

CORROSION: origin and prevention (1)

Eng. N.W. Buijs
Van Leeuwen Stainless, Beesd

Corrosion occurs in various forms and the constructor has to deal with it case by case. The origin and the prevention of corrosion are tightly connected to each other. In the past, ignorance has often led to notable damage. In two articles some clearness will be given about the origin and the prevention of corrosion.

Devices and installations have a technical and an economical lifetime. As far as the technical lifetime is decisive, it is mostly noticed that the corrosion phenomenon is the big troublemaker which eventually determines the lifetime. For this reason in our country every year hundreds of millions guilders are spent on renovating appliances and installations because the corrosion of the existing equipment had affected the technical function of the whole too much. From a marketing-technical point of view the replacement of systems has indeed also certain advantages, but the aspiration will always be to keep the technical lifetime as long as possible. It is also important not to 're-design' because in this case the technical lifetime will exceed the economical one. In itself this is not really needed because the device has to be replaced anyways in order to achieve the efficiency target. The aspiration of this article is to deliver a contribution in order to make an optimal choice as to the material and the process control.

Forms of corrosion

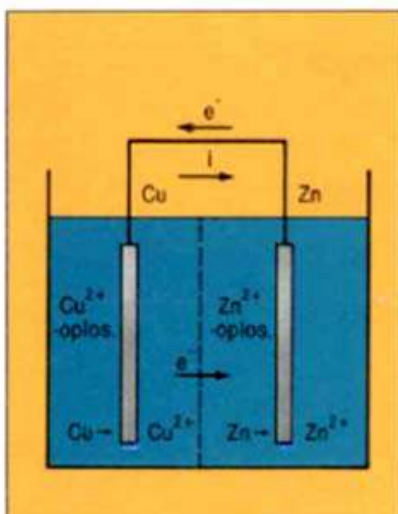
A largely used definition for corrosion is the undesired deterioration of a metal as a consequence of chemical- or electrochemical reactions on the metal surface through components which are present in its surroundings. Corrosion is a chemical reaction which will start spontaneously when the thermodynamic condition will induce this. The speed with which a similar reaction takes place is also decisive for the eventual use of a certain metal. The corrosion occurs in a variety of forms, each of which arises in a different way:

- general or smooth deterioration;
- split corrosion
- wander stream corrosion;
- grainborder corrosion;
- biological corrosion;
- pit corrosion;
- tension- or tear corrosion;
- weariness corrosion;
- erosion/corrosion.

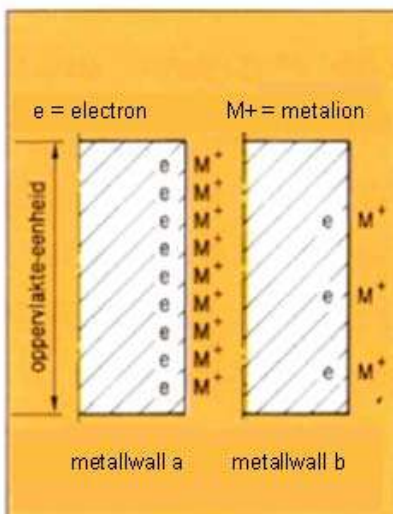
The general or smooth deterioration is a type of corrosion which is the least dangerous because the deterioration image expands over the whole surface

of a metallic object. The entity of the deterioration can easily be determined by, for example, expressing the loss of weight per time unity or surface unity (for example N/m²/hour) or a thickness decrease per time unity like mm/year. In practice, this last measure is the most used indicator. In this way it can be decided how much corrosion addition has to be given to a certain part in order to obtain the desired lifetime.

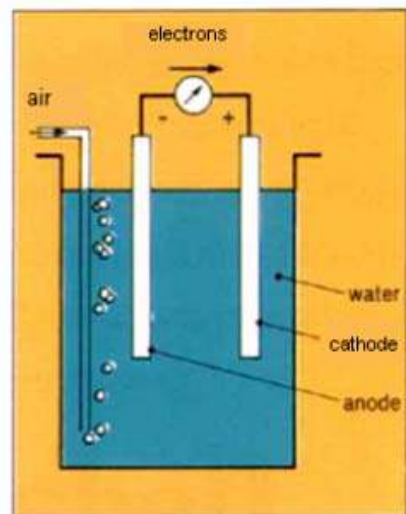
The galvanic corrosion is also called contact corrosion and is the result of an electric leading compound of two different metals which have come in touch with an aggressive environment. In this case, the least noble metal will be corroded much quicker than if it would have only been in touch with this environment. The metal which goes in dissolution is the anode of the galvanic element. Even in one metal you can have a form of this corrosion for example through a difference of potential which appears through differences of composition of the metal or environment. In such a case we



1. Schematical reproduction of the process of galvanic corrosion



2. Electric double layer



3. Example of corrosion element

speak about local element corrosion.

