

SIGRAFLEX® corrosion processes in sealing connections

Corrosion processes in static and dynamic sealing connections in piping systems, pumps, armatures and containers can cause significant costs and endanger the operational safety and service life of machinery and equipment.

Corrosion in sealing connections can be significantly reduced with the selection of suitable sealing materials and construction measures.

Firstly, adequate and evenly distributed surface pressure has to be observed during assembly of seals and gaskets. Secondly, great care has to be taken in the selection of adequate auxiliary materials, such as e.g. adhesives, release agents or lubricants, so that no corrosion-promoting side reactions do occur under operating conditions.

Although the appearance of various corrosion cases may often look similar at first glance, different corrosion mechanisms, which are triggered by different causes, have to be distinguished.

The most important corrosion types occurring in connection with sealing materials are:

- contact corrosion
- crevice corrosion
- electrochemical corrosion

Due to the fact that in practice these mechanisms hardly ever occur in isolation, it is often difficult to carry out a definite damage analysis.

In the following, we discuss corrosion phenomena on metallic sealing surfaces (flanges, armature spindles, etc.) which can occur in interaction with the sealing materials, resp. the sealing connection.

Contact corrosion

This form of corrosion develops primarily if a sealing material contains components which trigger a chemical reaction upon contact with a metallic sealing surface. Often, this form of corrosion appears in connection with crevice corrosion.

Probably the most common case of damage – both on armature spindles and flanges – occurs with flat gaskets or stuffing box packings, which cause pitting corrosion to Cr/Ni-steels due to high halogen (chloride, fluoride, bromide, iodide) content. These effects can be reduced significantly by changing the gasket material to a low halogen content flexible graphite. The typical halogen content of most flexible graphite sealing materials lies between 25 and 250 ppm, depending on the degree of purity. In the case of high purity SIGRAFLEX types typical values below 10 ppm are available.

Also, the sulphur content of a gasket material has to be taken into consideration. However, it must be distinguished between the forms in which the sulphur is present, in particular in which chemical valency stage. The valency stages -2 and +4 (sulphide and sulphite), also known as active sulphur, are considered to be critical. In the case of valency stage +6, one has to distinguish between free sulphuric acid, which is also considered critical, and sulphur which is present as sulphate [e. g. calcium sulphate], which is deemed less critical. Also, organic sulphur bound in e. g. rubber is not relevant.

When flexible graphite is used, it is recommended as a minimum requirement that the total sulphur content should not exceed 500 ppm, respectively that the content of "active sulphur" is lower than 200 ppm. Nearly 100% of the SIGRAFLEX product range has a total sulphur content of < 300 ppm, but even significantly lower maximum limits are available on request. Particularly in the power plant sector it has partly become customary to use only certain types of flexible graphite with total sulphur contents of less than 200 ppm in order to limit the detrimental effects of sulphur.

A further source for corrosion can be found in certain coatings or impregnations of gasket materials which release corrosive decomposition products under higher temperatures, mainly hydrochloric acid (HCl) in the case of organic compounds containing chlorine. In the case of PTFE, highly corrosive fluorine compounds are released. This decomposition process already starts at temperatures of around 300 °C/572 °F. Even though the short term resistance of PTFE lies at ca. 400 °C/752 °F, the temperature of permanent operation for gasket materials containing PTFE should not exceed 300 °C/572 °F.

Crevice corrosion

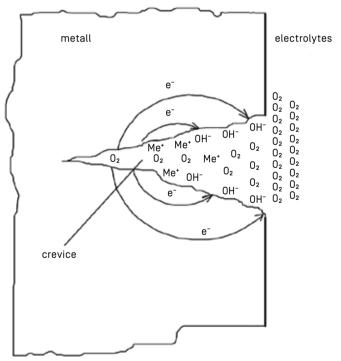
This type of corrosion should supposedly be the most common one in connection with gasket materials in electrolytic media. Even with highly pure, electrochemically inactive materials of high chemical and thermal stability, such as e.g. PTFE, strong corrosion effects can be observed under adverse installation conditions.

The corrosion mechanism is attributed to concentration differences (e.g. oxygen) in narrow crevices, as they can be commonly observed in sealing gaps, and thus resulting electrochemical potential differences. These potential differences permit electrochemical corrosion currents, with metal atoms being dissolved in the form of ions due to redox processes.

