10	880	985	1150	1285
316	7500	750	10	1020	1120	1325	1460

Table 6.5.2. Yearly costs of oil cooler

Material	Initial cost (£)	n (year)	C_{op} (£/y)	r=6%		r=12%	
				C_{eq} (£/y)	C_{tot} (£/y)	C_{eq} (£/y)	C_{tot} (£/y)
mild steel	1250	10	450	170	620	220	670
304	3000	10	450	410	860	530	980
Al. bronze + Cupronickel	3500	10	40	475	515	620	660

As discussed in section 6.3 corrosion protection is often achieved by painting. Sometimes this is combined with hot-dip galvanizing and we then speak of a *duplex system.* The initial costs are then higher, but the maintenance costs lower because repainting can be less frequent. We now compare the following systems:

a. *paint:* grit blasting followed by application of one coat of a zinc dust primer and two coats of an epoxy paint: cost of application £ 3.80 per m^2;
b. *duplex:* hot dip galvanizing followed by application of one coat epoxy paint: cost of application £ 4.70 per m^2.

In a moderately aggressive industrial or urban atmosphere repainting is necessary every 8 years for a. and every 12 years for b. in both cases costing £ 1.50 per m^2. In a very aggressive industrial atmosphere repainting is necessary every 5 years for a. and 8 years for b. also at a price of £ 1.50 per m^2. Assuming a total surface area to be protected of 10.000 m^2 this leads to the costs given in Table 6.5.3.

It is seen that under moderately aggressive circumstances a duplex system is only economically advantageous for installations with a long life and when the cost of capital is not too high. In a very aggressive atmosphere a duplex system is already advantageous for shorter lives and for long times also at a high cost of capital.

Of course these examples are only some of the very many which could have been given. In reference [14] some more cases are discussed along similar lines.

Table 6.5.3. Net present value of the cost of two protective systems under different circumstances.

System	Initial cost £	Cost of Repainting £	Aggressivity of atmosphere	Repainting period (year)	Total life (year)	Net present value of total cost (£) r=6%	r=12%
a. paint	38000	15000	moderate	8	20	53320	46510
				8	35	59350	47900
			severe	5	20	63850	54080
				5	35	74634	57020
b. duplex	47000	15000	moderate	12	20	54460	50850
				12	35	58170	51840
			severe	8	20	62320	55500
				8	35	68350	56890

The examples presented above show some of the most important aspects in the economic assessment of corrosion prevention and control: the necessity to balance initial cost against maintenance and operating costs and the importance of the cost of capital. The relative merits of the cases discussed here may well change when they are judged under different conditions of cost of capital and cost of labour and aggressivity of the environment.

Each case has to be judged on its own with all relevant circumstances taken into account (see chapter 8). There is certainly no universal answer to the question which is the best, in the sense of the cheapest method of corrosion prevention.

6.6. REFERENCES

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7. High temperature oxidation and its control

7.1. INTRODUCTION

In modern industrial practice high temperatures are increasingly being used. There are several reasons for this. The first is the well-known fact that the thermodynamic efficiency of heat engines increases with a larger difference between highest and lowest temperature. Increased maximum temperature thus leads to a saving of energy. This is applied, for example, in gas turbines, steam boilers and steam turbines and internal combustion engines. A second reason is that many chemical reactions have sufficiently high rates or are possible only at high temperatures. This has led to a large increase in high temperature processes in the chemical industry. A third reason is that the materials to be used for structures or containers at these high temperatures have to be fabricated or heat treated at even higher temperatures.

In the majority of these cases metals are in contact with a gaseous environment at high temperatures and the composition of the gas determines the type of reaction that will occur. In most cases the gas will contain oxygen causing *oxidation* of the metal. In the cracking of sulphur containing crude oils or in the combustion of sulphur containing fuels *sulphidation* will take place. If the environment contains chloride compounds, e.g., in the combustion gases of refuse incinerators where polyvinylchloride or similar plastics are present in the refuse, metal chlorides will be formed.

It is clear that the normal electrochemical type of corrosion, which was discussed in the previous chapters, cannot take place under these conditions, because the gases considered are not electrical conductors. Usually solid reaction products are formed; it is only in rare cases that the corrosion products are volatile or liquid. The presence of solid corrosion products on the surface may exert a strong influence on the kinetics of the corrosion, just as in passivation.

We will limit ourselves in this chapter to a discussion of high-temperature oxidation of metals because, on a tonnage basis of materials subject to high temperature corrosion, this is the most important type.

In section 2.2 we already discussed the thermodynamics of the reaction between oxygen and a metal. For nearly all metals which are used in practice the reaction

$$mM + \frac{n}{2}O_2 \rightarrow M_mO_n \qquad (7.1.1).$$

is spontaneous to the right at practically important temperatures and pressures. Nearly the only exceptions are Au which does not form an oxide at room temperature, Ag_2O (dissociates above 200°C) and HgO (dissociates above 270°C).

The same is true for the reaction of many metals with steam. For example for the reaction:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \qquad (7.1.2)$$

it can be calculated from the thermodynamic data of Appendix 2 that the equilibrium ratio p_{H_2}/p_{H_2O} at about 375°C is nearly 10. Thus, if this reaction were in thermodynamic equilibrium, a steel superheater would produce more hydrogen than steam! The experimental ratio p_{H_2}/p_{H_2O} is under 10^{-6} due to a kinetic barrier and is sometimes measured continuously as a check on whether serious corrosion takes place.

From this it follows that the suitability of metals to be used at high temperature under oxidizing conditions wholly depends on the kinetics of the oxidation.

7.2. KINETIC EQUATIONS FOR HIGH TEMPERATURE OXIDATION

From a practical point of view the two most important types of high temperature oxidation are described by the *parabolic* and by the *linear* rate equations. These are illustrated in Fig. 7.2.1.

Parabolic oxidation is found when a impervious adherent oxide layer is formed. The rate equation in this case has the form

$$(\Delta x)^2 = k_p t \qquad (7.2.1)$$

where Δx can be the weight gain during oxidation, the thickness of the oxide layer, or the weight loss of the metal after removal of the oxide, which are all proportional. A typical example of such an oxide layer is shown in Fig. 7.2.2. Because the rate, i.e., $d(\Delta x)/dt$, diminishes with time this is often called *protective kinetics.*

Linear oxidation is found when the oxide does not form an impervious layer or does not adhere to the metal. Oxidation then proceeds unhindered and the rate equation reads:

$$\Delta x = k_{\ell} t \qquad (7.2.2)$$

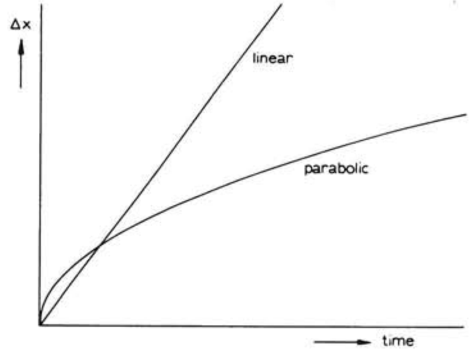

Figure 7.2.1. Linear and parabolic oxidation (Δx can be weight loss after removal of oxide, weight gain when oxide adheres to metal or thickness of oxide layer).

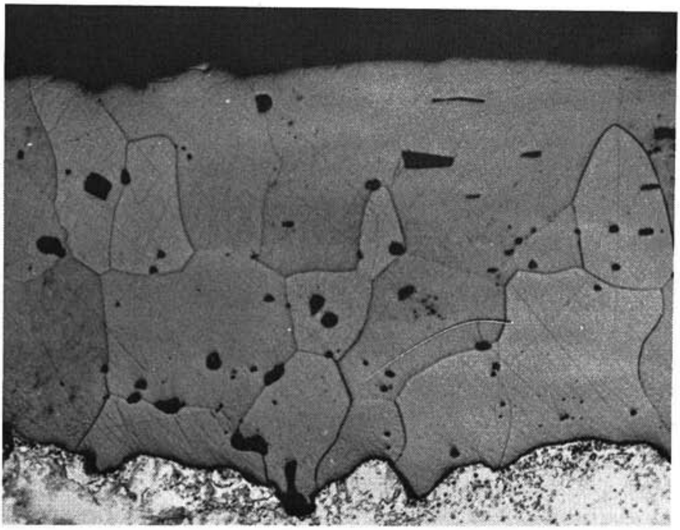

Figure 7.2.2. Microphotograph of a protective oxide layer on nickel (oxidized in air for 350 hrs at 1200°C, thickness of oxide 200μm).

The most important questions to be answered when control of high temperature oxidation is desired are:

a. when is parabolic oxidation to be expected,
b. what is the magnitude of the parabolic rate constant k_p.

The answers to these questions will be discussed in the subsequent sections of this chapter.

