Vysus Group

Whitepaper

Rust never sleeps

Abstract

The operation and maintenance of offshore facilities and onshore chemical plants and refineries is both expensive and time consuming. Corrosion and material degradation are the main problem areas. For offshore installations the level of exterior corrosion is enhanced due to the aggressive marine surroundings. In refineries and chemical plants, internal corrosion can be exacerbated due to increased temperature and aggressive chemical mixtures. The consequences of material failure in these locations can be devastating. Unfortunately the main construction and fabrication material used is steel. Steel, whilst being relatively cheap and easy to use is also inherently susceptible to corrosion. This paper discusses the various methods of deterioration and failure in land based and offshore systems. The various mechanisms, characteristics and methods involving corrosion and fatigue and their mitigation are detailed using basic principles, equations and theories. These include Cathodic and Anodic reactions, impressed current, sacrificial anodes, coating systems, and inspection techniques including Risk Based Inspection (RBI).

Keywords: Corrosion, Erosion–corrosion; Fatigue, Cathodic protection, Coatings, RBI

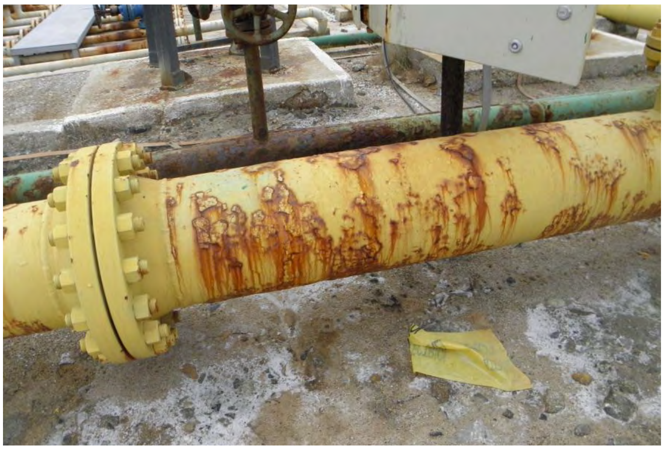


Fig. 1 - Paint breakdown and external corrosion

A better understanding of the problems associated with material degradation and the techniques to mitigate and eliminate them can go a long way to making the whole industry safer and environmentally friendlier.

For those old enough to remember, Neil Young is probably most famous for his song; “Southern Man”. However, he also wrote an album called; “Rust Never Sleeps”. Neil Young wasn’t a corrosion engineer but the title of his album could well be considered as one of the fundamental “laws” of degradation and failure of metallic components.

All steel components start off as iron ore, usually magnetite and hematite. Iron is one of the most abundant elements on our planet and has been used as a construction material for thousands of years. Unfortunately in order to make metallic iron from its ore requires energy. Hence, iron, and steel, which is basically iron with additional elemental additions, is thermodynamically unstable. That thermodynamic instability will ensure the metal will always try to return to its lower energy level. That process is generally called corrosion for metals and specifically called rusting for iron and steel.

Rusting is an oxidation process. This means that metallic iron will react with oxygen and form iron oxide. That reaction will progress at different rates depending on a number of conditions. In general, the worst conditions will be when the iron or steel is immersed in sea water. The corrosion reactions will involve a transfer of electrons and for that to happen an electrolyte will be needed. Sea water is a very good electrolyte because of its high salt concentration.

In order for iron and steel to rust, several reactions must take place.

The anodic reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

The cathodic reaction: $O_2 + 4e^- + 2\,H_2O \rightarrow 4\,OH^-$

Combining these gives: $Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2$

$Fe(OH)_2$ is an insoluble salt that precipitates at the cathode. It is then further oxidised by dissolved oxygen to hydrated ferric oxide, commonly known as rust.