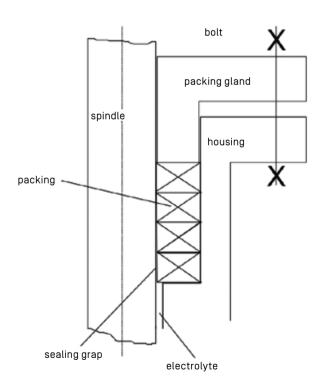
Through the enrichment of corrosion products a self-intensification effect sets in, which can finally result in the dissolution of substantial amounts of metal.

These effects markedly occur in stuffing box packings, in which there is always a more or less pronounced sealing gap as a result of their design. As operating pressure is relieved over the entire length of the packing, a reduction of process materials ensues from the operating pressure side towards the atmosphere side in the packing itself as well as alongside the gasket surfaces. Due to the fact that a packing seal usually suffers from a certain degree of leakage, additional enrichment of dissolved substances in the operating medium takes place here, primarily around the area of the outermost packing ring. Proper installation of the packing rings can at least alleviate those effects. E. g. with packings made from SIGRAFLEX flexible graphite, it is recommended to always individually precompress the packing rings in the packing space with a two-piece press sleeve.

By doing so, an even radial prestressing of each individual packing ring is achieved prior to exerting force through the packing gland. In this way, even the lowest ring considerably contributes to the sealing strength and the likelihood for a pronounced sealing gap is reduced.

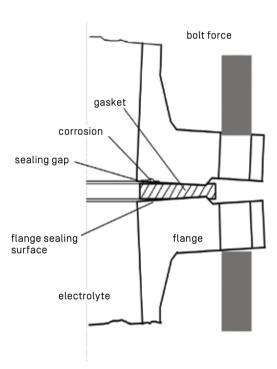


↑ Crevice corrosion ↑ Stuffing box packing



With flat gaskets, crevice corrosion processes are to be expected if there is an insufficient adaption of the gasket surface to the flange sealing surface. In the event of flange sheet bending or uneven flanges, particularly with relatively hard fibre gaskets, there is a chance that parts of the sealing surfaces (particularly at the inner diameter) suffer from insufficient pressure, allowing the formation of a sealing gap. These effects become even more critical if an improved behaviour of the gasket is attempted by a reduction of the gasket thickness (reduction of relaxation). It is recommended to use compressible gaskets of sufficient thickness to avoid above mentioned issues. Here, compressibility values greater than 15% should be the target as a minimum requirement.

In this situation, a high halogen content can have an intensifying effect. Long standing positive experience with soft and more adaptable materials, in particular with graphite gaskets based on SIGRAFLEX, demonstrate that this type of corrosion can be largely avoided.



↑ Flange gasket system

Electrochemical corrosion

Element	Normal potential E°H (Volt)
Mg/Mg ²⁺	- 2.40
Al/Al³+	- 1.70
Mn/Mn ²⁺	- 1.70
Cr/Cr ³⁺	-1.00
Zn/Zn²+	- 0.76
Fe/Fe ²⁺	- 0.44
Co/Co²+	- 0.29
Ni/Ni ²⁺	- 0.22
Sn/Sn ²⁺	
Pb/Pb ²⁺	- 0.12
H₂/2H ⁺	± 0.00
Cu/Cu ²⁺	+ 0.35
O₂/OH⁺	+ 0.40
C/C ₂ ⁺	+ 0.72 *
Ag/Ag⁺	+ 0.80
Hg/Hg ²⁺ 0	+ 0.86
Cl ₂ /Cl ⁻	+ 1.36
Au/Au³+	+ 1.50
Pt/Pt²+	+ 1.60

^{*} calculated values for: C + $\frac{1}{2}$ O₂ \rightarrow CO + 2e⁻

This form of corrosion is characterized by the occurrence of electrochemical processes in an ion-conducting phase [electrolyte]. Here, the corrosion does not have to be necessarily evoked by a direct electrolytic metal removal. It can also be generated by the reaction with an electrolytically produced intermediate [e. g. atomic hydrogen]. Characteristic for electrochemical corrosion is the dependency of the corrosion processes on the electrode potential, resp. on the electric current which flows through the phase boundary between material and medium. The explanation for this phenomenon can be deduced from the electrochemical voltage series of the elements.

The formation of galvanic cells, i. e. the certain arrangement of non-precious with precious elements, in particular metals, in the copresence of an electrolyte (electrically conductive aqueous solution by dissolved ions), causes the dissolution of non-precious element through a redox process (electron donation by the non-precious element, resp. electron acceptance by the more precious element).