(Several other rate equations have been observed such as those for cubic and for logarithmic oxidation. For a discussion of these we refer to the literature [1, 2]).

7.3. PARABOLIC OXIDATION

As stated above parabolic oxidation is observed when an impervious and adherent oxide layer is formed on a metal. That oxidation nevertheless continues, albeit at a diminishing rate, is due to diffusion processes in the oxide. For this diffusion process two extreme mechanisms can be distinguished.

a. An atom of metal M, which forms the oxide MO, gives off two electrons to the oxide with formation of an M^{2+}-ion. Both the metal ions and the electrons then migrate through the oxide to the oxide gas interface. The electrons are taken up by oxygen with formation of O^{2-}-ions. Together with the M^{2+}-ion these then cause the growth of the oxide. In this case the oxide layer is growing on the *outside* and this is shown schematically in Fig. 7.3.1a.

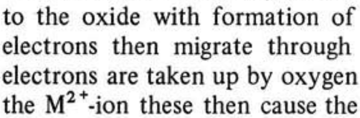

Figure 7.3.1. Processes taking place during high temperature oxidation: a. with diffusion of metal ions; b. with diffusion of oxygen ions.

b. An atom of the metal again gives off two electrons to the oxide with formation of an M^{2+}-ion. In this case only the electrons migrate to the oxide-gas interface where they again combine with oxygen to form O^{2-}-ions. These then migrate back to the metal oxide interface and together with the M^{2+}-ions form oxide. Here the growth occurs on the *inside* and this is shown schematically in Fig. 7.3.1b.

Whether or not a closed oxide layer is formed depends both on the mechanism ànd on the so-called *Pilling-Bedworth ratio* (PB):

$$\mathrm{PB} = \frac{\text{volume of oxide } M_mO_n}{\text{volume of metal oxidized}} = \frac{\mathrm{MW} \times d_m}{m \times \mathrm{AW} \times d_{ox}} \qquad (7.3.1)$$

with: MW = molecular mass of oxide, AW = atomic mass of metal, d_m = density of metal, d_{ox} = density of oxide.

If $PB < 1$ the oxide layer is not able to cover the metal completely and will be porous. This is the case for the alkali- and alkaline-earth metals and for some lanthanides. These metals accordingly nearly all show linear oxidation.

If $PB = 1$ a closed oxide layer can be formed without any internal stresses but this case is extremely rare. For most metals $PB > 1$, which means that in principle a closed oxide layer can be formed although in general this oxide layer will be under internal compressive stress. If the oxidation mechanism a. is followed these stresses are mainly limited to the outer layer and can in general be relieved easily. Then parabolic oxidation will occur. Metals which show this type of behavior are for example nickel ($PB_{NiO} = 1.52$), iron ($PB_{FeO} = 1.77$) and copper ($PB_{Cu_2O} = 1.68$). However, if mechanism b. is followed large stresses build up in the interior of the oxide layer, which are in general not easily relieved. The oxide layer will then crack off (*spalling*) and this can lead to accelerating or *break-away* oxidation. Examples of metals showing this type of behavior are zirconium ($PB_{ZrO_2} = 1.53$) and titanium ($PB_{TiO_2} = 1.95$). In this case an initial period of parabolic oxidation is followed by linear oxidation. In some cases of this type the oxidation resistance increases with increasing temperature. This is explained by an increasing plasticity of the oxide at higher temperatures which makes stress relief easier and cracking is delayed.

7.4. RATE OF PARABOLIC OXIDATION

Of course it is not sufficient to know only that parabolic oxidation occurs in a particular case. It is also necessary to know the rate at which it occurs and how this rate can be influenced. The generally accepted theory for this was first proposed by Wagner around 1930. One particular case will be discussed in this section as an example showing the main points of importance. The basic idea is that in all crystalline solids *defects* are present, i.e., deviations from the ideal crystal structure. The first type of defect is a *metal ion vacancy*, i.e., a place where a metal ion, which would be present in a perfect crystal, is missing. Similarly there may be *anion vacancies.* Furthermore there may be *electron holes*, i.e., ions which have lost an electron, such as when an Fe^{3+}-ion is present on a place which would be occupied by an Fe^{2+}-ion in the ideal crystal. Similarly there may be *free electrons.* (For a more complete discussion and description of defects see Appendix 15).

An important point is that there must be always such combinations of defects that the crystal as a whole remains electrically neutral. Thus when metal ion vacancies are present in an oxide, leading to a deficit of positive charge, these must be accompanied by an equivalent number of positively charged defects, such as electron holes. This particular combination of defects is found in oxides like FeO, CoO, NiO and Cu_2O. For the vacancy concentration, C_{vac}, it can be deduced (see Appendix 15) that:

$$C_{vac} = K' p_{O_2}{}^{1/n} \tag{7.4.1}$$

with n = 6 for FeO, CoO, NiO and n = 8 for Cu_2O and where K' is a constant.

As was discussed in section 2.2 for a metal in equilibrium with its oxide the equilibrium pressure of oxygen p_{O_2} (equil) is usually extremely small. At the oxide metal interface the oxygen pressure may be assumed to be equal to this equilibrium pressure as long as the oxidation is not too rapid. As the oxygen pressure on the outside will nearly always be much larger than this equilibrium pressure equation (7.4.1) predicts that a vacancy concentration gradient will be set up in the oxide layer. This means that the vacancies will diffuse through the oxide, which is equivalent to a flux of metal ions in the opposite direction. According to Fick's first law the vacancy diffusion rate will be proportional to this gradient, but this is also proportional to the rate of oxidation. When the conditions sketched in Fig. 7.4.1 apply we then find:

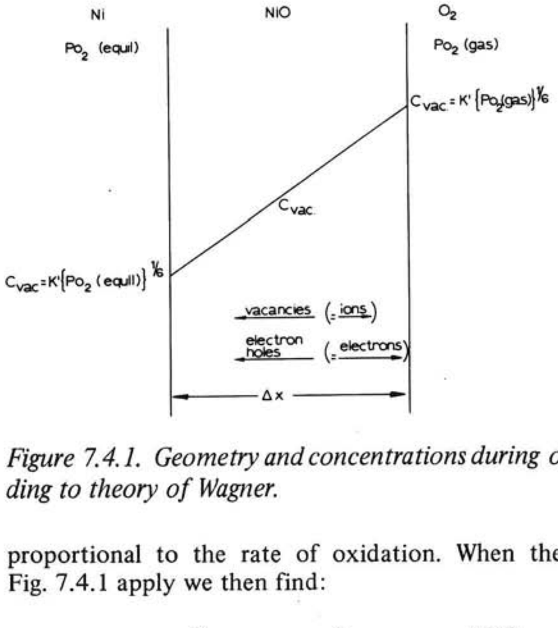

Figure 7.4.1. Geometry and concentrations during oxidation of nickel according to theory of Wagner.

$$\frac{d\Delta x}{dt} = AD \cdot \frac{C_{vac,outs} - C_{vac,\,ins}}{\Delta x} \simeq \frac{ADC_{vac,outs}}{\Delta x} \tag{7.4.2}$$

Here Δx = thickness of oxide, A = proportionality constant, D = diffusion coefficient, $C_{vac,outs}$ = vacancy concentration at gas oxide interface,

$C_{vac,ins}$ = vacancy concentration at oxide-metal interface. The second form of equation (7.4.2) is usually a good approximation because as a rule p_{O_2} (equil) $\ll p_{O_2}$ (gas).

By integrating equation (7.4.2) and putting $\Delta x = 0$ at $t = 0$ we at once obtain the parabolic rate equation:

$$(\Delta x)^2 = 2AD.C_{vac,outs}.t \tag{7.4.3}$$

where the second form of equation (7.4.2) has been used. Comparison with equation (7.2.1) shows that

$$k_p = 2ADC_{vac,\, outs} = 2ADK' p_{O_2}{}^{1/n} \tag{7.4.4}$$

where in the second form equation (7.4.1) has been used.

An important consequence of this result is that the parabolic rate constant diminishes with decreasing partial pressure of the oxygen in the atmosphere. But we also see that this decrease is much less than proportional. Both K', which in effect is an equilibrium constant, and D increase exponentially with increasing temperature. From equation (7.4.4) we thus see that this will also be the case for the oxidation rate.

Quite similar considerations and conclusions apply in the case of oxides with other types of defects although of course the details of the derivations differ. We will not go deeper into this but refer the reader interested in these cases to Appendix 15 and to the literature [1, 2].

With this theory it is also possible to explain the influence of alloying elements on the oxidation rate. For example if some chromium is added to nickel this enters the oxide as Cr^{3+}-ions. In order to preserve electrical neutrality the concentration of nickel vacancies increases and that of the electron holes decreases. This means that the vacancy concentration increases above the value given by equation (7.4.1) and thus leads to a corresponding increase in the parabolic rate constant. The data collected in Table 7.4.1 show that this is in agreement with experiment for a range of low chromium contents in the alloy.

