

Corrosion inhibitors in graphite packing

The valve stem is by far the most challenging component of a valve when trying to keep the process fluid out of the environment. There are different methods to seal the moving stem on a valve, with compression packing, elastomeric seals, or bellow seals. At higher temperatures, compression packing is the predominant method and graphite is most commonly used.

By Hans Dekker

Graphite has many advantages over alternative materials. It is chemically resistant, temperature resistant, mechanically relatively stable in comparison with some alternatives, and flexible/expanded graphite has good sealing properties. Graphite is used as a packing material in different forms:

- Braided expanded graphite
- Braided graphite yarns
- Hybrid braids
- Die-formed expanded graphite rings

The way packing works is easily explained. An axial gland force is being applied and converted into a radial force according to Poisson's Law (Figure 1). This radial force gives the packing its sealing capability and it creates a frictional force between packing and valve stem (and stuffing box). This is the reason that the gland force that is received by every packing ring, and the consequential radial force, diminishes going deeper into the stuffing box (Figure 2).

The forces are applied to the packing rings after the valve assembly has been completed. The valve is often hydrotested with high-pressure water. This is done to assure that pressure containment requirements are met.

Problem description

A known phenomenon that many valve operators are familiar with is valve stem pitting corrosion. Small pits have formed on the surface of the valve stem that can give the valve stem a very rough finish (see figure 3). This pitting corrosion is causing several issues. First, it can weaken the valve stem when the erosion becomes very severe. A much bigger problem is that this rough, corroded stem surface can damage the stem seal, resulting in leakage and potential plant shutdowns. The irony is that this type of valve corrosion may be caused by the valve packing itself. It is often caused by galvanic corrosion resulting in pitting in which the (graphite) packing plays a predomi-

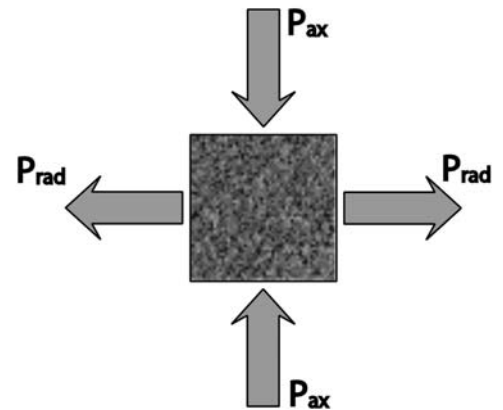


Figure 1

nant role. This issue calls for corrosion control methods.

Corrosion basics

Corrosion is the electrochemical degradation of a material (metal or alloy) due to a reaction with its environment. Corrosion of metals (Fe, Cu, Zn, Mg) occurs as metallic elements go into ionic solution, which is known as "dissociation".

The rate of dissociation or corrosion varies with the electrolytic/corrosive reaction present. Corrosion can be slowed or halted through materials selection, cathodic protection, protective coating, inhibitors, or design process modification.

The above explains why valve stems corrode. The position of steel and graphite are visible in the galvanic scale where steel (the valve stem) represents the anode, graphite (the packing) represents the cathode. Remaining water from - for example - a hydrostatic pressure test or the process medium

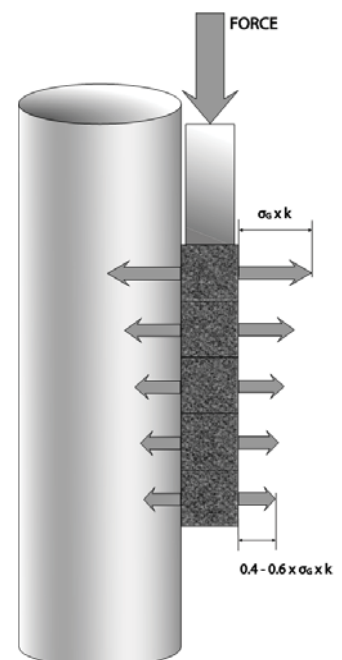


Figure 2

The corrosion process can be explained by showing a corrosion cell (see figure 4). The corrosion cell consists of four elements:

1. Anode
2. Cathode
3. Electrical Connection
4. Electrolyte

All these four elements must exist for corrosion to occur. Therefore, corrosion can be prevented by taking one of these elements away. Oxidation takes place at the anode; the anode is losing electrons. Reduction takes place at the cathode; the cathode is gaining electrons. The position of the metals in relation to each other determines which metal takes the role of anode and which metal takes the role of cathode. This relation is visualized on the galvanic table (see figure 5).

