

A CASE STUDY ON CORROSION OF STAINLESS STEEL IN FIREWATER MAINS

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Abstract

Traditionally, many firewater mains were made of carbon steel or cast iron. At present, more and more stainless steel is used as material for firewater pipes due to usually better corrosion resistance in natural waters than iron or carbon steel. In some few cases, however, unexpected corrosion failures in systems using austenitic stainless steels were observed only after a relatively short time of usage ranging from a few weeks to a few years. Most of these corrosion damages were found on the weld nuggets or in the heat-affected zones of on-site girth welds. One of the most important factors affecting the corrosion resistance of stainless steel at welds and in heat-affected zones are the surface oxide films originating from the welding heat in the presence of oxygen (heat tints). Therefore, proper root shielding is important especially when welding pipes for fire protection systems where the water is taken from natural sources (e.g. from rivers, lakes or tap water), as microbially induced corrosion (MIC) can increase the risk for corrosion damages significantly. Two failure cases in fire protection systems, one in a stainless steel factory and one in a power plant have been studied and are described in this paper. A proposal for the mechanism is suggested and general recommendations how to avoid or diminish the risk for unexpected localised corrosion failures are given.

Introduction

Carbon steel or cast iron are traditional materials for firewater mains. Clogged tubes due to corrosion of these materials have caused problems over the years and alternative materials have been considered. Stainless steel has nowadays started to be used in firewater piping. Stainless steel has usually an excellent corrosion resistance in cold, flowing, low-chloride containing water. In stagnant water, like it is usually found in firewater systems, the corrosion resistance evidently diminishes. This is the case also when the temperature or the chloride content increases. Thiosulphate is known to have a detrimental effect on the pitting corrosion resistance of stainless steel if it exists in a proper ratio to chloride and/or sulphate [1,2].

Corrosion of stainless steels in natural waters and in systems using such water is typically localised corrosion. In welded structures, corrosion is often concentrated in the weld nugget itself or in the heat-affected zone. The openings of the corrosion pits are typically very small but large subsurface cavities are often formed. Especially on-site welds, like welded butt joints of pipes, are vulnerable to such pitting failures. On-site welds are usually welded from the outside of the pipe using shielding gas inside. Normally it is difficult or even impossible to clean the root of the weld after welding properly. If the shielding gas contains already a relatively small amount of oxygen, heat tint layers (coloured oxides) will be formed close to the weld. The pit initiation potential in these areas as well as on the weld itself is usually lower than on the base metal.

These heat tint layers promote the initiation and growth of corrosion pits even in seemingly harmless environments [3,4].

Natural waters contain always a diversity of microbes and thus these seemingly harmless environments might turn out to be aggressive. Microbes can change the environment's corrosiveness either chemically or physically. This phenomenon is called microbially induced corrosion (MIC). It is generally accepted that the ennoblement (increase of the open circuit potential) of stainless steel surfaces detected all over the world in ocean waters, brackish waters, rivers and even tap water is caused by microbial colonisation. This ennoblement can exceed the pit initiation potential. However, the mechanism of ennoblement is not clear and many different hypotheses and theories have been suggested during the years. One of these is the role of manganese oxidising bacteria, which can oxidise Mn^{2+} to the strong oxidant Mn^{4+} causing the potential of the metal to rise. Sulphate reducing bacteria (SRB) have often been detected together with iron and manganese oxidising bacteria on failure areas of stainless steels. SRBs can lower the redox potential within the deposits on the surface by producing sulphides (S^{2-}). Another way for SRBs to enhance the corrosion of stainless steel is to form thiosulphate ($S_2O_3^{2-}$). SRBs consume sulphate (SO_4^{2-}) by reducing it to sulphide, which can be oxidised to thiosulphate in the presence of air. In simulated paper machine water, it has been demonstrated that thiosulphate produced by the metabolic activity of SRBs caused severe pitting corrosion to stainless steel [2].

In this paper, failure analyses of two case histories of fire protection systems suspected to be caused by MIC are presented.

