

CORROSION

- WORLDWIDE 1 TON OF STEEL TURNS TO RUST EVERY 90 SEC.
- ENERGY NEEDED TO MAKE 1 TON STEEL = ONE MONTH'S ENERGY NEED OF AVERAGE FAMILY
- 50% OF WORLD'S STEEL PRODUCTION IS FOR REPLACEMENT OF CORRODED STEEL

pH VALUE

pH VALUE

4

CORROSION

- CHEMICAL REACTIONS ARE NOT TO BE CONFUSED WITH PHYSICAL CHANGE
- CHEMICAL REACTIONS ARE EITHER EXOTHERMIC OR ENDOTHERMIC
- ENERGY IS VITAL TO CHANGE OF CHEMICAL PROPERTIES

pH VALUE

pH VALUE

5

CORROSION

- ALL MATERIAL CORRODE - NOT ONLY METALS
- ORGANIC MATERIALS LIKE WOOD, STONE, PLASTICS ETC. AS WELL
- VISIBLE SIGNS ARE:
 - IRON = REDDISH-BROWN (RUST)
 - COPPER = GREENISH (VERDEGRIS)
 - ZINC = WHITISH (WHITE RUST)

pH VALUE

pH VALUE

6

CORROSION

VERDEGRIS



pH VALUE

pH VALUE

7

CORROSION

WHITE
RUST



pH VALUE

8

CORROSION

- In order for corrosion to take place, the following basic elements are necessary:

- OXYGEN
- ELECTROLYTE
- METALS WITH DIFFERING POTENTIALS

pH VALUE

pH VALUE

9

CORROSION

- All elements consist of positive, negative and neutral particles forming an electrically neutral atom
- A metal can only be attacked by corrosion when the metal atom is changed to a positively charged particle through electron emission

pH VALUE

pH VALUE

10

CORROSION

ELECTRON EMISSION

pH VALUE

pH VALUE

11

CORROSION

- ELECTROLYTE IS A LIQUID WHICH IS ELECTRICALLY CONDUCTIVE
 - ◆ ANODE
 - ◆ CATHODE
 - ◆ FLOW OF ELECTRONS
 - ◆ DISSOLUTION

pH VALUE

pH VALUE

12

CORROSION

■ IONS IN SEA WATER:

- ◆ Sodium (Na^+)
- ◆ Chloride (Cl^-)
- ◆ Magnesium (Mg^{++})
- ◆ Sulphate (SO_4)
- ◆ Bromide (Br^-)
- ◆ Bicarbonate (HCO_3^-)
- ◆ Calcium (Ca^{++})

Typical salt concentrations in sea water:

36,000 ppm of which 26,000 ppm is sodium chloride

The ions create conductivity in the sea water

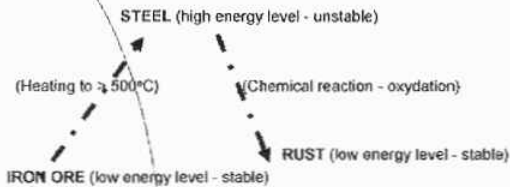
pH VALUE

pH VALUE

13

CORROSION

■ ENERGY LEVELS OF IRON:



pH VALUE

pH VALUE

14

CORROSION

- GALVANIC SERIES
- POTENTIAL OF METALS IN SEA WATER (V)
- NOBLE vs IGNOBLE
- DIFFERENCES IN POTENTIAL

pH VALUE

pH VALUE

15

CORROSION

■ ELECTROLYTIC CELL:

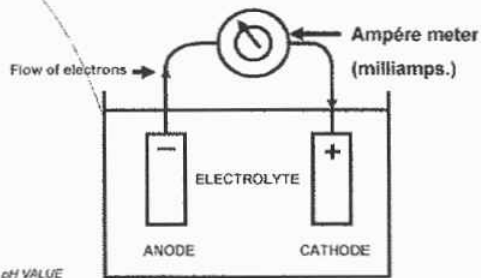
- ◆ Electrons are released at the anode as the anode material is consumed
- ◆ Electrons are absorbed by the cathode

pH VALUE

pH VALUE

16

CORROSION

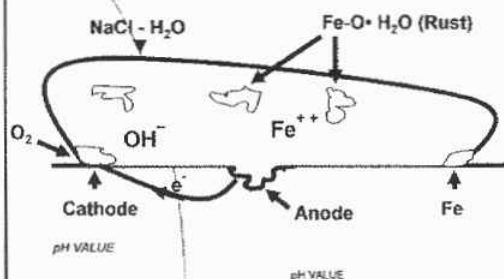


Electrolytic cell (principle)

17

CORROSION

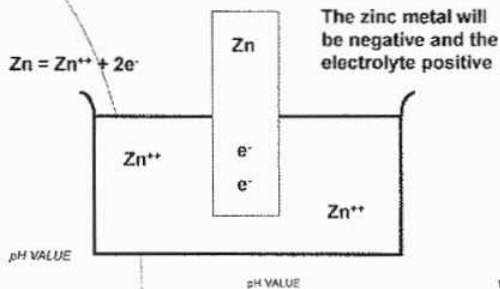
Electrolytic cell - corrosion of steel



18

CORROSION

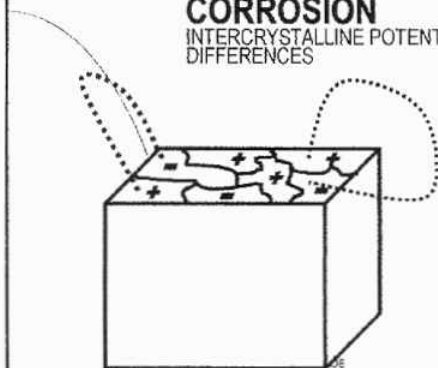
Electrolytic cell - corrosion of zinc



19

CORROSION

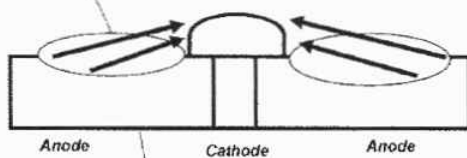
INTERCRYSTALLINE POTENTIAL DIFFERENCES



20

CORROSION

LARGE ANODE - SMALL CATHODE



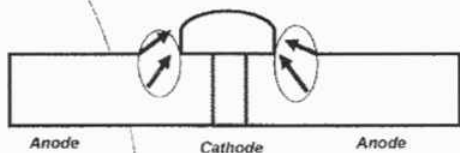
ELECTROLYTE WITH HIGH CONDUCTIVITY

pH VALUE

21

CORROSION

LARGE ANODE - SMALL CATHODE



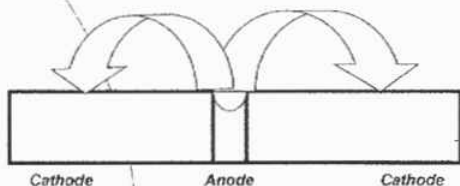
ELECTROLYTE WITH LOW CONDUCTIVITY

pH VALUE

22

CORROSION

LARGE CATHODE - SMALL ANODE



ELECTROLYTE WITH LOW CONDUCTIVITY

pH VALUE

23

CORROSION

- FACTORS INFLUENCING THE CORROSION RATE:
 - OXYGEN SUPPLY
 - CONDUCTIVITY OF ELECTROLYTE
 - FLOW RATE OF ELECTROLYTE
 - DIRECT METALLIC CONTACT
 - DIFFERENCE IN POTENTIAL
 - RELATIVE SIZES OF AREAS
 - PURITY OF METALS
 - INFLUENCE OF pH
 - TEMPERATURE

pH VALUE

pH VALUE

24

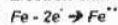
CORROSION

■ OXYDATION

Oxygen addition:



Electron emission:



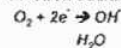
■ REDUCTION

Oxygen

dissociation:



Electron addition:



pH VALUE

pH VALUE

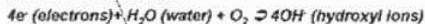
25

CORROSION

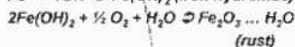
ANODIC REACTION:



CATHODIC REACTION:



COMBINED REACTION:



(rust)

pH VALUE

pH VALUE

26

CORROSION

■ GALVANIC SERIES:

If two metals with differing potentials are in direct contact in an electrolyte, the metal with the lowest potential will protect the metal with the highest potential (i.e. the most noble one)

pH VALUE

pH VALUE

27

CORROSION

GALVANIC SERIES (in sea water):

Platinum
Gold
Graphite
Titanium
Silver
Stainless steel (passive)
Nickel (passive)
Bronze alloys
Copper
Brass alloys
Nickel (active)
Tin
Lead
Stainless steel (active)
Cast iron
Steel (or iron)
Aluminium alloys
Cadmium
Pure aluminium
Zinc
Magnesium alloys
Pure Magnesium

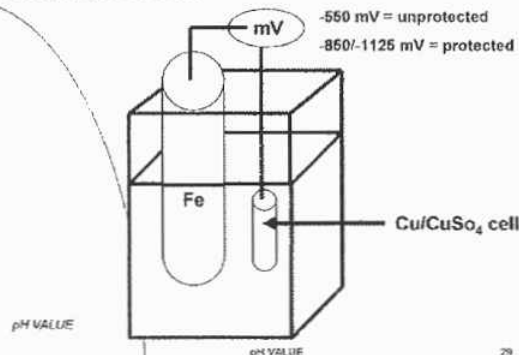
NOBLE

IGNOBLE

pH VALUE

28

CORROSION



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CORROSION

ELECTRODE	ELECTROLYTE	POTENTIAL
Silver/silverchloride (Ag/AgCl)	Sea water	approx. + 0.24V
Copper/coppersulphate (Cu/CuSO ₄)	Sea water	approx. + 0.30V

pH VALUE

pH VALUE

30

CORROSION

- STEEL AND COPPER IN DIRECT CONTACT IN SEA WATER:

Copper is more noble than steel and will receive electrons from the latter. The copper is protected from corrosion and the steel will corrode

pH VALUE

pH VALUE

31

CORROSION

- STEEL AND ZINC IN DIRECT CONTACT IN SEA WATER:

Zinc is less noble than steel and will transfer electrons to the latter. The steel is protected from corrosion and the zinc will corrode

pH VALUE

pH VALUE

32

CORROSION

- pH-SCALE
- ACIDIC via NEUTRAL to ALKALINE

← 0 7 14 →

- PROBLEM TODAY LIES IN AIR AND WATER BORNE POLLUTION

pH VALUE

pH VALUE

33

CORROSION

■ pH-SCALE.

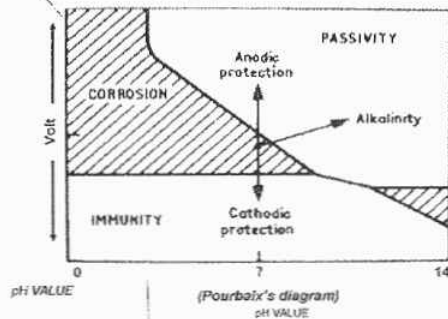
Completely pure water has a pH-value of 7, which indicates that the solution is neutral. pH-values below 7 indicates acidic solutions, whereas pH-values above 7 indicates alkaline solutions. The pH-scale is logarithmic in construction, which means that one unit step up or down from neutral increases the strength of the solution by a factor of 10. A solution with a pH-value of 4 will be $10 \times 10 \times 10 = 1000$ times as concentrated as a solution with a pH-value of 7.

pH VALUE

pH VALUE

34

CORROSION



35

CORROSION

Introduction

Corrosion is the natural deterioration or destruction of a material as result of its interaction with its environment. Corrosion mainly occurs in metals and the term is applied to their reaction with oxygen. Most people connect the term corrosion with rusting, however, all materials are subject to surface deterioration. Generally the processes are chemical or electrochemical, although physical and mechanical factors contribute.