$Fe(OH)_2 + O_2 + H2O \dashrightarrow Fe_2O_3.H_2O$ (rust)

Fig. 3 - Paint breakdown and external corrosion

Fig. 2 - Corrosion at pipe supports

One of the most important aspects of rust is that it is autocatalytic. This means that once rusting starts it will continue unabated unless something is done to stop it. So what can be done to stop it? Well, the easiest way is to prevent it in the first place.

Looking at the Cathodic reaction above it can be seen that it involves oxygen. If we can remove oxygen from the equation then the whole oxidation process cannot happen. This is where impervious coatings come into play. One example of this is the thick bitumen coatings used on marine pipelines. The coating actually serves two purposes in this case. It will act as a physical barrier to both oxygen and moisture. Moisture being the electrolyte needed for the reaction to take place. Many paints perform the same function, however, most paints have a secondary method of corrosion prevention and that is the “sacrificial anode” effect.

In order to understand the principles of a sacrificial anode we need to look at the Galvanic Series. Just about everyone knows that Gold is the most unreactive or noble metal. Gold does not form an oxide. At the other end of the scale Potassium is one of the most reactive. It will oxidise explosively and is so reactive it needs to be stored under oil or de-aerated conditions.

Depending on how reactive a metal is will dictate where on the Galvanic Series it comes. More reactive, then closer to Potassium. Less reactive, then closer to Gold. The interesting thing is that if two dissimilar metals are connected in an electrolyte the more reactive metal will corrode and the less reactive one will not. Quite literally, the more reactive metal will sacrifice itself to save the nobler one and is known as Galvanic Corrosion.

This is the fundamental principle behind sacrificial anodes and why large aluminum anodes are attached to ships and offshore platforms. It is also how many paints help prevent corrosion. Even though a paint film will reduce the amount of oxygen and moisture contacting the metal surface, it will not eliminate it completely. However, if the paint contains minute flecks of a more reactive metal, such as zinc, these will corrode in preference to the underlying steel structure.

In a sacrificial anode system the more reactive metal will corrode and according to the anodic reaction, produce electrons. It is this increase in electron density which inhibits the anodic reaction in the more noble metal. This property is the principle behind an impressed current system of corrosion prevention called “Cathodic Protection”. This method dispenses with a sacrificial anode, instead using an electric current, to deliver electrons into the structure to be protected.

As a general rule of thumb, standard constructional steel will require a potential of approximately -850mV. This voltage level will normally ensure that the corrosion process is stopped or slowed to a very low rate. However, while the Impressed Current system is very effective there can be problems with it. These problems become more serious with higher strength steels and arise if the voltage drops below -850mV. At potentials more negative than -850mV (e.g. -1000mV) we enter the area of overprotection. The increased negative potential causes the production of hydrogen. Unfortunately hydrogen and steel are not a good mix. Hydrogen embrittlement can occur which may reduce the fatigue life of a component by orders of magnitude.