Table 7.4.1. Parabolic rate constants (in $g^2.cm^{-4}.min^{-1}$) for nickel alloys at 1000°C

wt % Cr	k_p	atmosphere	k_p
0	$3.8\text{x}10^{-10}$	O_2	$2.5\text{x}10^{-10}$
0.3	$15\text{x}10^{-10}$	O_2+Li_2O	$5.8\text{x}10^{-11}$
1.0	$28\text{x}10^{-10}$		
3.0	$36\text{x}10^{-10}$		
10.0	$5\text{x}10^{-10}$		

If Li^+-ions are taken up in the oxide, which is possible by performing the oxidation in the presence of gaseous Li_2O, the reverse happens as is also shown in Table 7.4.1.

At higher chromium contents this theory breaks down because then another type of oxide is formed. This happens because chromium has a much greater affinity for oxygen than nickel (see Appendix 6) and preferential oxidation of chromium occurs at higher chromium concentrations. The chromium concentration in the oxide is much higher than in the alloy and instead of a NiO-type oxide an oxide of the $NiCr_2O_4$-type is formed. The diffusion in this oxide is much slower which explains the decrease in oxidation rate above chromium contents of about 5 to 6%

7.5. PREVENTION AND CONTROL OF HIGH TEMPERATURE OXIDATION

As was already indicated in section 7.4 one way to decrease the rate of high temperature oxidation is to decrease the oxygen partial pressure. But to obtain a reduction in rate of one order of magnitude the oxygen pressure, as indicated in equation (7.4.4) must be lowered by four to eight orders of magnitude (see section 7.8, problem 2).

In furnace installations a lowering of oxygen pressure in the combustion gases can in some cases be achieved by controlling the combustion process so that stoichiometric amounts of fuel and oxygen are used. The combustion gases are then practically oxygen free leading to diminished oxidation. In practice this can be achieved only with liquid or gaseous fuels because with solid fuels combustion generally is uneven. This leads both to inefficient use of fuel and residual oxygen in the combustion gases.

Furthermore, as was stated in section 7.1 (see also problem 9 of section - 2.11), oxidation may also be caused by gases other than oxygen. The most important of these are steam and carbon dioxide. The occurrence of oxidation of course depends on the metal and on the circumstances such as temperature and partial pressure of the gas.

Heat treatment of fabricated parts is often done in controlled atmospheres to prevent oxidation. Examples of such atmospheres are nitrogen with 5% hydrogen, cracked ammonia or argon. Furnace brazing of metals like stainless steel or titanium is performed in high vacuum. As this is not sufficient to remove any oxide layers already present on the surface, which prevent wetting by the solder, fluxes are also used. At ordinary oxygen pressure reoxidation is so rapid, however, that brazing is not possible. In a sufficiently high vacuum the oxidation rate becomes so low that wetting is faster than reoxidation.

Obviously it is impossible in these two cases to combat the high temperature oxidation by choosing a more resistant material: this choice is dictated by other requirements. However, for parts or constructions which must be used continuously at high temperatures it is of course possible to choose materials which are more resistant to high temperature oxidation. As shown in section 7.4 (see also Appendix 15) the oxidation resistance of a metal may be improved by the addition of suitable alloying elements. These can have one of two effects: they may either diminish diffusion in the oxide or cause the formation of a different, more protective oxide. In fact the latter phenomenon is used in the majority of cases. Typical examples are chromium, aluminium and silicon in iron, chromium and aluminium in nickel, aluminium in copper, etc.

Table 7.5.1 gives the maximum service temperature of a number of alloys commonly used at high temperatures in oxidizing atmospheres.

Table 7.5.1. Maximum temperature of use of different alloys without excessive oxidation (metal loss about 0.1 $mm.year^{-1}$*)*

Alloy	Typical tradename	Maximum service temperature
mild steel		500–550°
iron with 1%Cr, 0.5%Mo		600°
iron with 4–6%Cr		650°
iron with 9%Cr		750°
iron with 13%Cr		750–850°
iron with 17%Cr		850–900°
iron with 18%Cr, 8%Ni		900°
iron with 27%Cr		1050–1100°
iron with 25%Cr, 20% Ni		1150°
iron with 25%Cr, 1%Y		1350°
iron with 30%Cr, 5%Al, 0.5%Si	megapyr	1300°
iron with 24%Cr, 5.5%Al, 2%Co	kanthal A	1300°
nickel		900–950°
nickel with 20%Cr	nichrome 20	1100°
nickel with 16%Cr, 7%Fe	inconel	1050°
nickel with 10%Cr	chromel P	1100°
nickel with 2%Al, 2%Mn, 1%Si	alumel	1100°
platinum with 10%Rh		1400°

It is also possible to prevent high temperature oxidation by applying protective coatings. However, these are now limited to metallic and inorganic coatings. An example of the former is the *aluminizing* of steel. This is performed by covering the steel with a thin layer of aluminium and subsequently giving this a heat treatment to form a surface layer of iron-aluminium intermetallic compounds. These have much higher melting points than aluminium (about 650°C) in combination with a high oxidation resistance.

As non-metallic coatings special enamels and paints based on a silicate can be used. This is a rather specialized field, also in connection with other requirements such as thermal shock resistance, mechanical strength, etc., so that general rules are not easily given.

Finally here too the design is very important. High temperature oxidation resistance depends on the presence of an impervious oxide layer. If this is locally damaged or weakened, oxidation will be accelerated. Local differences in temperature, for example, may lead to thermal stresses high enough to cause cracks in the oxide. An example for this is shown in Fig. 7.5.1. This concerns superheater tubes which fitted rather closely in steel sheets. These sheets acted as heating ribs causing the tube wall locally to have a much higher temperature than expected on the basis of the steam temperature. This in itself already leads to accelerated oxidation. But the temperature differences also caused cracking of the oxide layer which led to linear oxidation kinetics and the very early failure after only a few months.

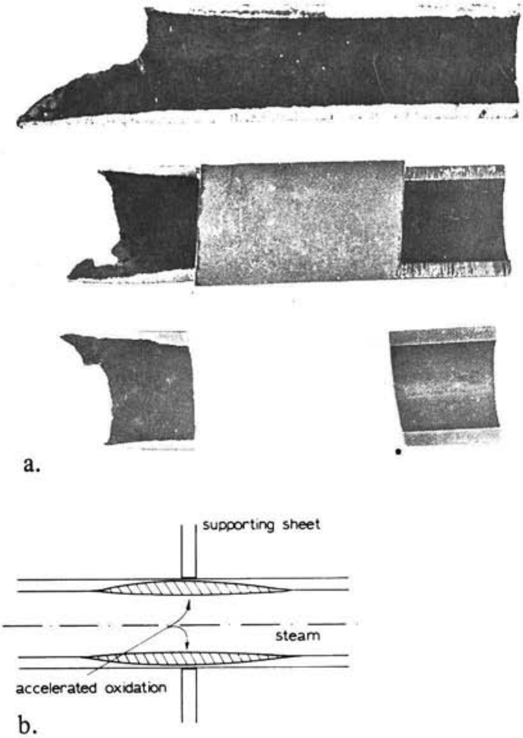

Figure 7.5.1. Locally accelerated oxidation of superheater tube: a. photograph of tubes after failure; b. Sketch of construction.

Finally it is necessary to stress again that oxidation resistance is *always* due to the presence of an impervious, protective oxide layer. Anything which may cause (local) removal, damage or weakening of this layer, such as mechanical damage, sudden large temperature changes (thermal shock), large local temperature differences, etc. thus has to be avoided.

No high temperature material is better than its oxide skin.

7.6. DEW POINT CORROSION

A special type of corrosion which in certain respects is intermediate between electrochemical corrosion and high temperature oxidation is *dew point corrosion.* One example of this was already mentioned in section 6.4 (see Fig. 6.4.8). It occurs when hot gases, in most cases combustion products, are cooled so much that condensation starts to occur.

In particular when sulphur dioxide or sulphur trioxide are present, for example with sulphur containing fuels, the dew point may be as high as 150–200°C. The acid condensates formed in these cases are highly aggressive and cause heavy corrosion of mild steel.