Case Histories

Case 1: Fire Protection System in a Stainless Steel Plant

The fire extinguishing system in a stainless steel plant had been earlier made of carbon steel and is gradually being changed to stainless steel type EN 1.4301. The removed carbon steel pipes were heavily corroded and had huge amounts of reddish brown deposit and tubercles inside the pipes after 20 years of usage. The examined stainless steel parts have been installed in the cold rolling plant in 2002 and some failures occurred after less than three years of usage. The raw water comes from a river nearby, is not specially treated and stays stagnant most of the time. The temperature varies from about 5-10°C in some staircases during winter times to up to 50°C over furnaces of the annealing lines. Stainless steel is also partly used in the hot rolling plant's fire protection system (FPS). The water comes from the same source but the water in the system is used for washing about once a week instead of the stagnant situation at the cold roll mill. No failures have been detected in these stainless steel pipings after over 15 years of usage. The chloride content of the river is usually very low (~1 mg/l). Only very seldom higher chloride values have been measured, when brackish water (~1000 mg/l of Cl^-) from the sea nearby is mixed with river water during times of strong southern wind. The sulphate content in the river water is also low (~3 mg/l); its alkalinity is low (~0.35 mmol/l) as well as its hardness (~0.17 mmol/l); pH is neutral (~7.0); the amount of manganese is low (~0.006 mg/l) and that of iron is rather high (~0.5 mg/l). The pressure in the system is 13 bar due to the height of some buildings.

Case 2: Fire Protection System in a Power Plant

In Case 2, the pipes of the system were also originally constructed from carbon steel and had been gradually replaced by austenitic stainless steel pipes (both EN 1.4301 and EN 1.4401). There were still some parts made of carbon steel or cast iron in the system and the water contained high amounts of precipitated iron. The water used in this fire extinguishing system was tap water with a low chloride concentration. The water was treated with chloramine when the system was filled with water. The water stayed stagnant most of the time and was changed only

once a year. Unexpected pitting corrosion in stainless steel pipes of this FPS was observed after just a few years of service. The pits detected were situated in the welds or in the heat-affected zones. The first perforations were detected in EN 1.4401 stainless steel pipes after two years of operation. Later on, several pits causing leaks were also detected in the EN 1.4301 material. The pressure in the piping system was 10 bar and the temperature was ambient (20...25°C).

Experimental Procedures

Metal samples were removed from the systems and were examined visually and under a stereomicroscope. The chemical compositions of the pipe material and the weld metal were analysed with an optical emission spectrometer (OES). Metallurgical examinations consisted of optical light microscopy of cross sections prepared from the samples, scanning electron microscopy (SEM) studies from failure areas and energy dispersive spectroscopy (EDS) of corrosion products or of the deposits on the inner surfaces of the pipes. In Case 1, the metal samples were completely dry when arriving at the laboratory. Therefore, traditional methods like cultivation could not be applied to detect possible bacteria. However, preliminary trials with a new PCR-method were performed with one sample showing corrosion failure. In Case 2, microbiological assays were also performed. The total counts of aerobic and anaerobic bacteria and the amount of sulphate reducing bacteria were analysed by cultivation from the samples taken at site, from the water inside the pipes as well as from the deposits on the surfaces of the pipes. Samples were scraped from several places on the surface of the opened pipe. The system had been opened half an hour before the sampling.

Results

Case 1

The failures of the removed metal pipes (EN 1.4301) occurred in less than three years of usage. Some pits already perforated the pipe wall. Most of the corrosion attacks detected were either in the fusion line or in the heat affected zone, Figure 1. Although the weld itself was uneven and partly incomplete in some cases, the corrosion did not occur especially in those areas. Instead, colourful heat tint areas could be seen on the failed pipes. The heat tint colours ranged from very dark blue to dark brown.