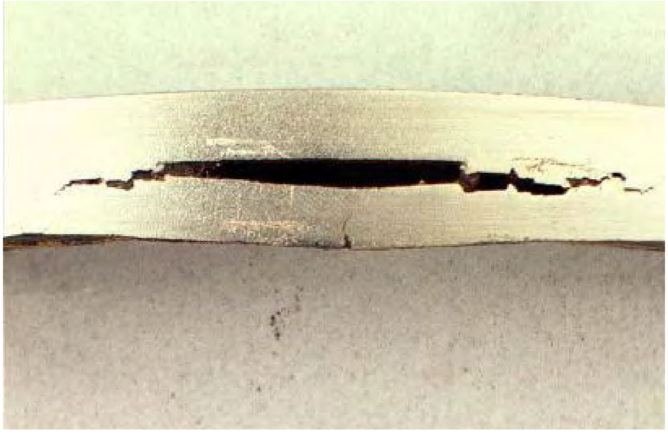


Fig. 4 - Hydrogen Induced Cracking in linepipe steel

Fatigue is a degradation process where cyclic loads reduce the strength of a material and eventually cause failure. It can be easily demonstrated by taking a paper clip and bending it back and forth several times. It will start to become more pliable and then break in two. This failure is called Fatigue because when the phenomenon was first analysed it was thought that the metal got tired. The name stuck even after the mechanism was understood. What makes fatigue so onerous is that the cyclic loads applied can be much less than the Ultimate Tensile Stress and even the Yield Stress of the material and still failure can occur. Reducing the magnitude of the cyclic stress increases the number of cycles before the component fails, but it will still eventually fail. As bad as the problem of fatigue is, it is much worse when corrosion is introduced producing a phenomenon called Corrosion Fatigue. The effect of Corrosion Fatigue is termed synergistic. In simple language this means that the effect of both conditions taken together are greater than the sum of them when taken separately. In essence; 2 + 2 = 5.

It is widely recognised that sea water is one of the most aggressive natural environments on the planet. However, many refineries and chemical plants contain chemical mixtures which can destroy “ordinary” constructional materials in a very short time. In these cases it is necessary to use “exotic” materials such as highly alloyed stainless steels or alloys with high concentrations of Nickel and Copper such as Inconel or Monel. Many of these alloys form inert and tenacious oxide films which form barriers to whatever aggressive medium they are in contact with. These materials tend to be very expensive and require extra care in fabrication, especially welding, but in many situations there are few alternatives.

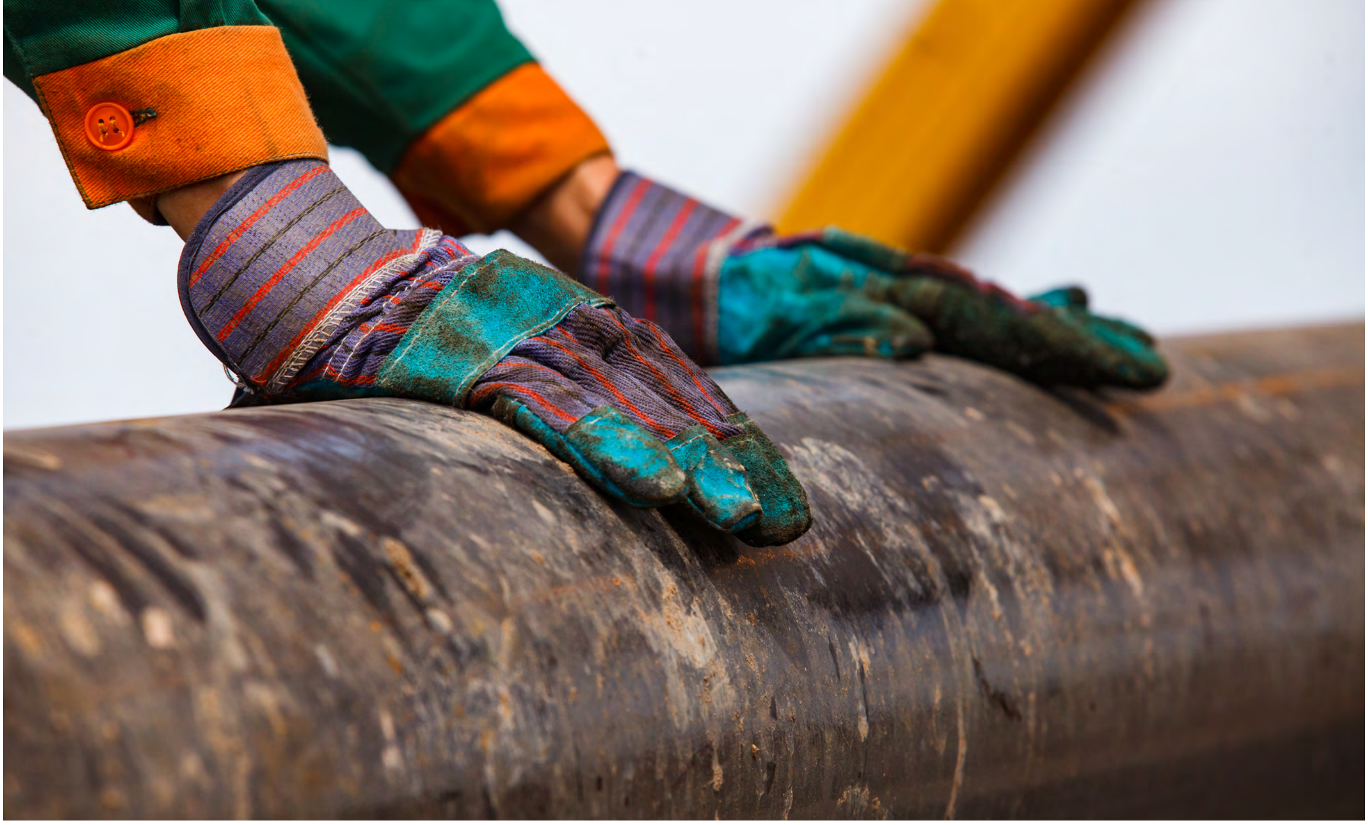
One of the major problem areas on offshore platforms is Corrosion Under Insulation (CUI). An offshore platform presents a particularly harsh environment for steel. Pipework needs to be protected either by wrapping or coatings. Some pipework also needs to be wrapped because the contents are at a very high temperature and the wrapping will be used for either insulation or protection or both. Unfortunately it is very difficult to