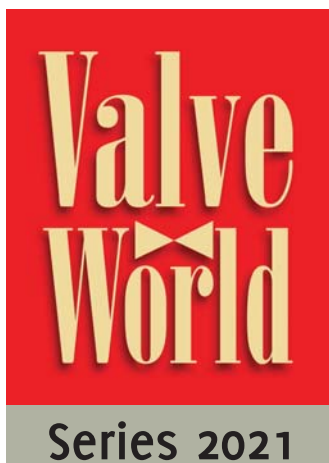




Figure 3

represents the electrolyte, making the corrosion cell complete.

Corrosion prevention

When metals are manufactured, they are created from their ore by adding energy. This puts the metals in a metastable state. This metastable state can be disturbed by corrosion initiators which can be present in various forms.

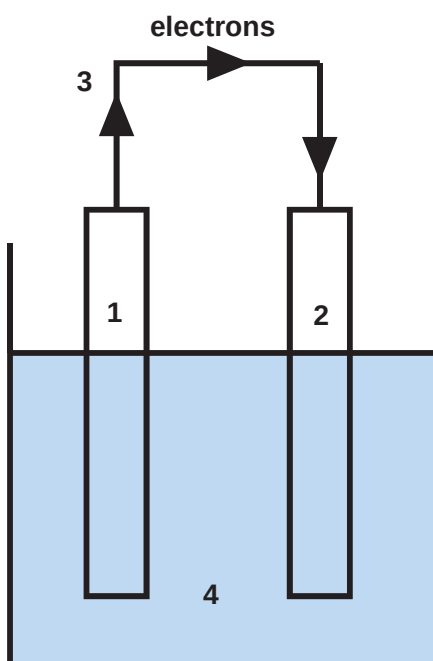


Figure 4

Corrosion can be prevented by the elimination of corrosion initiators, or by taking away one of the four elements of the corrosion cell. Graphite impurities could act as a corrosion initiator. Using high-purity graphite limits the impurities being present that could potentially act as a corrosion initiator. Halogens for instance are related to pitting and crevice corrosion in metals. They can act as a

pitting initiator and although the exact process that takes place is not very well understood, we know that it takes place. This is the reason that nuclear plants limit the presence of halogens to avoid these to get into nuclear cells where they could cause corrosion. This is the reason that chlorides are banned as well because they can cause the presence of micro-environments where hydrochloric acid can cause pitting corrosion. Sulfur is another element that is often banned depending on its present valency (sulfide, sulfite, or sulfate).

Cathodic protection

Cathodic protection is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell. A simple method of protection connects the metal with a more easily corrosive (more reactive) "sacrificial metal" to act as the anode (see figure 6). Sometimes this sacrificial metal is referred to as a sacrificial inhibitor though this is not a correct term from a scientific point of view. Zinc powder or wire is sometimes added to graphite packing to act as a "sacrificial inhibitor".

Passivation

Passivating corrosion inhibitors increase the anodic polarization, hence reducing the potential/current between cathode and anode. This reduction inhibits corrosion through an electrochemical process called passivation.