The cost of corrosion to society through replacing corroded structures and protecting existing structures is estimated to be some 2-4% of a country's GNP per annum, however, this percentage may well be on the high side, however, if correct this would mean an annual cost to Norway of some \$3 billion. In the USA the cost of corrosion was calculated to be in excess of \$10 billion in 1985. The correct figure being as it may, it is quite clear that the cost of corrosion to society each year is substantial. A large portion of these costs may be substantially reduced, however, as a large portion of the damages seen are due to people having insufficient knowledge of corrosion and the conditions which promote corrosion. The choice of materials is often not well founded and the protection of the same materials often insufficient.

Corrosion of metals is generally confined to the surface. In some cases, such as that of aluminium, a layer of oxide is formed that serves as a barrier to prevent further contact with oxygen, thus suppressing corrosion. The oxide layer on iron in dry air is so thin that is invisible to the naked eye and protects the iron. However, in the presence of moisture, hydrates of iron oxide are formed, the iron becomes porous to oxygen and corrosion proceeds.

Great efforts have been made throughout decades to inhibit or arrest the corrosion of metals through adding other substances to the virgin metal, with varying degree of success. Trace substances added to iron can accelerate corrosion, whereas other substance may inhibit it. Aluminium is added to brass to make it more corrosion resistant. The drawback of solving corrosion problems through utilizing less corrosion prone materials, is often either loss of physical properties as compared to the original metal, or increased costs due to the cost of the alloy.

The most common means of thwarting corrosion is to apply a resistant surface coating (or lining) to the metal in question. The material used for such coatings vary greatly, however, the most commonly used are paints, plastics, rubbers, ceramics and other metals such as aluminium, zinc, chrome or nickel applied through various methods

such as, e.g. electroplating, hot dip galvanising, painting.

In protecting metal structures against corrosion through the use of protective paint systems, all persons involved, from the designer of the structure through the painter to the paint inspector, must have at least basic knowledge of corrosion and the factors influencing this phenomenon. In this certain knowledge of chemistry is inevitable and needed.

Chemical reactions

The study of chemical reactions forms basis for all chemistry, both organic and inorganic. All chemical reactions involve formation and breaking of chemical bonds in or between molecules to form different substances. Chemistry has been defined as the science of substances - their composition, structure and properties, as well as their reactions with themselves or other substances resulting in new or changed substances.

A simple chemical reaction occurs when hydrogen gas combines with oxygen gas to form the compound we call water. On the molecular level this is due to two hydrogen atoms establishing a chemical bond with one oxygen atom to produce two molecules of water (H_2O).

Chemical reactions are often confused with **physical change** and this should be avoided. Change in state is the physical change which most often is confused with chemical change.

Water, as most substances, can exist in various states induced by external influences such as, e.g. pressure, temperature. Water, when heated above the boiling point turns into steam and when cooled below the freezing point, turns into ice. Water in its various states have very different forms with different physical properties, however, it remains H_2O .

Chemical reactions always involve **energy** and in any chemical reaction energy is either needed to initiate or maintain the reaction, or the reaction will liberate energy. Chemical reactions releasing energy are called **exothermic** whereas reactions requiring energy are called **endothermic**. The energy involved in chemical reactions may be in the form of heat, pressure, radiation, electricity etc., however, when we are specifically discussing chemical reactions in paints we are mainly dealing with energy in the form of heat.

The reaction between hydrogen and oxygen to form water releases substantial quantities of energy in the form of heat. The reaction is therefore exothermic. Once the water molecules are formed, we cannot break the chemical bond between the atoms by just cooling the water down (withdrawing energy). The bond must be broken through returning an equal amount of energy as that which was released in the original reaction, to the water (f.i. in the form of electrical

energy) to break the bond that holds the hydrogen and the oxygen atoms together. Such a reaction as the latter is termed endothermic.

Chemical reactions are identified by the changes in the **chemical properties** of the substances during the course of the reaction. Such changes in properties can be very profound and are usually durable.

Table salt (NaCl), when melted, can be decomposed to its elements by passing a direct electrical current through the melt. At the negative electrode we will get formation of the silvery molten metal sodium (Na) and at the positive electrode we will get release of the poisonous greenish-yellow gas chlorine (Cl).