In sealing connections, galvanic cells are often formed through the interaction of various materials and metals, resp. alloys.

This can be attributed to:

- different flange materials
 [e.g. connection of pipes to apparatuses]
- different materials within a component
 [e.g. armature spindle and housing material]
- the gasket material itself

In the latter case, this could be e.g. a metal gasket made of materials which are unsuitable for the intended purpose, or metal inlays in the soft gasket sheet. And lastly, also the soft gasket sheet itself could become electrochemically active.

In any case, an electrolyte has to be present that both transport processes and the corresponding electrochemical reactions can take place. In mere steam systems, however, the danger for this type of corrosion is generally considered low due to the absence of electrolytically active ions.

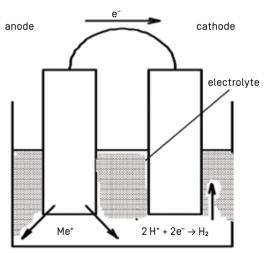
Owing to the fact that graphite is ranked as a relatively precious element in the electrochemical voltage series, which, however, is incapable of forming ions and therefore cannot accept electrons, the material assumes an exceptional position. Direct redox reactions with the carbon are not possible, as they only take place in the presence of other reducible elements such as e.g. oxygen.

In the case of armatures, the material combination Cr/Ni steel-spindle and grey cast iron housing is widely used, however, also various other materials for both components can be found. By using electrochemically more precious materials such as e.g. graphite, various electrochemical potentials are in interference with each other depending on the paired materials so that a definite analysis of the cause in the event of damage is often not possible.

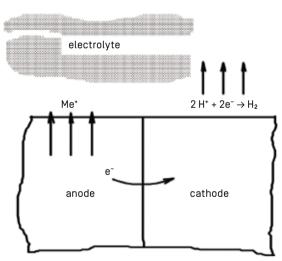
Corrosion at valve spindles can occur in some special cases with both graphite and PTFE packings.

Various causes for corrosion are, for example:

- · crevice corrosion
- enrichment of impurities and corrosion products from the piping system
- impure graphites with high contents of e.g. chlorides, fluorides or sulphur
- structural disturbances within the steels
- halogen containing media



↑ Galvanic chain



↑ Corrosion element

These causes cannot always be clearly identified due to the complex processes within a packing sealing gap. However, once a corrosion process is in progress – for whatever reason – it is assumed that the graphite has a certain promoting effect.

If such damages to the spindles, which generally take the form of pitting corrosion, cannot be tolerated in special cases, graphite packings made from barium molybdate inhibited graphite foil [SIGRAFLEX AQ or SIGRAFLEX ZX] should be used. For more than 30 years now, very positive experiences in power plant engineering have been made with this special "anti-corrosion type". Notably, this type is mandatory in many nuclear power plants [e.g. at EDF].

The presence of molybdate ions [MoO_4^{-2}] improves the corrosion resistance of passivating Cr/Ni steels against pitting in such a way that the repassivation potential is shifted towards higher values. With stuffing box packings made from graphite foil, it is recommended to go without zinc-containing supplements [principle of the sacrificial anode]. The formation of zinc oxide as a by-product causes an increase in volume of the packing during operation, which can result in spindle blockage. In general, this kind of inhibition leads to friction problems between packing and spindle.

In flanges and piping made from carbon steel, the corrosion process caused by the gasket is negligible due to the geometrical surface-area-to-volume ratio (small electrochemically active cathode surface of the gasket [inner circumference x gasket thickness] versus the entire anodically active inner surface of the piping system) and the resulting miniscule current density of the corrosion.

With flanges made from **austenitic steels**, electrochemical corrosion processes can exclusively occur with **aqueous electrolytic media**.

To prevent the formation of corrosion in sealing connections, the following is recommended:

- avoidance of disadvantageous metal pairings
- utilization of high-grade Cr/Ni steels with better pitting corrosion resistance (higher molybdenum content)
- utilization of gasket material with low contents of critical impurities (chloride, fluoride, sulphur)
- application of flexible graphite with high purity (low ash content)
- stuffing box packings: utilization of graphite foils with barium molybdate inhibitor
- flange connections: ensuring even and sufficient surface pressure throughout the entire sealing surface
- \bullet selection of a gasket material with sufficient compressibility in excess of 15 %
- adequate training resp. qualification of the assembly personnel



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