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MICROBIOLOGICALLY INDUCED CORROSION (MIC) IN X2CRNI19-11 COOLING WATER COIL IN A NO_X ABSORBER OF A NITRIC ACID PLANT

Case 2, continuation on Technical Bulletin 2005/11

Introduction

After completion of the erection of a new nitric acid plant a test run with cooling water was performed in the cooling water coils of a NO_X absorber of a nitric acid plant. This cooling water, originating from the river Maas, contains some 50 to 100 ppm chlorides.
However, as a result of a recession the plant start-up was delayed for some 6 months. It was overlooked to flush the cooling water coil with demineralised water to remove the chlorides.

Leakage in cooling water coil due to MIC

About half a year after the test run with cooling water the plant start up was initiated. During this start up entrainment of nitric acid was observed in the cooling water as a result of serious pitting in the X2CrNi19-11 cooling water coils of the NO_X absorber. The pitting started from the inside (cooling water side) of the coil in an area with abundant porous oxide scaling (heat tint) as a result of external field welding as shown in figure 1 and photo 1.

Photo 1
Pitting due to MIC in cooling water coil of NO_x absorber.

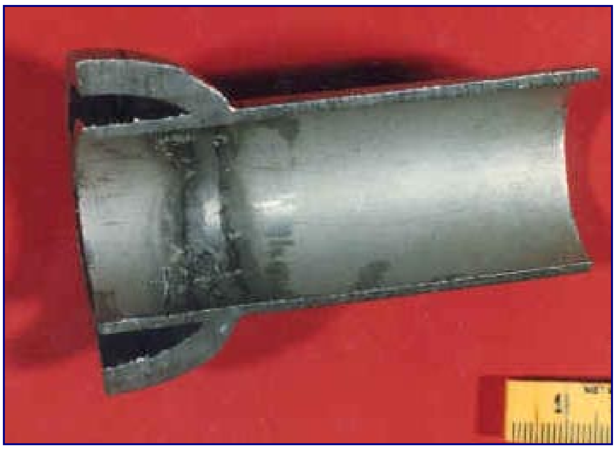
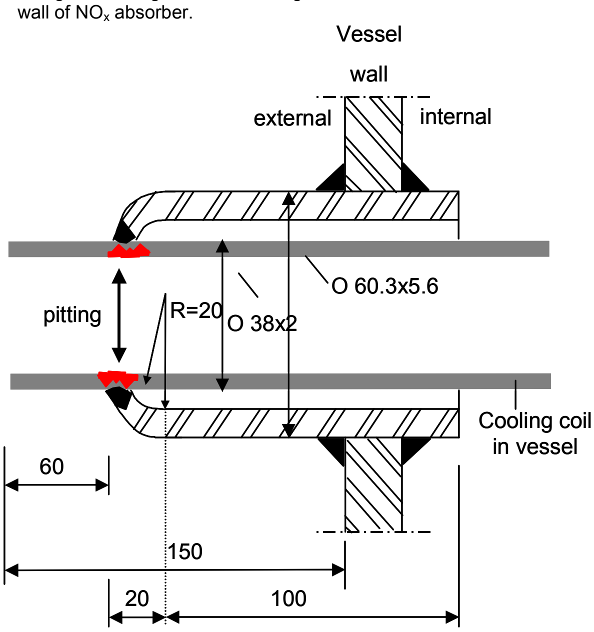


Figure 1
Design of cooling water coil through the wall of NO_x absorber.



Obviously, the heat tints were not removed despite recommendations in the specification.
The stagnant cooling water, the presence of the porous oxide scale and formation of a biological slime film in the stagnant cooling water caused the rapid perforation of the coil. It was recognized that this extremely rapid pitting attack was influenced by microbiological processes.

Mechanism of Microbiologically Induced Corrosion

Microbiologically Induced Corrosion (MIC) is the term used for the failure mode in which the corrosion is initiated, propagated and/or accelerated by micro-organisms like bacteria, algae, fungi, etc. Generally, the morphology of the failure mode is pitting or a crater type attack. MIC is a widely recognized failure mode in water systems, especially in cooling water systems in which, generally, sufficient nutrients are present.