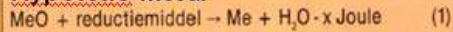
Splitcorrosion only appears in narrow splits due to a difference in potential which is caused by the relatively low oxygen content in the split. This form of corrosion is really feared because it takes place in such a hidden way. It can even occur in splits which are not bigger than 0.03 mm (for example non-narrowly adjacent packs on metal flanges). It is clear that in this case the dissolving electrode is the metal split (the anode). When a metal conduct, which is placed in the soil, is in the area of a streamleading network a portion of this stream can flow back to the net. Corrosion will arise on the spot where the stream quits the duct (wanderstream corrosion). A similar corrosion occurs frequently on rails on behalf of trains which have been taken up in an electric circuit.

Grainborder corrosion, also called intercrystalline corrosion, is the consequence of a potential difference between the borders of the metal crystals and the crystal itself. There is no point in using corrosion additives here. The measure which is used is penetration per time unity. The corrosion speed in general is high. The big danger of this form of corrosion is that through deterioration of the borders the mutual connection of the crystals gets lost whereby the grains in the end lie loose. There are three main reasons through which the borders become sensitive to corrosion. First of all through precipitation of alloy elements which at a certain saturation and a slow chilling can separate themselves on the grain border. An example is the formation of chromecarbides in stainless steel which nestle on the grain border because of the undesired 'friendliness' to germs of similar zones. Chromecarbides are very un-noble and dissolve relatively quickly because of the difference in potential with the matrix with all the related consequences. A second disadvantage of this phenomenon is that in this way chrome is subtracted to the matrix and it will be the question whether enough chrome remains present in order to keep the stainless steel (locally) passive.

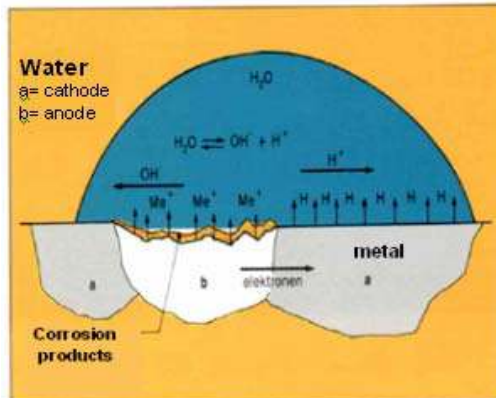
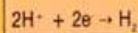
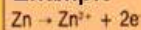
The second cause which can be mentioned is that crystals which lie next to each other can cause dislocations because of their reciprocal positions, which is an easy inducement for the metalions to quit that spot. As third point, crystals can form themselves whereby impurities are expelled before the coagulation front (segregation);

Corrosion Process

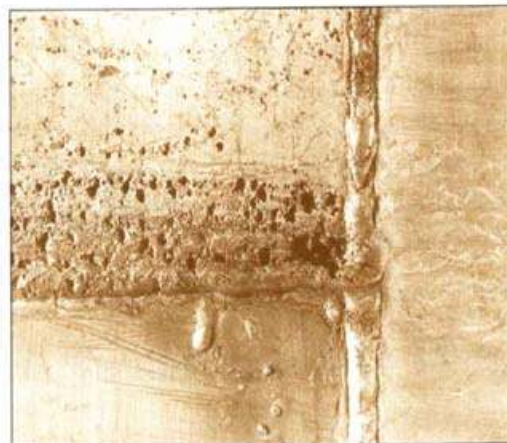
Hypotetic metal



Example



4. Schematic Imagination of corrosion-element (drop)



5. Pitting corrosion of stainless steel

these will eventually nestle on the grain borders. Similar impurities almost always react anodic in a chemical environment and for this reason the border always corrodes. High temperature corrosion is also called oxidation because it is the matter of reacting with oxygen at elevated temperatures. In this way on the

material arise oxide peels which possess a different expansion than the mother material so that when there is mechanical tension (for example because of large temperature differences) this peel will break off the ground layer. By alloying this kind of metal in the right way with certain elements the oxidation firmness can enormously be increased. In case micro-organisms die oxygen is needed to permute these organic materials in carbon and hydrogen. For this reason it is very important that bacteria and similar cannot delimit themselves in dead corners of systems, because this kind of corrosion can appear in these locations. It will be clear that regular cleaning of similar constructions is a need.