One of the most important methods to prevent this type of corrosion of course is to keep the temperature everywhere above the dew point. A typical case is illustrated in Fig. 7.6.1 which shows the original and the improved design of a silencer for a diesel-locomotive. To improve sound damping the original design was double walled with a perforated steel sheet as inner wall. Between the inner and outer sheets a layer of glass wool was used for extra damping of sound. However, this also acted as thermal insu-

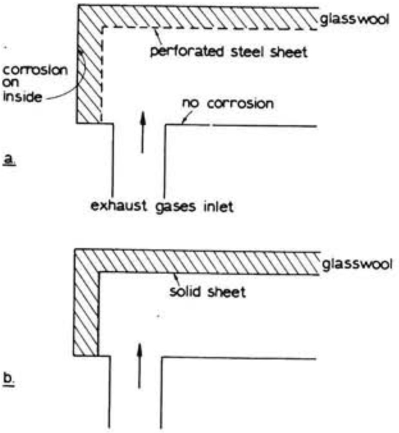

Figure 7.6.1. Sketch of cross section of part of a silencer of a diesel locomotive: a. original design; b. improved design.

lator so that the outer sheet became so cool that condensation and heavy corrosion occurred from the inside. By using a full sheet as inner wall penetration of the combustion gases was prevented in the improved design and the corrosion was completely prevented.

A second method to prevent or at least diminish this type of corrosion is the use of fuels which form no aggressive substances on combustion.

If neither of these methods can be applied it is necessary to use either another material or a coating or lining. The choice of these methods depends on economic considerations and on the size of the installation. There is quite a difference between an industrial stack of perhaps 4 m diameter and a height of 75 m and the exhaust of an automobile!

7.7. REFERENCES

1. P. Kofstad, *High temperature oxidation of metals,* New York, John Wiley (1966).
2. O. Kubaschewski and B.E. Hopkins, *Oxidation of metals and alloys,* London, Butterworths (1962).

7.8. PROBLEMS

1. Calculate the Pilling-Bedworth ratio for Al_2O_3 on Al, MgO on Mg and Na_2O on Na. Do you expect these oxides to be protective?
2. Calculate the factor by which the oxidation rate of nickel is decreased when it is oxidized in air at a pressure of 0.1 mm Hg instead of at atmospheric pressure. Do the same calculation for a pressure of 10^{-5} mm Hg.

8 Epilogue: How to Prevent or Control Corrosion

In section 1.1. it is stated that the term *corrosion* is understood to refer either to the process or the damage caused by that process.

In the subsequent parts of this book many different methods of the prevention and control of corrosion, in both meanings, are discussed, together with the theoretical background thereof. Of course in any particular practical situation only a limited number of these methods will be applicable. In order to apply the knowledge gained it is always necessary:

a. to decide which methods are applicable in a particular case;
b. to choose thàt method which gives the greatest chance of success and is at the same time economically acceptable.

The purpose of this chapter is to give a survey of the different possibilities for corrosion prevention and control and to give an indication of the process needed to reach a decision in particular practical situations. As a guide in this survey it is helpful to use the outline sketched in Fig. 8.1.

The function and desired lifetime of a certain piece of equipment for which corrosion prevention or control is necessary are in this discussion considered as 'given'. The first step then is to obtain a correct interpretation of the environment or environments in which the equipment is to operate. Because the behavior of materials may be influenced strongly by components present in small amounts, e.g., copper and copper alloys are very sensitive to even small amounts of ammonium ions, it is not sufficient only to have a general idea of the composition of the environment(s). Furthermore it is of course necessary to know the temperature range in the equipment, velocity of liquid flow, presence of suspended solids and other conditions such as intermittent or continuous wetting by liquids, etc. In certain cases, such as in internal combustion engines different parts of the equipment are in contact with different environments and operate under different conditions, which means that these must all be known.

The next step is to obtain and interpret corrosion data of different materials in these environment(s) under the given conditions. This is done by using the methods discussed in section 6.2, i.e., using published data if these are available or performing experiments, if possible, under practical conditions.

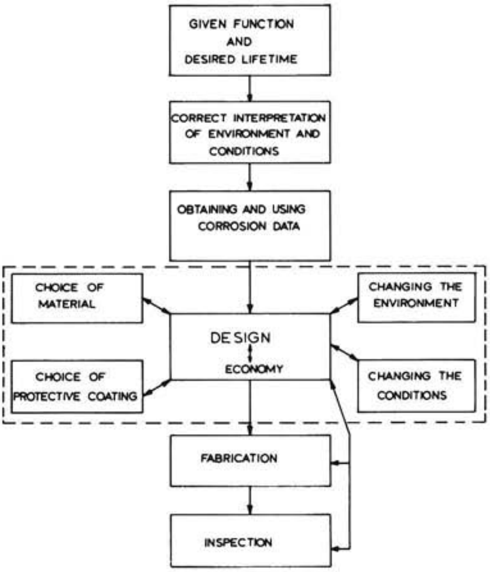

Figure 8.1. General aspects of corrosion prevention and control.

These results are then used in the detailed design of the equipment under consideration. Of course the corrosion data have to be combined with other data related to other requirements, which are not discussed here, such as mechanical properties, workability, etc.

As indicated in Fig. 8.1 the design includes not only geometrical design but also choice of material, of protective coating and decisions about changes in environment and conditions. Even though these are shown separately in Fig. 8.1 these show a very strong interdependence and in reality form one single activity. This is suggested by the box formed by the broken line. During the design stage the economic merit of different alternatives also has to be studied, for example by applying the methods discussed in section 6.5.

The choice of material is based primarily on the data obtained along the lines given in section 6.2. If no material is found which is resistant against the environment under the given conditions the application of some method of corrosion protection is necessary as will be discussed below. If one or more materials are sufficiently corrosion resistant it is necessary to consider whether these materials fulfill other requirements such as mechanical properties, workability, weldability, price, etc. In any case it will be necessary to compare the costs of using an expensive material without or a cheaper material with additional corrosion protection.

If corrosion prevention is considered to be necessary the different general possiblities are: applying a protective coating, changing the environment or changing the conditions or possibly a combination of these.

The most important types of protective coatings were discussed in section 6.3 together with some of their uses, properties and methods of application. The importance of adequate surface preparation and the influence of design (see also section 6.4) were also stressed. It is important to know that temporary corrosion preventives may be incompatible with certain types of paint resulting in softening and swelling of these paints. This means that already at the design stage these and other types of interaction have to be reckoned with.

Corrosion prevention by changing the environment can be achieved in a number of different ways as discussed in particular in chapters 4, 5 and 7. Lowering the electrolyte concentration usually leads to decreased corrosion rates due to increased electrical resistance (section 4.5). Increase of pH often causes diminished attack. This may be due to a diminished contribution of the hydrogen evolution reaction to the cathodic current (section 4.3) or by facilitating the formation of a passive layer (section 4.8). Addition of inhibitors (section 4.3) or passivators (section 4.8) also leads to a decreased corrosion rate. Removal of oxygen leads to diminished corrosion if oxygen reduction is the cathodic reaction (section 4.4) and also in high temperature oxidation (Chapter 7).

Finally one may also change the conditions. Direct methods are cathodic and anodic protection (section 4.7 and section 4.8). Cathodic protection can often be combined with painting. An important variable is the velocity of liquid flow. If there is danger of pitting corrosion this may be decreased by increasing the velocity (section 5.3) but if there is risk of erosion- or cavitation corrosion the velocity must be decreased (section 5.8). Other conditions which can be influenced by the design are stresses which have to be kept low in order to prevent stress corrosion cracking (section 5.7) and eliminating or diminishing vibration and relative movement of parts in order to prevent fretting corrosion (section 5.9).

When all these points have been studied and a decision has been reached fabrication must start. As mentioned in section 6.4 this has to conform to the design. This means in the first place that complete and clear instructions have to be given to the workshop. But it also means that regular *inspection* is necessary. This is an important but often overlooked activity. Not only must everything be thoroughly inspected after completion but this must also be done *during* construction. There must be a regular feedback to the design stage. As unexpected difficulties often arise which necessitate changes in design it is clearly necessary that the implications of these changes with respect to the corrosion behaviour of the equipment are considered too!

From the above it follows that it is impossible to give a formula for a universal solution to all corrosion problems. Each practical case has to be studied in detail and usually it is impossible to find a complete solution in the corrosion literature. But if the activities relating to design, fabrication and inspection are organized along the lines sketched in Fig. 8.1 as discussed in this chapter and are based upon an understanding of corrosion processes and the ways in which these can be influenced, it will be possible in nearly all cases to find a satisfactory solution. This will in turn make it possible to realize the savings indicated in Appendix 1 by preventing unnecessary corrosion costs through the application of existing knowledge about corrosion protection and control.

Appendices

A.1. POTENTIAL SAVINGS OF CORROSION COSTS IN GREAT BRITAIN

Of the total estimated corrosion costs in Great Britain of £ 1365 million about 25% can be saved and the potential savings together with the changes required to achieve them are given in the table.
(Taken from: Report of the Committee on Corrosion and Protection, Chairman Dr. T.P. Hoar, London, HMSO, 1971).