We see from the above example that the melting of the table salt did not bring about anything other than physical change and that we only achieved a change in the chemical properties when we passed the current through the melt. The change was very profound indeed as the split of the bond between the two elements changes the table salt from a harmless substance to two basic elements, of which one is highly poisonous.

What is corrosion?

For most people corrosion is pure and simply the **reddish-brownish rust** which is formed as a by-product when iron or steel corrodes. Although this rust is the most common corrosion by-product, we have all seen the **greenish rust** (verdegrijs) which forms when copper corrodes (although this rust is mostly seen as a desirable "patina") and the **whitish "rust"** which is formed when zinc corrodes.

Why do the materials we use in constructions deteriorate in this fashion? Turning to the metals, we see that most are formed through our adding large amounts of energy to the ore. In its natural state the ore is bonded to various other elements such as, e.g. carbon or sulphur. The condition of the metal in nature is the most stable one and not very prone to corrosion.

In the production of metals such as steel or aluminium we are changing the natural condition of the ore by exposing it to large amounts of energy, either in blast-furnaces, electrical furnaces or in electrolytic processes. This energy is added to the ore which separates into its single elements forming molten virgin metal and other unwanted residual products which we commonly term **slag**. The metal is separated from the slag and cooled to a solid state. In this solid state the metal is very prone to corrosion and is at a residual high energy level.

Fabrication processes such as, e.g. rolling or extruding may impart additional energy to the metal. Rolling of steel plates will bring the red-hot steel into contact with oxygen and an oxide layer is formed on the steel surface. This layer of iron oxide is called **mill scale**. The mill scale, while intact, will protect the steel, however, the scale is very

brittle and in outdoors exposure will crack and break down rapidly, thus exposing the steel to corrosion. The corrosion by-product, rust, is very similar in composition to iron ore and thus more stable than either iron or steel. Rust is at a lower energy level than both the latter and very close to the energy level at which iron ore exist in nature.

Corrosion theory

Corrosion of metals is an electrochemical process requiring an electrically conducting liquid or substance, which we term **electrolyte** and oxygen. Water very often is an electrolyte (sea water is an excellent electrolyte) and even condensation or rain water may become electrically conductive through absorption of particles from pollution in the air or on the substrate.

An electrolyte is a liquid which is electrically conductive.

Metals tend to emit electrically charged particles called **electrons** when in contact with a conductor, such as other metals or an electrolyte. Substances which have emitted one or more electrons, take on a positive charge due to the presence of positrons in the atom core. Substances which absorb electrons take on a negative charge due to the negative charge of the electron. Substances with either a positive or a negative charge are termed **ions**. In some metals this tendency is very weak like in, e.g. platinum or gold. Such metals with low emission of electrons are designated **noble metals**. Other metals with a strong tendency to emit ions, like, e.g. aluminium or zinc, are designated **ignoble metals**.

If two metals are submerged in an electrolyte without any direct contact between the two metals, both will corrode at a certain rate, however, if the two metals are placed in direct, electrical connection to each other, the rate of corrosion will increase significantly for the most ignoble of the metals, whereas the corrosion rate for the most noble of the metals will slow down or be arrested. The rate of corrosion is dependant on a number of factors like, e.g. which metals are involved, exposure time in the electrolyte, composition of the electrolyte, contamination on the substrate etc.

Imagine steel directly connected to copper and immersed in an electrolyte. When an iron atom is released on the surface, it will emit two electrons and become an iron ion (Fe^{++}). Places where such emissions take place are called **anodes**. Through corrosion anodes are consumed. Electrons (negatively charged) are transmitted through the steel to the copper, which thus becomes the cathode. At the cathode hydroxyl ions are formed. These ions will react with the iron ions and thereafter with the oxygen in the air or in the electrolyte, forming rust, or water containing **iron oxides** (Fe_2O_3 ; $\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$).