There are several types of MIC, one of these types being MIC due to increase of the electrode (metal) potential under slime formation.

Aerobically produced biofilms catalyze the cathodic reduction of dissolved oxygen probably via intermediate formation of hydrogen peroxide. The peroxide is further reduced to hydroxyl ions.

$O_2 + 2H_2O + 2e \Leftrightarrow H_2O_2 + 2OH^-$

$H_2O_2 + 2e \Leftrightarrow 2OH^-$

As a consequence the electrode potential is raised. This potential is likely to exceed the critical potential for pitting in stainless steel when chlorides are present.

In experiments performed in the laboratories of DSM TechnoPartners it was found that the potential of a 304L stainless steel (X2CrNi19-11) electrode exposed to cooling water (originating from the river Maas) increased substantially within a couple of days.

The susceptibility of stainless steels to (microbiologically induced) pitting corrosion can be explained by means of a cyclic voltamogram as shown in Figure 2.

In the cyclic voltammetry experiment the potential of the test electrode is shifted relatively slowly and anodically (e.g. at 1 mV/sec) from a low cathodic value (e.g. 100 mV below the free corrosion potential). The current increases strongly when the so-called pitting potential (E_{pit}) is exceeded (dependent on type of material, pH and temperature). When the anodic current exceeds a preset value (e.g. 1 mA/cm^2), the scan direction is reversed and the scan proceeds cathodically until the starting potential is reached.

Even when the potential decreases, the corrosion process continues (often the current even increases) because of the increased corrosiveness of the occluded solution.

Eventually, the potential becomes too low to sustain corrosion and the process is stopped. The potential where the corrosion current becomes lower than the passive current is called the protection potential (E_{prot}). Usually, the pitting potential is more or less well defined, but the protection potential is also dependent of the amount of damage during the pitting process.

With higher chloride content the E_{pit} and the E_{prot} values decrease and as a consequence the tendency for pitting increases. In the porous oxide layer chlorides will be selectively adsorbed and the pH will drop. The slime formation led to a rise of the potential of the stainless steel pipe above its critical pitting potential.

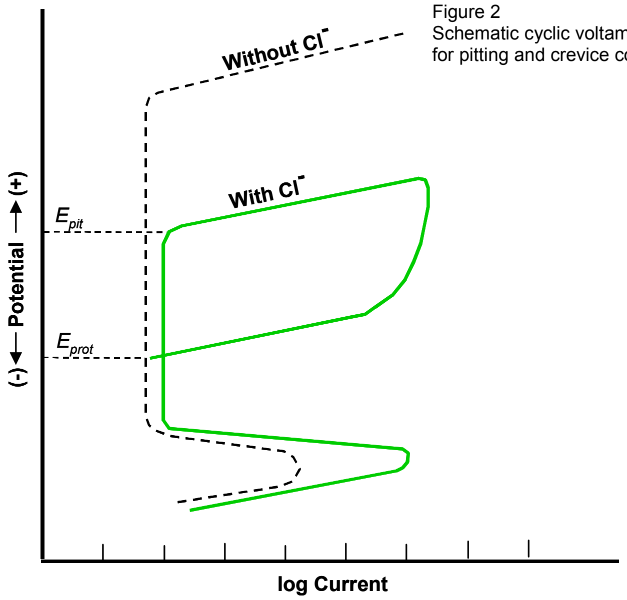


Figure 2
Schematic cyclic voltamogram for pitting and crevice corrosion.

Conclusions and recommendations

- The rapid perforation by pitting of the cooling water coil is due to the stagnant, chloride containing cooling water, the presence of heat tints and formation of a biological slime in the stagnant cooling water.
- To avoid or minimize the risk of microbiological induced pitting corrosion heat tints should be removed.

Literature

Susan Watkins Borenstein
Microbiologically Induced Corrosion Handbook

Author: G. Notten (Senior Corrosion Engineer)
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