Industry or agency	Estimated Potential saving (£M)	Changes required to achieve savings
Building and construction	50	More awareness in selection, specification and control of application of protectives.
Food	4	More awareness in selection of equipment and protection methods
General engineering	35	Greater awareness of corrosion hazards at design stage and throughout manufacture.
Government departments	20	Mainly on defence side by better design and procedures.
Marine	55	Improved design, awareness and application
Metal refining and semifabrication	2	Improved awareness in plant and product protection.
Oil and chemical	15	Improved effectiveness in selection of materials and protection.
Power	25	Greater use of cathodic protection and improved awareness at design stage of operating conditions.
Transport	100	Change of exhaust system material and improved awareness at design stage.
Water	4	Improved awareness of corrosion and protection.
TOTAL	310	

A.2. SOME USEFUL CONSTANTS AND CONVERSION FACTORS.

Gas constant	$R = 8.314$ J.mole^{-1}.degree^{-1}
Faraday	$F = 96487$ C gm.equivalent^{-1}
2.303 RT/F (25°C)	= 59.2 mV
pressure	1 atm = 1.013×10^5 N.m^{-2}
energy	1 cal = 4.184 J
	1 l. atm = 101.33 J
length	1 inch = 2.54 cm
time	1 day = 8.616×10^4 sec.
	1 year = 3.156×10^7 sec.

A.3. CONVERSION TABLE FOR CORROSION RATES

In the table the factors are given to convert a unit on the left of the table into one of those above, e.g.

1cm.year^{-1} = 0.394 ipy.

Legend:

ipy = inches per year
mdd = mg.dm^{-2}.day^{-1}
n = valency of metal under consideration
M = atomic mass of metal under consideration
d = density (g.cm^{-3}) of metal under consideration

	mA.cm^{-2}	cm.year^{-1}	ipy	mdd	g.m^{-2}.day^{-1}
mA.cm^{-2}	1	$0.326 \frac{M}{nd}$	$0.129 \frac{M}{nd}$	$89.2 \left\|\frac{M}{n}\right\|$	$8.92 \left\|\frac{M}{n}\right\|$
cm.year^{-1}	$3.06 \frac{nd}{M}$	1	0.394	274 d	27.4 d
ipy	$7.75 \frac{nd}{M}$	2.54	1	694d	69.4 d
mdd	$0.0112 \frac{n}{M}$	$\frac{0.00365}{d}$	$\frac{0.00144}{d}$	1	0.1
g.m.$^{-2}$.day^{-1}	$0.112 \frac{n}{M}$	$\frac{0.0365}{d}$	$\frac{0.0144}{d}$	10	1

For a typical metal such as iron, copper, zinc, etc. with $M \simeq 60$, $d \simeq 7.5$ g.cm^{-3} and $n = 2$ this gives the following table, which is accurate enough for most practical purposes.

	$mA.cm^{-2}$	$cm.year^{-1}$	ipy	mdd	$g.m^{-2}.day^{-1}$
$mA.cm^{-2}$	1	1.3	0.52	2676	268
$cm.year^{-1}$	0.77	1	0.394	2050	205
ipy	1.92	2.54	1	5200	520
mdd	$3.6x10^{-4}$	$4.9x10^{-4}$	$1.92x10^{-4}$	1	0.1
$g.m^{-2}.day^{-1}$	$3.6x10^{-3}$	$4.9x10^{-3}$	$1.92x10^{-3}$	10	1

A.4. SOME GENERAL PROPERTIES OF METALS AND THEIR OXIDES

Metal	Name	Atomic Mass $kg.kmol^{-1}$	Density $kg.m^{-3}$	Common oxide(s)	Density of oxide $kg.m^{-3}$
Ag	silver	107.88	$10.5\ x10^3$	Ag_2O	7.143×10^3
Al	aluminium	26.98	$2.702x10^3$	Al_2O_3	3.97×10^3
Cr	Chromium	52.01	$7.20\ x10^3$	Cr_2O_3	5.21×10^3
Co	cobalt	58.94	$8.9\ x10^3$	CoO	$5.7-6.7 \times 10^3$
				Co_3O_4	6.07×10^3
Cu	copper	63.54	$8.92\ x10^3$	Cu_2O	6.0×10^3
				CuO	6.40×10^3
Fe	iron	55.85	$7.86\ x10^3$	FeO	5.7×10^3
				Fe_3O_4	5.18×10^3
				Fe_2O_3	5.24×10^3
Mg	magnesium	24.32	$1.74\ x10^3$	MgO	3.58×10^3
Na	sodium	22.99	$0.97\ x10^3$	Na_2O	2.27×10^3
Ni	nickel	58.71	$8.90\ x10^3$	NiO	7.45×10^3
Ti	titanium	47.90	$4.5\ x10^3$	TiO_2	4.26×10^3
Zn	zinc	65.30	$7.14\ x10^3$	ZnO	5.47×10^3
Zr	zirconium	91.22	$6.4\ x10^3$	ZrO_2	5.6×10^3

Molecular Mass of Oxide $M_aO_b = a \times$ (atomic mass of M) $+ b \times 16.00$.

A.5. FREE ENTHALPY CHANGE OF REACTIONS

We consider a reaction between reactants A and B giving the product P, where A and P are pure solids and B is a gas:

$$aA + bB = pP \qquad (A5\text{-}1)$$

The change in free enthalpy is the difference between the total free enthalpy of the product minus that of the reactants:

$$\Delta g = - a\mu_A - b\mu_B + p\mu_P \qquad \text{(A5-2).}$$

By definition we have for any compound X:

$$\mu_X = h_X - Ts_X \qquad \text{(A5-3).}$$

where h_X and s_X are the enthalpy and entropy per mole of X. For pure solids these are only slightly dependent upon temperature and pressure and may be put equal to their standard values $h_x^\ominus$ and $s_x^\ominus$ at a standard temperature and pressure (25°C = 298 K and 1 atm). From (A5–3) we then obtain:

$$\mu_X^\ominus (298\text{ K, } 1\text{ atm.}) = h_X^\ominus - 298\, s_X^\ominus$$

and for any other temperature T we define

$$\begin{aligned} \mu_X^\ominus (T) &= h_X^\ominus - Ts_X^\ominus \\ &= \mu_X^\ominus (298) - (T-298)\, s_X^\ominus \qquad \text{(A5-4).} \end{aligned}$$

For ideal gases (in corrosion work we may assume gases to behave ideally) the molar enthalpy is independent of pressure and nearly so of temperature. However, the molar entropy is strongly dependent upon pressure (or in mixture of gases upon the partial pressure of the gas considered) and we have

$$s_X\,(\text{gas}) = s_X^\ominus - R \ln p_X \qquad \text{(A5-5).}$$

where p_X is the (partial) pressure. The standard molar entropy $s_X^\ominus$ is the entropy of one mole of the gas at a standard pressure, usually 1 atm. This equation can be understood from the fact that at low pressures a larger volume is occupied and this means a correspondingly larger randomness.

From equations (A5–4) and (A5–5) we thus find for a gas:

$$\mu_X (T) = \mu_X^\ominus (T) + RT \ln p_X \qquad \text{(A5-6).}$$

Applying this to equation (A5–2) we obtain for the change in free enthalpy of reaction (A5–1):

$$\Delta g = (-a\mu_A^\ominus - b\mu_B^\ominus + p\mu_P^\ominus) - b\, RT \ln p_B$$

or

$$\Delta g = \Delta g^\ominus - b\, RT \ln p_B \qquad \text{(A5-7).}$$

For a reaction such as

$$aA + bB = pP + qQ \qquad \text{(A5-8).}$$

the free enthalpy change is

$$\Delta g = -a\mu_A - b\mu_B + p\mu_P + q\mu_Q \qquad \text{(A5-9).}$$

We consider the case that A and P are again pure solids but now B and Q are present in solution. The thermodynamic potential for dissolved substances is quite similar to that of gases as given by equation (A5–6) with, however, the concentration [X] taking the place of the pressure:

$$\mu_X\,(\text{sol}) = \mu_X^{\ominus} + RT\ln[X] \qquad \text{(A5-10).}$$

Here the standard thermodynamic potential is defined for a certain standard temperature and standard concentration $[A] = 1$ mole.l^{-1}. If another concentration unit is chosen, the numerical value of $\mu_A^{\ominus}$ will of course be changed, see problem 7 Chapter 2.

Using equation (A5–10) we obtain from equation (A5–9):

$$\Delta g = (-a\mu_A^{\ominus} - b\mu_B^{\ominus} + p\mu_P^{\ominus} + q\mu_Q^{\ominus}) + \frac{q}{b}RT\ln\frac{[Q]}{[B]}$$

or

$$\Delta g = \Delta g^{\ominus} + \frac{q}{b}\,RT\ln\frac{[Q]}{[B]} \qquad \text{(A5-11).}$$

as the change in free enthalpy of reaction (A5–8).