We are utilizing this phenomenon in electrical batteries. A conventional battery consists of a carbon or a graphite rod immersed in an electrically conductive substance (electrolyte). The rod and the electrolyte are surrounded by a zinc container. Both the

rod and the zinc container have connection points for electrical cables (poles). If a small and suitable light bulb is coupled to the two poles, it will give off light. The battery is emitting electrical current. After some time this emission will stop as the zinc container (the anode) is consumed through **dissolution** (e.g. corrosion).

The most ignoble metal is dissolved and electrical energy is released at the anode. This energy is absorbed at the cathode.

For corrosion to occur it is not necessary to have two different metals connected as in the above example. Steel, which in reality is an alloy, corrodes when exposed in an outdoors environment. This is due to steel not being microscopically homogenous in composition. Any steel contains minute areas with noble and ignoble particles. If the steel is left uncoated and exposed to an electrolyte, particles of mill scale, graphite or other noble substances will form small cathodes, whereas the steel itself will become the anode. Such areas will form minute "batteries" which will corrode. The corrosion will dissolve the anode (the steel itself) and leave the cathodes intact. However, it should be noted that the electrolyte around the cathodes will change and become alkaline in nature (the pH-value will increase).

The reaction process may be described as follows:



Reactions other than the formation of hydroxyl ions at the cathode may occur. In acid solutions or acids, hydrogen gas will form. Deposition of noble metals from a solution onto the metal of the cathode is another possibility.

Galvanic series

A metal's resistance to corrosion is an expression of that metal's ability to withstand corrosion in an environment. The durability of the metal or an alloy is dependant on the metal and the influences brought to bear upon it.

All metals or alloys contain a certain amount of residual energy. This residual energy may be measured (in volts). Such measurements are called potential or electrical tension measurements. The difference in potential between two metals may be measured by means of a volt metre, however, if we want to measure one metal's potential either by itself or together, we will need to use a reference electrode. A reference electrode works in a way like a zero calibration. Such a reference electrode is referred to as a **standard hydrogen electrode (SHE)**. It has a current potential of zero volt in a defined electrolyte at a temperature of 0°C.

For measuring potentials in sea water, the reference electrodes listed below are used.

ELECTRODE	ELECTROLYTE	POTENTIAL
Silver/silver chloride Ag/AgCl	Sea water	approx. + 0.25 V
Copper/copper sulphate Cu/CuSO ₄	Sea water	approx. + 0.30 V

Both reference electrodes have a potential greater than the hydrogen electrode.

Metal and metallic alloys may be ranged according to their corrosion resistance in what we term **galvanic series**. Such galvanic series are established by measuring the electrical tension or the potential of a metal or an alloy in a defined environment.

The galvanic series of metals immersed in sea water is the most common one and through this we can quickly establish which metal will corrode when coupled to another metal. A metal with a lower potential than another metal is termed more ignoble than the latter. When two metals are joined, it is desirable to have as little corrosion as possible. If it is not possible to isolate the metals from direct electrical contact, one should then see to it that the potentials of the two metals are as close as possible. The driving force of corrosion processes is the difference in potential between the metals, as mentioned. The greater the difference in potential is, the greater the corrosion of the most ignoble of the metals will be. Corrosion due to difference in potential between two metals or to differences in potential within the alloy itself, is termed **galvanic/bimetallic corrosion**.

Corrosion attack on metals is highly dependant on the medium the metal is exposed to. Aluminium alloys and stainless steels will not corrode significantly in a city or an industrial atmosphere. The corrosion will become significant, however, if the same metals are exposed to sea water.

Some metal or alloys may have varying potentials. This is due to these metals being covered by a thin, protective oxide layer. As long as this oxide layer is intact, it contributes to the metal being what we term as **passivated**. If the oxide film is damaged or removed, the potential of the metal will change, and the metal will become what we term as **active**. The corrosion resistance has been lowered through the removal of the oxide film.

Alloys with such passivating oxide films are, e.g. stainless and acid resistance steels, nickel and aluminium alloys. Sufficient supply of water and oxygen will cause the oxide film to reform, however, if the metal surface is contaminated or dirty, supply of oxygen may be impaired and corrosion will occur.