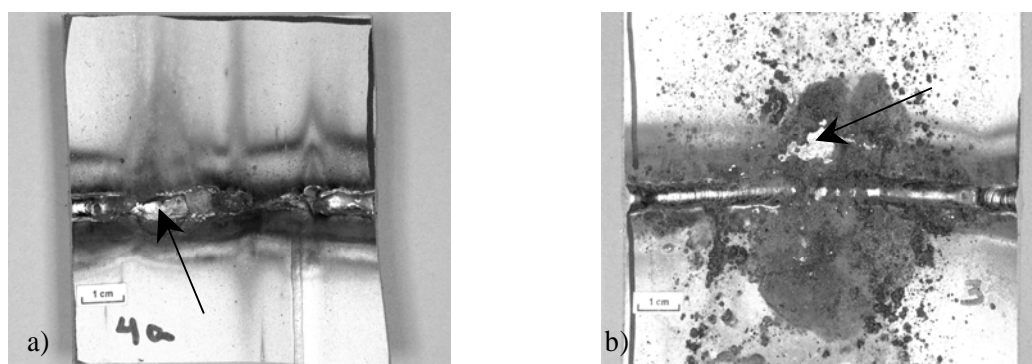


Figure 1. Pits (black arrows) a) in the fusion line and b) in the heat-affected zone of the weld.

For the common stainless steels types EN 1.4301 and 1.4401, it is usually considered that a slightly straw-yellow heat tint and otherwise clean weld indicate that the shielding gas protection has been satisfactory. All other colours indicate significant decrease in corrosion resistance [5]. In Figure 1a, also multicoloured areas linked to corrosion besides the heat tint areas can be seen. Iron, oxygen and carbon were the main elements of the EDS-analyses of the deposits on the inner surfaces. Moreover, chromium and nickel as components of stainless steel as well as

manganese, sulphur and occasionally also phosphorus and chlorine originating from the environment were detected. High amounts of iron, manganese and chlorine had been detected earlier in deposits of MIC failure cases of stainless steels. Also the presence of sulphur and phosphorus can be regarded as an indication of bacterial involvement. Microbiological results taken from the failure area of one of the samples showed signs of bacteria. From this sample, bacterial DNA was isolated and multiplied with PCR using eu-bacteria primers. However, it was not possible to identify the different species without sequencing. The metallographic examination did not reveal any abnormalities in the normal austenitic microstructures of the studied samples.

Case 2

The first perforating pits in this fire extinguishing system were observed in a type EN 1.4401 stainless steel pipe with a diameter of 140 mm and a wall thickness of 3 mm. The leaks were situated near a girth weld. Visual inspection of the pipe sample revealed two perforations that were located in the heat-affected zone close to the fusion line of the on-site weld. Plenty of reddish brown deposit was found on the opposite inner side (Figure 2a). Similar reddish brown deposits and deposit rings were observed on the inner surfaces of type EN 1.4301 stainless steel pipes removed from the fire extinguishing system later. Typically, the openings of the pits were very small having large subsurface cavities (Figure 2b). The chemical compositions of the type EN 1.4301 stainless steel samples were according to the specifications within the ASTM standard boundaries except for some of the samples, which contained less than 18 % Cr (17 and 17.7 %). The microstructure of both materials was normal austenitic. The pits were typically situated close to or in the transversal on-site welds. There were clear signs of oxidation of heat-affected zones (heat tints) but no other signs for welding defects were found in the failure areas.