A.6. THERMODYNAMIC DATA FOR SOME OXIDES

oxide	$\Delta g^{\ominus}$ (298) kJ. mole^{-1}	$\Delta h^{\ominus}$ (298) kJ.mole^{-1}	$\Delta s^{\ominus}$ (298) J.mole^{-1} K^{-1}
Ag_2O	− 11.2	− 31.1	− 66.5
Al_2O_3	− 1582.4	− 1675.7	− 312.9
Cr_2O_3	− 1058.1	− 1139.7	− 273.6
Cu_2O	− 146.0	− 168.6	− 75.8
CuO	− 129.7	− 157.3	− 92.6
FeO	− 245.1	− 266.3	− 70.9
Fe_3O_4	− 1015.5	− 1118.4	− 345.2
Fe_2O_3	− 742.2	− 824.2	− 275.0
NiO	− 211.7	− 239.7	− 94.0
TiO_2	− 852.7	− 912.1	− 199.3
ZnO	− 318.3	− 348.3	− 100.5
ZrO_2	− 1022.6	− 1080.3	− 193.7
H_2O(liq)	− 237.2	− 285.8	− 163.2
H_2O(gas)	− 228.6	− 241.8	− 44.4

Note: $\Delta g^{\ominus}$, $\Delta h^{\ominus}$ and $\Delta s^{\ominus}$ in this table are defined for the formation of one mole of oxide at 298°K according to the reaction

$$mM + \frac{n}{2} O_2 = M_mO_n$$

Furthermore we may put approximately:

$$\Delta g^{\ominus}(T) \simeq \Delta h^{\ominus}(298) - T\Delta s^{\ominus}(298)$$

$$\simeq \Delta g^{\ominus}(298) - (T\text{-}298)\,\Delta s^{\ominus}(298)$$

if T does not differ too much from 298°K. In other cases more exact equations have to be used which are tabulated in the literature (see ref [2] of chapter 2).

A.7. ACID AND ALKALINE SOLUTIONS

The classic definition for an acid is that this is a compound which upon dissolution in water produces H^+-ions. Conversely an alkali gives OH^--ions Water itself, even when completely pure, contains H^+- and OH^--ions which is due to the so-called self ionization of water according to the equation:

$$H_2O = H^+ + OH^- \qquad (A7\text{-}1).$$

The dissociation product is defined as the product of the concentrations of H^+ and OH^-ions:

$$K_W = [H^+]\,[OH^-] \qquad (A7\text{-}2).$$

and at room temperature $K_W = 10^{-14}$. This means that in pure water, where the concentrations of H^+- and OH^--ions must obviously be equal, we have

$$[H^+] = [OH^-] = 10^{-7} \text{ mole.} l^{-1} \qquad (A7\text{-}3).$$

Using this we may now define an acid solution as one which has a H^+-ion concentration greater than 10^{-7} mole.l^{-1} and an alkaline one which has a OH^--ion concentration greater than this amount. From equation (A4.2) it then follows that in acid solutions $[OH^-] < 10^{-7}$ mole.l^{-1} and in alkaline solutions $[H^+] < 10^{-7}$ mole.l^{-1}.

The acidity or alkalinity of a solution is conveniently designated by the so-called pH value which is defined as:

$$pH = -\log\,[H^+] \qquad (A7\text{-}4).$$

For a neutral solution we thus have $pH = 7$, for acid solutions $pH < 7$ and for alkaline solutions $pH > 7$.

A more complete treatment of acids, alkalies and the uses of pH is given in most physical chemistry textbooks.

A.8. CELL TENSIONS AND ELECTRODE POTENTIALS

In order to reach an unambiguous assignment of the sign of a cell tension and of electrode potentials the following rules have been internationally agreed upon.

1. The cell and the cell-reaction are written in the same order, i.e., the metal atoms occur on the same side of the reaction equation as the corresponding electrode in the cell.
   For example

   cell: $Fe \mid Fe^{2+}(aq) \mid Cu^{2+}(aq) \mid Cu$
   Reaction: $Fe + Cu^{2+} = Fe^{2+} + Cu$

2. The sign of the cell tension is the polarity of the right-hand electrode on open circiut. If $E > 0$ for the cell-reaction then $\Delta g < 0$ and the reaction tends to proceed spontaneously to the right.
3. When the H_2-electrode is used as standard electrode it is placed on the left-hand side of the cell. Molecular H_2 thus also occurs on the left-hand side in the cell reaction equation.
4. The standard tension of such a cell, again taken with the sign of the polarity of the right-hand electrode, is called the standard potential of that electrode.
   The standard tension of the cell

   $H_2 \mid H^+(aq) \mid Cu^{2+}(aq) \mid Cu$

   with the cell reaction

   $H_2 + Cu^{2+} = 2H^+ + Cu$

   is the standard potential of copper.
5. The cell tension is obtained from the equilibrium potentials of the constituent electrodes by substracting the electrode potential of the left-hand electrode from that of the right-hand electrode.
   For example for the cell

   $Zn \mid Zn^{2+}(aq) \mid Fe^{2+}(aq) \mid Fe$

   we have

   $E_{cell} = E_{Fe} - E_{Zn}$.

A.9. ELECTROCHEMICAL SERIES OF METALS

electrode reaction	$E^{\ominus}$ (volt)
$K^+ + e^- = K$	−2.92
$Ca^{2+} + 2e^- = Ca$	−2.87
$Na^+ + e^- = Na$	−2.71
$Mg^{2+} + 2e^- = Mg$	−2.34
$Al^{3+} + 3e^- = Al$	−1.67
$Zn^{2+} + 2e^- = Zn$	−0.76
$Cr^{3+} + 3e^- = Cr$	−0.71
$Fe^{2+} + 2e^- = Fe$	−0.44
$Cd^{2+} + 2e^- = Cd$	−0.40
$Ni^{2+} + 2e^- = Ni$	−0.25
$Sn^{2+} + 2e^- = Sn$	−0.14
$Pb^{2+} + 2e^- = Pb$	−0.13
$2H^+ + 2e^- = H_2$	0.00
$Cu^{2+} + 2e^- = Cu$	+0.34
$Ag^{2+} + e^- = Ag$	+0.80
$Hg^{2+} + 2e^- = Hg$	+0.85
$Pt^{2+} + 2e^- = Pt$	+1.2
$Au^+ + e^- = Au$	+1.68

Note: In some books a different sign convention is chosen which reverses the signs given here. This is found particularly in the older American literature.

A.10. STANDARD POTENTIALS OF SOME REDOX REACTIONS

electrode reaction	$E^{\ominus}$ (volt)
$Cr^{3+} + e^- = Cr^{2+}$	−0.41
$Cu^{2+} + e^- = Cu^+$	0.153
$Fe(CN)_6{}^{3-} + e^- = Fe(CN)_6{}^{4-}$	0.356
$O_2 + 2H_2O + 4e^- = 4OH^-$	0.401
$I_2 + 2e^- = 2I$	0.53
$O_2 + 2H^+ + 2e^- = H_2O_2$	0.69
$Fe^{3+} + e^- = Fe^{2+}$	0.771
$Br_2 + 2e^- = 2Br^-$	1.06
$O_2 + 4H^+ + 4e^- = 2H_2O$	1.23
$Cl_2 + 2e^- = 2Cl$	1.36
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.77
$F_2 + 2e^- = 2F^-$	2.85

A.11. PRACTICAL GALVANIC SERIES FOR A NUMBER OF METALS AND ALLOYS IN AIR SATURATED, NEUTRAL SEAWATER

metal	potential (volt)
magnesium	−1.32
zinc alloy zamak Z400	−0.94
zinc	−0.78
aluminium 99.5%	−0.67
mild steel	−0.40
cast iron GG-22	−0.35
13% Cr-steel (active)	appr. −0.30
18% Cr-8% Ni-steel (active)	appr. −0.30
lead 99.9%	−0.26
brass 60-40	−0.07
copper	+0.10
monel K	+0.12
70-30 cupronickel	+0.34
chromium and chromium-nickel steels (passive)	appr. +0.40