Galvanic/bimetallic corrosion may also occur if external conditions influence two like metals so that their potential is changed. Change in the supply of oxygen is one

example of such external influences.

The below table show the galvanic series in sea water for certain metallic materials in commercial use, listed with the highest potentials at the top of the list. Increased potential means increased corrosion resistance.

NOBLE (cathodic)
Platinum
Gold
Graphite
Titanium
Silver
Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)
Hastelloy C (62 Ni, 17 Cr, 15 Mo)
18-8-3 stainless steel (passivated)
18-8 stainless steel (passivated)
Inconel (80 Ni, 13 Cr, 7 Fe)
Nickel (passivated)
Silver solder
Monel (70 Ni, 30 Cu)
Cu-Ni alloys (60-90 Cu, 40-10 Ni)
Bronze alloys (Cu-Sn)
Copper
Brass alloys (Cu-Zn)
Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
Inconel (active)
Nickel (active)
Tin
Lead
Lead-tin solder
18-8-3 stainless steel (active)
18-8 stainless steel (active)
Ni-resist cast iron
Chrome based stainless steel 11-30 Cr (active)
Cast iron
Steel or iron
2024 Aluminium (4.5 Cu, 1.5 Mg, 0.6 Mn)
Cadmium
Pure aluminium
Zinc
Magnesium and magnesium alloys
IGNOBLE (ANODIC)

Alloys grouped together in the table may be used together without undue risk of significant galvanic corrosion of either metal.

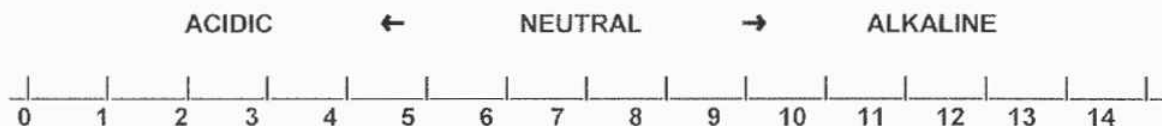
Corrosive environments and the influence of the pH-value

In dry interior spaces the risk of corrosion is minute. However, exposure outdoors to environmental influences like, e.g. sun, rain and air borne pollution will change the conditions, usually providing factors increasing the corrosion rate of most metals.

Especially air borne pollution will have detrimental effects. Quite a number of the gases emitted into the atmosphere from industry either are or will be changed into acidic or alkaline substances. Such substances - usually aqueous solutions - will attack metals as well as other construction materials.

When we wish to indicate if a solution is either acidic or alkaline we measure the pH-value of the solution. This value is usually measured within a frame of 0-14 like the below.

THE pH-SCALE:



Completely pure water has a pH-value of 7 which indicates that the solution is neutral. pH-values below 7 indicate acidic solutions, whereas pH-values above 7 indicate alkaline solutions. The pH-scale is logarithmic in construction which means that one unit step up or down from neutral increases the strength of the solution by a factor of 10. A solution with a pH-value of 4 will be $10 \times 10 \times 10 = 1000$ times as concentrated as a solution with a pH-value of 7.

Usually corrosion of metals increase in acidic or alkaline solutions. Aluminium and zinc will corrode at an accelerated rate in alkalies, whereas steel, when exposed to alkalies will be passivated through the formation of a thin film of iron oxide on the steel surface. This passivating film provides quite good protection against corrosion. Most metals will be quickly consumed in acids.

The passivating of steel in an alkaline environment is seen in the case of steel reinforcement bars imbedded in concrete. As long as the concrete remains alkaline, the rebars will not corrode significantly.

Due to the air borne pollution being dissolved in water from rain or condensation, acids are

commonly formed which leads to attack on the substrate. Heavy rain will wash off such contaminants, however, light rain and condensation will not. Contaminants in the form of dust and salts attract moisture (the contaminants are hygroscopic) thus prolonging the moisture time. This is the reason why structures in areas with little precipitation but a general high level and humidity may corrode severely.

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