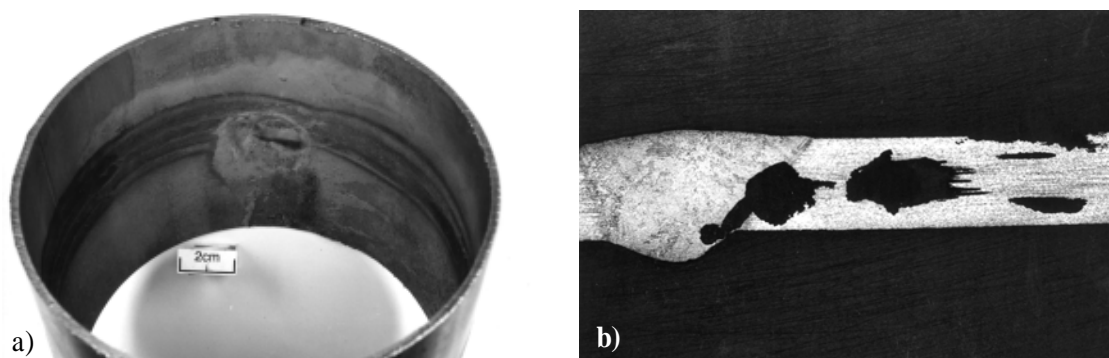


Figure 2. a) Reddish brown deposit on the inner surface of a stainless steel type EN 1.4401 pipe section removed from the fire extinguishing system. b) Optical micrograph of a trough-wall, mainly subsurface corrosion pit in an EN 1.4401 type of stainless steel pipe after two years of service in fire extinguishing water.

The pits were typically surrounded by dark brown circular deposit rings and the inner surfaces of the pipes were mostly covered with a thin and rather smooth layer of yellowish brown deposit. Sulphur and occasionally also high amounts of manganese as well as small amounts of phosphate were detected in the deposits in or surrounding the pits.

The results of the water analysis from a water sample taken a few months after the first leaks occurred (water A) is given in Table 1. In the same table, also the analysis of a water sample taken from the same fire extinguishing system two years later in relation to the leakage of the type 1.4301 pipes (water B) is listed. Water C is used as feeding water for the fire extinguishing system and can be regarded as typical drinking water.

Table 1. Chemical analysis of the water samples taken from the fire extinguishing system of the power plant.

Water	pH	Fe mg/l	Mn mg/l	Ca mg/l	Mg mg/l	Cl ⁻ mg/l	SO ₄ ²⁻ mg/l	HCO ₃ ⁻ mg/l	NO ₂ ⁻ mg/l	NO ₃ ⁻ mg/l
A	6.0	0.01	0.40	8.8	4.0	28	n.a.*	n.a.*	n.a.*	n.a.*
B	7.2	0.44	0.53	12.0	4.4	21	34	20	<0.01	1
C	7.8	0.05	0.02	12.0	4.7	24	27	26	<0.01	<1

* not analyzed

The total count of aerobic bacteria in samples taken directly from the surfaces of the opened system was clearly higher (from 1.1×10^3 to 7.3×10^3 cfu/ml) than in the water sample (32...50 cfu/ml). SBRs could be detected from the pipe sample, which had been delivered to the laboratory with a moist deposit still on its surface. Also the amount of aerobic bacteria in this sample was rather high, namely 4.3×10^6 cfu/cm², which was clearly higher than that in the pipe sample with dried deposit (20 cfu/cm²). Both samples contained through-wall pits. The presence of iron bacteria was verified from the sample delivered to the laboratory and the water taken simultaneously from the fire extinguishing system under consideration. The amount of heterotrophic aerobic bacteria was quite high (4.3×10^5 and 2.4×10^5 cfu/ml respectively). Plenty of individual rod-shaped bacteria as well as cell aggregates and starting biofilm formation on the stainless steel coupons incubated six days in an iron bacteria culture medium could be seen under the epifluorescence microscope. The presence of manganese oxidising bacteria was not checked.