A. 12. ELECTROCHEMICAL EQUIVALENTS OF SOME ELEMENTS

element	reaction	$\mathrm{kg.C^{-1}}$	$\mathrm{kg.A^{-1}.h^{-1}}$
Ag	$Ag^+ + e^- = Ag$	1.118×10^{-6}	4.025×10^{-3}
Au	$Au^{3+} + 3e^- = Au$	0.681	2.452
	$Au^+ + e^- = Au$	2.044	7.357
Ba	$Ba^{2+} + 2e^- = Ba$	0.712	2.562
Br_2	$Br_2 + 2e^- = 2Br^-$	1.756	5.962
Ca	$Ca^{2+} + 2e^- = Ca$	0.2077	0.7476
Cd	$Cd^{2+} + 2e^- = Cd$	0.5824	2.097
Cl_2	$Cl_2 + 2e^- = 2Cl^-$	0.7348	2.646
Co	$Co^{2+} + 2e^- = Co$	0.3054	1.099
Cr	$Cr^{6+} + 6e^- = Cr$	0.0898	0.3234
	$Cr^{3+} + 3e^- = Cr$	0.1797	0.6468
F_2	$F_2 + 2e^- = 2F^-$	0.3937	1.417
Fe	$Fe^{3+} + 3e^- = Fe$	0.1929	0.6945
	$Fe^{2+} + 2e^- = Fe$	0.2894	1.042
H_2	$2H^+ + 2e^- = H_2$	0.02089	0.0752
Mg	$Mg^{2+} + 2e^- = Mg$	0.1260	0.4536
Mn	$Mn^{2+} + 2e^- = Mn$	0.2846	1.025
Na	$Na^+ + e^- = Na$	0.2383	0.8579
Ni	$Ni^{2+} + 2e^- = Ni$	0.3041	1.095
O_2	$O_2 + 2H_2O + 4e^- = 4OH^-$	0.3316	1.194
O_2	$O_2 + 2H^+ + 2e^- = H_2O_2$	0.1658	0.597
Pb	$Pb^{4+} + 4e^- = Pb$	0.5368	1.933
	$Pb^{2+} + 2e^- = Pb$	1.074	3.865
Sn	$Sn^{4+} + 4e^- = Sn$	0.3075	1.107
Zn	$Zn^{2+} + 2e^- = Zn$	0.3388	1.219

A. 13. SIGN OF OVERVOLTAGE

For a cell reaction such as

$$A + B^{+} = B + A^{+} \qquad \text{(A13-1).}$$

we have according to equation (2.4.2):

$$\Delta g = -nFE \qquad \text{(A13-2).}$$

where the sign of the cell tension E is determined using the conventions of Appendix 5.

When reaction (A13-1) is a spontaneous reaction to the right we have from equation (2.1.2) $\Delta g < 0$ which together with equation (A13-2) gives:

$$E > 0 \qquad \text{(A13-3).}$$

When this reaction goes to the right the current flows from electrode B to electrode A, i.e., from the positive to the negative electrode and thus

$$E \times I > 0 \qquad \text{(A13-4).}$$

If it is assumed that the potential of electrode B is unaffected by the current, which is true in a good approximation when its surface area is much larger than that of electrode A, the cell tension is equal to the overvoltage of electrode A and

$$\eta_A \times I > 0 \qquad \text{(A13-5).}$$

Similarly when the reaction proceeds spontaneously to the left the sign of Δg and E and the direction of the current are reversed and equations (A13-4) and (A13-5) thus remain valid.

A. 14. ANNUAL EXPENDITURE ON PROTECTIVE COATINGS IN GREAT BRITAIN

(Taken from: Report of the Committee on Corrosion and Protection, Chairman Dr. T.P. Hoar, London, HMSO, 1971).

type of coating	cost of paint (a) £M	application cost factor (b)	total £M
1. Organic Market breakdown by main users.			
Industrial finishes	28.7	x 8	229.6
Can coatings	1.8	x 3	5.4
Marine	12.0	x 20	240.0
Construction	17.0	x 10	170.0
2. Galvanizing	–	–	39 (c)
3. Tinplating	–	–	75 (d)
4. Electroplating (all metals)	–	–	13 (e)

a. Based on board of Trade census (1963) and 'A profile of the United Kingdom Paint Industry' (1968).

b. Estimates of appropriate experts and includes costs of surface preparation, special facilities, loss of use, etc.

c. Figure supplied by the Zinc Development Association.

d. Figure supplied by the British Steel Corporation.

e. This assumes that only 50 percent of all electroplating is for anti-corrosion purposes.

A. 15. ELEMENTS OF DEFECT CHEMISTRY

At all temperatures above absolute zero a thermodynamic argument shows that all crystals contain a finite number of defects. For metals the simplest types of defects are the *vacancy*, i.e., a lattice position where the metal atom is absent and the *interstitial*, i.e., a metal atom in a position which is empty in the ideal crystal. It can be shown that, when the concentration x of the defects is not too high, this is given by

$$x = e^{-E/RT} \qquad (A15\text{-}1).$$

Here E is the energy necessary to create the defect. If, for example, $E = 40$ kJ.mole^{-1} we have at 300 K: $x \simeq 10^{-7}$, at 1000 K: $x \simeq 10^{-2}$.

In ionic crystals, such as metal oxides, single defects are not possible because electrical neutrality of the crystal as a whole must be preserved. In stoichiometric crystals the simplest types of defects are a pair of vacancies or *Schottky-defect*, illustrated schematically in Fig. A15.1b, and an interstitial ion plus a corresponding vacancy or *Frenkel-defect*, shown schematically in Fig. A15.1c.

Of great practical importance is non-stoichiometry in oxides because this often has a decisive influence on oxidation kinetics. Three common examples are shown schematically in Fig. A15.2. The first of these is nickel oxide, NiO, which has a nickel deficit in the form of Ni^{2+}-vacancies. In

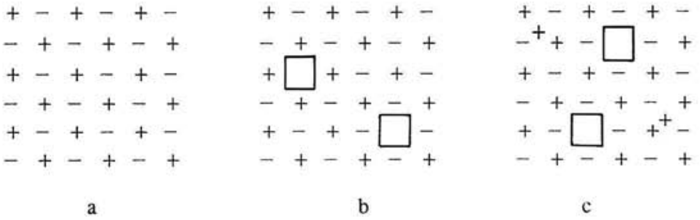

Figure A15.1. Point defect in stoichiometric crystals: a. ideal crystal; b. Schottky-defect; c. Frenkel-defect.

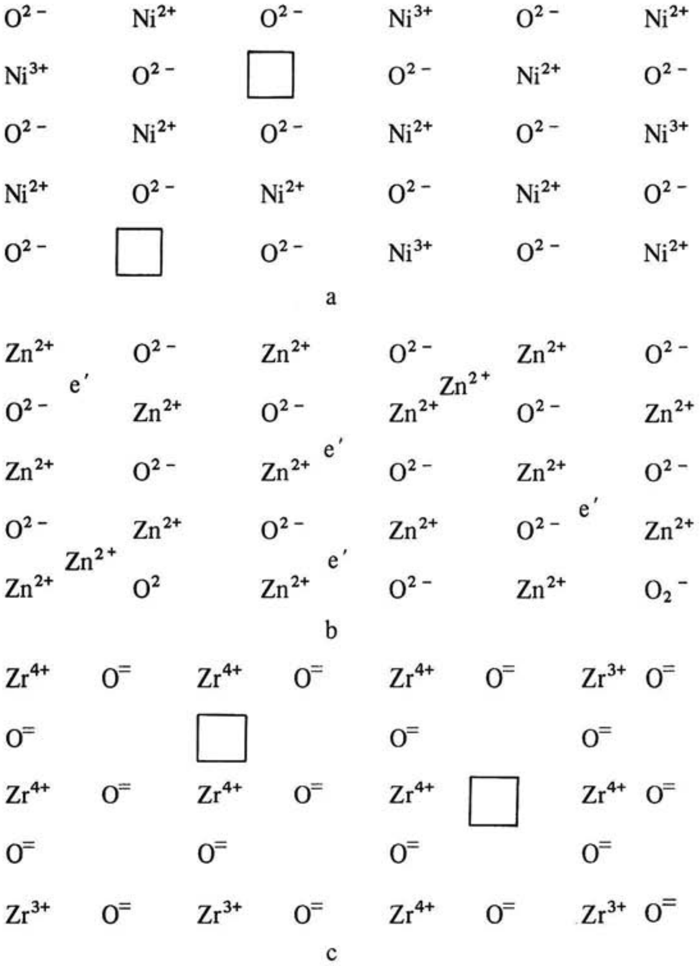

Figure A15.2. Point defects in non-stoichiometric crystals: a. NiO: metal deficit; b. ZnO: metal excess; c. ZrO_2: oxygen deficit.

order to compensate for the corresponding deficit in positive charge an equivalent number of Ni^{2+}-ions have lost an electron and have become a Ni^{3+}-ion. The nickel ion vacancy is denoted by the symbol V_{Ni}'' where the double prime indicates an effective negative charge of magnitude 2. The Ni^{3+}-ions have *electron holes* associated with them and are denoted by the symbol $h^{\cdot}$ where the dot indicates an effective positive charge of magnitude 1. The effective charges are defined with respect to the ideal crystal as reference.