Fig. 5 - Corrosion Under Insulation

examine pipes which are covered with any kind of wrapping and from a corrosion point of view, it has been very much a case of “out of sight, out of mind”. If the wrapping becomes perforated and water is allowed to collect inside the wrapping then there is a very high likelihood of increased corrosion activity. The best way to inspect for CUI is to completely remove the covering; however, this can be time consuming, costly and impractical in many cases. This is where experience and efficient monitoring systems can be extremely beneficial. Previous experience of similar systems will identify locations of high susceptibility, for example, low spots in the line and areas which have a temperature profile which means water will remain in liquid form and not evaporate off. These areas can be ranked and given a risk factor.

It is this allocation of risk which is providing tremendous benefits in terms of efficiency and cost savings over traditional inspection methods. Risk Based Inspection software will utilise current and historical information and produce a prioritised inspection regime. It is by prioritisation that cost savings and efficiency can be achieved. Without prioritisation, inspection can fall into the “shotgun” or “hit and miss” approach which really only results in what is termed “firefighting”. Areas are inspected because they are easy to get at or they have been problematic in the past. The actual efficiency of the inspection regime will be quite low because many potential problem areas will be missed. We will spend a lot of time, energy and resources doing this “firefighting”. The smarter way to deal with the problem is to stand back and have a look at the whole system and determine what causes the “fires” to occur in the first place. We can then address the instigators of these problems and if we take care of those then effectively the problems never arise. Part of that “stand back and have a look” necessitates an effective inspection regime.

Effective inspection regimes involve; identification, prioritisation and systemisation.



Identification involves ascertaining where the problem areas are and what failure mechanisms are involved. Internal corrosion / erosion, external corrosion, CUI, corrosion fatigue, stress corrosion cracking and hydrogen induced cracking are a few of the major failure mechanisms.

Prioritisation involves a process of ranking the different consequences of failure unveiled in the identification step and incorporating a measure of probability of them occurring. There are a number of different ways in which to rank and prioritise. These include loss of life, loss of revenue and environmental impact.

Systemisation involves both being systematic and covering all the relevant systems. This will necessitate effective allocation of time and resources which may be a bigger obstacle than it seems. A great example is trying to organise offshore inspections in a geographical region which is subject to excessive bad weather i.e. fog or rain. Helicopters get cancelled and vessel movements are disrupted which invariably leads to the inspection regime being compromised.

Ultimately the Oil and Gas industry is full of challenges which can consume large amounts of time, money and resources. A better understanding of the problems associated with material degradation and the techniques to mitigate and eliminate them can go a long way to making the whole industry safer and environmentally friendlier.

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