Sometimes the metal itself fights against biological corrosion i.e. when ions arise which inhibit the growth of similar organisms like for example by copper ions. The well corrosion is distinguished by its local character. The symptoms are deterioration in well form (pitting) which usually form themselves quite quickly and deeply. The main cause is usually a local damage of the passive oxide hide whereby an aggressive environment can do a devastating work on those spots. Imperfections in a such a hide or unwished embedding of different parts in the surface can also be the reason of pit-corrosion (think of steel polish particles which penetrate a stainless steel surface). An

important reason is also the penetration of specific components from an environment like chlorine- and halogeniones. Therefore, besides the pH value and the conduction ability of the electrolyte, it is also important to know how big is the percentage of chlorine ions. Additional reasons are wander streams and stream differences which usually originate because of turbulences whereby differences will arise in the oxygen content.

Combined corrosion

Above some individual corrosion phenomena have been described shortly; in practice it can also happen that combined corrosion phenomena appear, like for example:

- stress (tear) corrosion;
- weariness corrosion;
- erosion/corrosion.

A combination of mechanical stress and a corroding environment causes a quicker corrosion on the spots where the stress is highest wherefore cracks

arise relatively quickly whereas the material surrounding it is completely sound.

Sometimes the cracks run along the grain border (intercrystalline) and sometimes even through the grains (trans-crystalline); this arises depending on the kind of metal and the exposed environment.

The reason for which corrosion focuses so intensely on a stress area can be explained by the fact that due to the stress small cracks originate on the surface hide whereby there will be a difference in potential between the often oxidized hide and the blank metal in the cracks. In this way there is a relatively small active fracture surface on one hand and a big passive smooth one on the other. Besides this and through the notch effect in the small cracks stress in the metal is locally very high, whereby the crack formation can propagate with a fast pace and eventually will lead to fracture. In practice hydrogen friability is an example of this form of corrosion. The word fatigue corrosion already tells that here there is a combination of metal fatigue as a consequence of a long persisting variable stress and the presence of a corroding environment which is an inducement for accelerated corrosion on those spots which function as anodes.

The erosion/corrosion is the combination which is also called cavitation corrosion and also leads to accelerated corrosion which often concerns a general deterioration. The main cause is usually that the passive metal hide is ravelled out by an abrasive means and that the metal will therefore not have a chance to passivate itself again whereby it corrodes in a much faster way.

Theory about corrosion

Metals, with a few exceptions (like gold, platinum and silver), are mined as ores or with other words in combination with another element or other elements. This means that from a thermo-dynamic point of view this is a situation of equilibrium or in other words the material is in a lowest energy condition towards which, as a nature law teaches us, every system aims.

If a reduction remedy is added plus energy such a metal can be liberated from its ore. A famous example is the iron preparation in a blast furnace with cokes as a reduction remedy and energy which is added. If we call a hypothetical metal Me the reaction basically takes place following (1) in frame.

A similar reaction is an endothermic reaction because heat is needed to have this reaction happen. In this way the metal is brought to a higher energy condition which on itself is not a

condition of equilibrium. If the metal sees the opportunity to loose the energy again, this happens spontaneously under heat delivery (exothermic reaction).

This process is the corroding or oxidizing ('incinerating'). This corrosion process progresses faster as the metal is less noble. The corrosion products which originate from it, as to their structure, are indeed dependent from the kind of environment where the corrosion has taken place.

What actually happens during corrosion is clear from the frame. The reaction (2) is oxidation of a metal or in other words the metal combines with the element oxygen. The underlying partial reactions are (3) (4) and (5). Adding up leads to the total reaction: (6). The actual oxidation reaction is thus (3). Basically it does not make any difference whether this oxidation has taken place with the help of oxygen or another oxidation means. In principle, a similar reaction makes that a metal changes into a positive ion and a specific solution. The free electrons, as a rule, are carried directly into the system.

When a metal bar is placed in a solution of its own ions this yields an equilibrium reaction (7). If the reaction progresses to the left, the metal is loaded positively with regard to the solution and is loaded negatively when the reaction progresses to the right. Setting up this difference in potential will prevent further progressing of the reaction unless a second reaction which originates at the same time can eliminate this difference in potential again. As can be seen from the example in frame 1 the reaction carries on and the zinc bar corrodes completely. The appearance of reduction reaction is essential for corrosion to appear.