The second case is that of ZnO with interstitial zinc ions ($\mathrm{Zn}_i^{\cdot\cdot}$) and free electrons ($e'$). Finally zirconium dioxide, ZrO_2, has oxygen vacancies ($V_O^{\cdot\cdot}$) and free electrons (e'). Table A15-1 gives a survey of the different types of defects and the symbols used to designate them. With these symbols we can, just as with the symbols for the chemical elements, write reaction equations for the formation and disappearance of defects.

Table A15-1. Types and symbols of defects.

defect	symbol	remarks
vacant M position	V_M''	MX with bivalent ions taken as example
M on proper lattice position	M_M	
X on proper lattice position	X_X	
vacant X position	$V_X^{\cdot\cdot}$	$\cdot$ = effective positive charge
interstitial M-ion	$M_i^{\cdot\cdot}$	
interstitial X-ion	X_i''	
electron	e'	$'$ = effective negative charge
electron hole	$h^{\cdot}$	
trivalent ion N on lattice position of M	$N_M^{\cdot}$	
monovalent ion A on lattice position of M	A'_M	

When we consider nickel oxide in contact with gaseous oxygen we can write:

$$\tfrac{1}{2}\mathrm{O}_2\ (g) \rightleftharpoons V_{Ni}'' + 2h^{\cdot} + O_O \qquad \text{(A15-2).}$$

With this equation we denote the process by which one O-atom takes up two electrons, creating two electron holes, and becomes an O^{2-}-ion which is taken up by the lattice. Then a nickel ion could also be taken up, i.e., a nickel ion vacancy is formed. The equilibrium constant for reaction (A15.2) can be written:

$$K = \frac{[V_{Ni}''][h^{\cdot}]^2\ [O_O]}{p_{O_2}{}^{1/2}} \qquad \text{(A15-3).}$$

or, because $[O_O]$ = constant

$$K = \frac{[V_{Ni}''][h^{\cdot}]^2}{p_{O_2}{}^{1/2}} \qquad \text{(A15-4).}$$

In order to calculate concentrations a second equation is needed because equation (A15-4) still contains two unknowns. This second equation arises from the electroneutrality condition:
This expresses the fact that in order to preserve electrical neutrality there must be two electron holes for each nickel ion vacancy, i.e., the number (and thus also the concentration) of electron holes is twice that of the nickel ion vacancies. Substitution of (A15-5) then gives after some rearrangement:

$$[V_{Ni}''] = (4K)^{1/3}\ p_{O_2}{}^{1/6} \qquad \text{(A15-6).}$$

Similar considerations are possible for other oxides. For the other two examples of figure A15.2 the corresponding reaction equations are:

$$\text{ZnO}: \tfrac{1}{2}O_2\ (g) + Zn_i^{\cdot\cdot} + 2e' \rightleftharpoons O_O + Zn_{Zn} \qquad \text{(A15-7).}$$

$$\text{ZrO}_2: \tfrac{1}{2}O_2\ (g) + V_O^{\cdot\cdot} + 2e' \rightleftharpoons O_O \qquad \text{(A15-8).}$$

Note: Because non stoichiometric oxides usually are semiconductors, oxides with electron holes are sometimes called *p-type oxides* and those with excess electrons *n-type oxides.*

If alloying elements are present they influence the defect concentrations if their valency differs from that of the host ion. For example if Cr^{3+}-ions are built into a NiO lattice they occupy nickel ion positions and can thus be written $Cr_{Ni}^{\cdot}$. This means that the electroneutrality condition (A15-5)is changed and must now be written:

$$[h^{\cdot}] + [Cr_{Ni}^{\cdot}] = 2\,[V_{Ni}''] \qquad \text{(A15-9).}$$

Using this together with equation (A15-4) at once shows that an increasing chromium concentration causes an increase in the concentration of nickel ion vacancies. Analogously lithium, being monovalent, is built in as Li_{Ni}', i.e., with an effective negative charge. Then the electroneutrality condition becomes:

$$[h^{\cdot}] = 2\,[V_{Ni}''] + [Li_{Ni}'] \qquad \text{(A15-10).}$$

Thus now the nickel ion vacancy concentration decreases with increasing lithium concentration.

Similar effects can be deduced of course for other oxides such as ZnO and ZrO_2.

Problems

1. Show that the oxidation rate of Zn will increase if it is alloyed with a monovalent metal, such as Li, and decrease upon alloying with a trivalent metal, such as Al.
2. Show that the concentration of oxygen vacancies in ZrO_2 is proportional to $p_{O_2}^{-1/6}$.
3. Explain why decreasing oxygen pressure leads to a decreased rate of oxidation of zirconium, even though the concentration of oxygen vacancies increases with oxygen pressure.

A.16. PRESENT VALUE TABLE.

n	$P_{n,r}$ (Present value of £1)		$A_{n,r}$ (Present value of £1 per period)	
	r = 6%	r = 12%	r = 6%	r = 12%
1	0.9434	0.8929	0.9434	0.8929
2	0.8900	0.7972	1.8334	1.6901
3	0.8396	0.7118	2.6730	2.4018
4	0.7921	0.6355	3.4651	3.0373
5	0.7473	0.5674	4.2124	3.6048
6	0.7050	0.5066	4.9173	4.1114
7	0.6651	0.4523	5.5824	4.5638
8	0.6274	0.4039	6.2098	4.9676
9	0.5919	0.3606	6.8017	5.3282
10	0.5584	0.3220	7.3601	5.6502
11	0.5268	0.2875	7.8869	5.9377
12	0.4970	0.2567	8.3838	6.1944
13	0.4688	0.2292	8.8527	6.4235
14	0.4423	0.2046	9.2950	6.6282
15	0.4173	0.1827	9.7122	6.8109
16	0.3936	0.1631	10.1059	6.9740
17	0.3714	0.1456	10.4773	7.1196
18	0.3503	0.1300	10.8276	7.2497
19	0.3305	0.1161	11.1581	7.3658
20	0.3118	0.1037	11.4699	7.4694
21	0.2942	0.0926	11.7641	7.5620
22	0.2775	0.0826	12.0416	7.6446
23	0.2618	0.0738	12.3034	7.7184
24	0.2470	0.0659	12.5504	7.7843

n	$P_{n,r}$ (Present value of £1)		$A_{n,r}$ (present value of £1 per period)	
	r = 6%	r = 12%	r = 6%	r = 12%
25	0.2330	0.0588	12.7834	7.8431
26	0.2198	0.0525	13.0032	7.8957
27	0.2074	0.0469	13.2105	7.9426
28	0.1956	0.0419	13.4062	7.9844
29	0.1846	0.0374	13.5907	8.0218
30	0.1741	0.0334	13.7648	8.0552
31	0.1643	0.0298	13.9291	8.0850
32	0.1550	0.0266	14.0840	8.1116
33	0.1462	0.0238	14.2302	8.1354
34	0.1379	0.0212	14.3681	8.1566
35	0.1301	0.0189	14.4982	8.1755
36	0.1227	0.0169	14.6210	8.1924
37	0.1158	0.0151	14.7368	8.2075
38	0.1092	0.0135	14.8460	8.2210
39	0.1031	0.0120	14.9491	8.2330
40	0.0972	0.0107	15.0463	8.2438
41	0.0917	0.0096	15.1380	8.2534
42	0.0865	0.0086	15.2245	8.2619
43	0.0816	0.0076	15.3062	8.2696
44	0.0770	0.0068	15.3832	8.2764
45	0.0727	0.0061	15.4558	8.2825
46	0.0685	0.0054	15.5244	8.2880
47	0.0647	0.0049	15.5880	8.2928
48	0.0610	0.0043	15.6500	8.2972
49	0.0575	0.0039	15.7076	8.3010
50	0.0543	0.0035	15.7619	8.3045

A.17. REQUIRED LEVEL OF CHEMISTRY KNOWLEDGE.

Secondary school chemistry books which approximately represent the level of chemistry knowledge desirable for studying this book as a whole. For the categories of students a. and b. of the preface a less extensive preknowledge is sufficient.

Denmark:

K. Ranche Madsen: *Laerbog i Kemi* (ISBN 8712 74 230 9)

Netherlands:

J.F.C. Schouten and J. Tromp, *Kernmethode scheikunde 1 & 2*, Zutphen, Thieme (1975, 1976).

Norway:

Hans Holtan, *Generell Kjemi*, Universitetsforlaget (1970).

Sweden:

S. Andersson, I. Leden and A. Sonesson, *Gymnasiekemi 1, 2, & 3*, Stockholm, (Esselte Studium) (1975, 1976).

or

B. Borén, O. Moll, B. Hellström, S. Lillieborg and T. Lif, *Kemi NT 1, 2 & 3*, Stockholm (Esselte Studium) (1974, 1975, 1976).

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