Discussion

Both failure cases occurred after a short time of usage in water with low chloride content. Under normal conditions, these types of water are not regarded as corrosive to the stainless steel types EN 1.4301 or EN 1.4401. However in these cases, the water was stagnant most of the time and only occasionally used. In stagnant waters with the possibility for deposit formation, the corrosion resistance of stainless steels is clearly diminished. During long stagnant periods, the stainless steel surface is not cleaned and bacterial activity may increase. The presence of bacteria was verified for Case 2 and indications of bacteria growth were found also in Case 1. It is generally accepted that the noble shift of the open circuit potential of stainless steels detected all over the world in natural waters is caused by microbial colonisation. This ennoblement can exceed the pit initiation potential even in low chloride waters. Usually the pit initiation potential on the weld and on the heat-affected zone is lower than on the base metal. Therefore, pitting corrosion starts often in these areas. Heat tint layers are also rich in iron and manganese oxides, which might explain why harmful bacteria tend to attach to these areas as well. Ennoblement alone cannot cause pitting corrosion. There has to be also some anions able to produce strong acid solutions inside the pit. Chlorides are the most common anions causing pitting corrosion of stainless steels by forming concentrated metal chloride solutions inside the pits. In typical pure drinking waters having low chloride concentrations (6...30 mg/l) the pitting potential for stainless steels at room temperature is very high (>1000 mV_{SCE}). In our earlier study [3], the effects of heat tints on pitting corrosion were examined in chloride solutions at room temperature. It was shown that pits could initiate at substantially lower potentials in heat tint areas than in areas without heat tints. However, the potentials required for continued growth of open pits in a dilute (106 mg/l Cl) plain chloride environment were considered still quite high for serious pitting in seemingly harmless environments to be explained by the presence of heat tints alone. In the presence of sulphates, the needed amount of chlorides to initiate corrosion is even higher and is depending on the molar ratio of chlorides and sulphates.

In many cases where pitting corrosion of stainless steels in fresh waters occurred, manganese and/or iron oxidising bacteria (like *Leptothrix*, *Siderocapsa*, *Gallionella*) had been detected. Iron oxidising bacteria can oxidize ferrous iron to ferric iron, which then reacts with the chloride ions

producing ferric chloride [6]. Ferric chloride is extremely aggressive causing pitting corrosion on stainless steel. The deposits from the bacteria are rich in ferric chloride and attack aggressively austenitic stainless steels. Manganese oxidising bacteria oxidise Mn^{2+} to Mn^{4+} , which is a strong oxidiser as well. In the studied cases, indications of iron oxidising bacteria were detected from the deposits. The presence of manganese oxidising bacteria was not tested. Anaerobic SRBs were also found in failure areas often together with manganese- and iron-oxidising bacteria, as was shown also in our Case 2.

Another mechanism of how microbes can affect the initiation of pitting corrosion of stainless steels is the formation of thiosulphate. This type of pitting does not need the ennoblement of the steel but can occur at lower potentials than in pure chloride environments. SRBs consume sulphate by reducing it to sulphide and which in the presence of air can be oxidized to thiosulphate. During the stagnant periods in the system, anaerobic bacteria like SRBs produce sulphide. During occasional usage of the fire extinguishing system when oxygen or oxygen containing new water can enter the system, thiosulphate is formed. In simulated paper machine water, it has been demonstrated that thiosulphate produced by the metabolic activity of SRBs caused severe pitting corrosion of stainless steel type EN 1.4301 [2].

The waters in both cases contained also a high amount of precipitated iron. The high concentration of iron in the water can offer suitable conditions for iron oxidising bacteria. Besides iron hydroxides can behave as anion selective membrane at neutral pH and had been shown [7] playing a certain role for the occurrence of localised attack of stainless steel.

Conclusions and Recommendations

The influence of microbial activity played a decisive role in these pitting corrosion cases of stainless steel piping in firewater mains. The presence of precipitated iron and heat tint areas of welded structures increased the danger for corrosion failure.

The best way to prevent the formation of deleterious oxide layers is to remove oxygen from the piping by shielding gas flushing before welding and using backing gas during the whole welding process and some time afterwards. The oxidation of the weld root can be reduced also by using root paste. This paste reacts with the welding heat and forms a slag layer on the root side of the weld. However, the results achieved with root paste are not anywhere near the results achieved by using backing gas. Alternatively, heat tints can be removed by pickling after welding. However, this is not always possible when considering the welding of piping containing natural waters. To avoid this kind of failures one should use water as clean as possible with low amounts of solids, chlorides, manganese and iron as well as a low amount of organic substances. Additionally, stagnant conditions or very low flow rates should be avoided as well. If continuous flow is not possible, the water should be changed frequently enough and the amounts of bacteria should be checked regularly. When necessary, the water should be treated to minimise bacterial activity. In Case 1, no failures had been detected in the system using the same water with regular use (once a week). In Case 2, the problems had been solved by using very clean demineralised water and circulation.

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