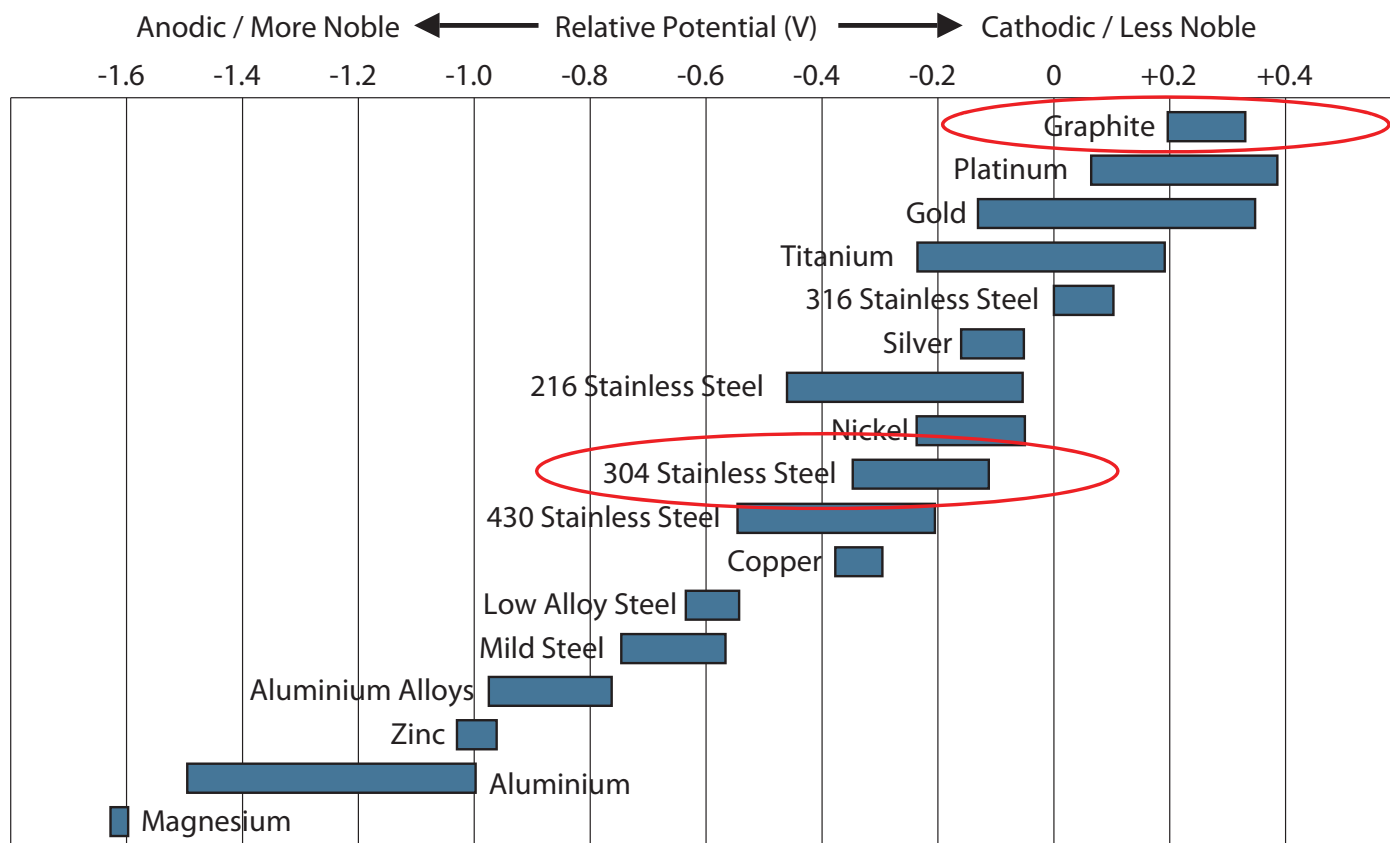


Figure 5

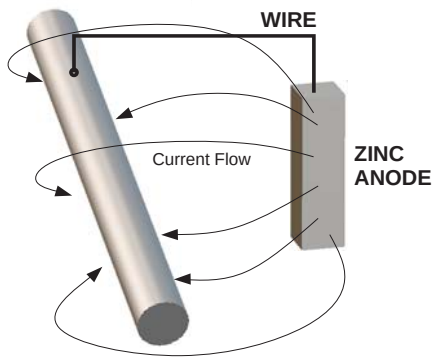


Figure 6

Passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. They are adsorbed on the metal surface forming a protective film or barrier. Passivating inhibitors are usually crystalline salts such as sodium chromate, phosphate, or molybdate. Only the negative anions of these compounds are involved in reducing metal corrosion. At one potential the metal is corroding. At another potential, the metal will stop corroding. Passivation brings the metal into an electrochemical position where it will not lose electrons. An example of a passivating corrosion inhibitor used in graphite packings is barium sulfate.

Pros and cons

All the above-mentioned prevention techniques have their pros and cons. Cathodic protection such as the addition of zinc in graphite packings, whilst being a low-cost option, puts a short expiry date on the packing. There are also concerns with steel embrittlement due to the presence of zinc in some industries. Passivating inhibitors are in that respect much longer lasting and therefore an excellent solution in graphite packings.

Putting purity requirements on graphite packings is common in the nuclear and gas & oil industries. Whilst this removes the presence of corrosion initiators, this might prohibit the use of crucial additives and therefore cause additional challenges.

Pure graphite packings might be able to seal to $\leq 10^{-2} \text{ mg s}^{-1} \text{ m}^{-1}$ (the class CH requirement in ISO 15848-1), but modern fugitive emission legislation require lower leak levels. The combination of graphite purity in combination with low emissions requirements is in some cases impossible to fulfill.

Compromise

For this reason, to make graphite packing seal to Low E emission levels, additives,

amongst which PTFE, are added. Without these additives, the graphite packing will not seal to the low level required in modern emission standards.

Some oil companies demand a very pure graphite packing whilst demanding at the same time very low emissions levels. These requirements are contradictory. Sometimes this issue is solved by allowing exceptions to the end-user's own specification. This is usually done by compromising on the purity requirements. By using a compression packing that is protected by passivating corrosion inhibitors, a valve user can assure that no corrosion will take place whilst being able to seal to low emissions levels.

About the author

Hans Dekker graduated as a Bachelor of Engineering at the Saxion Polytechnic in the Netherlands. He is the EMEA Product Line Manager for Packing and Gaskets for A.W. Chesterton Company.