Prevention of this corrosion can be reached by:

- taking away the electrolyte (aggressive environment)
- covering the zinc bar with coating (for ex. paint layer)
- lowering the potential of the zinc bar artificially with the assistance of an external stress source whereby the oxidation reaction cannot happen anymore.

If we place a copper bar in a copper (Cu²⁺) solution and a zinc bar in a zinc solution and separate these two solutions from each other with a diaphragm which will not let through metal ions but only electrons (electrical power) both bars will take a potential with regard to the solution (independently from each other). The difference in potential which we can measure appears to be 1.1 Volt where the half precious copper is positive with regard to the base zinc. After we have

linked the two bars electrically, a stream will flow from Cu to Zn (picture 1). The copper electrode will have a reduction of Cu²⁺ ions). Per definition the electrode where the reduction has taken place is called anode.

In the sketched set up of picture 1 the zinc bar goes in solution. This can be fought against in three ways, i.e.:

- isolating the zinc bar (covering it with a coating)
- breaking the connection wire;
- taking away the Cu²⁺ ions making the cathodic and consequently also the anodic reaction impossible.

The set up is an example of galvanic corrosion. Above mentioned remedies to stop galvanic corrosion will be examined more closely later. The explanation is more finalized to better clarify the corrosion mechanism in its generalities.

Potential

The concept of potential is the electric tension (in Volt) which a metal assumes when it is immersed in a fluid. This tension is caused by the quantity of metal ions which go in dissolution and their equivalent quantity of electrons which are present per surface-unity of the metal (electrical doublelayer). The difference in potential between metal a and the fluid in picture 2 is bigger than the one of metal b.

The dimension of the tension is determined by the preciousness of the metal or with other words how many metal ions go in dissolution. The more ions dissolve the more base is the metal. For example platinum and gold do not have any ions which go in dissolution, half-precious metals like copper and nickel have relatively few and with base metals like zinc and magnesium many to extremely many metal ions can go in dissolution.

In this way originates a succession of preciousness which can be set in a series. Observing a corrosion element like the one in picture 3 it can be spoken about a potential of the anode with regard to the fluid and the potential of the cathode with regard to the fluid. The electromotive power of the corrosion-element is the difference of the potentials. However, it is not possible to measure the difference in potential between the electrode and the liquid wherein this has been immersed. Therefore a reference electrode has been defined.

In practice the normal hydrogen electrode is usually used which per definition has received the potential 0. In this way the difference in potential can always be measured both for the anode and for the cathode comparing it to the normal-hydrogen electrode.

With the assistance of thermodynamics a formula has been developed in order to calculate all these differences in potential. These values are represented in figure 1; this is called the electrochemical tension series. The series shows the degree of preciousness of the various metals. Sodium and potassium are thus base and therefore dissolve very easily. For this reason they can spontaneously catch fire. Gold and platinum react with a lot of difficulties because of the very precious nature. The more the normal potential decreases the more base is the metal. There is also the fact that two different metals which have been electrically connected in an electrolyte will behave in such a way towards each other that the least precious metal will go in dissolution. The precious metal consequently will be protected by the less precious one until the latter is totally dissolved. Some examples are the zinc anodes on a steel ship which have to be renewed from time to time. This form of protection is also called cathodic protection.

for example, the acid degree (pH) of a specific environment is also a decisive factor.

Single metal

The above mentioned mechanism can also be 'translated' to only one single metal. On a metal surface various tiny local elements can be present for various causes like differences in structure (for example α and β crystals (...)) differences in tension and environment variations.

In this way with the aid of an electrolyte the small anodic spot can dissolve in favour of the cathode spots whereby local corrosion will originate. As time goes the cathode spots will however lie loose whereby they will disappear and in this way new anodic spots will come in touch with the environment. (Pict 4). In this way the corrosion process will stride forward and general corrosion is a reality.

Even though a lot can be written about the different corrosion mechanisms we limit ourselves to the above concise exposition. The practical question on how to fight against corrosion is often more relevant. Besides the various mechanisms to fight against corrosion also the material choice is very important and so is the way the structure is built. In practice there is often 'over-designing' and needless expensive metals are chosen whilst the solution could better be sought in a total different construction or set up of the whole.

Naturally, also the metal choice remains of great importance and therefore a dialogue between a metal expert, a constructor and the consumer is absolutely necessary in order to take an optimal decision. The advice of a chemist can also be important because,