Unexpected corrosion of stainless steel in low chloride waters – microbial aspects

Lisbeth Rischel HILBERT[1], **Leena CARPÉN**[2], **Per MØLLER**[3], **Frank FONTENAY**[1], **Troels MATHIESEN**[1]

[1]FORCE Technology, Denmark, LTH@force.dk
[2]VTT, Finland, Leena.Carpen@vtt.fi
[3]Technical University of Denmark, Denmark, pm@mek.dtu.dk

Abstract

Stainless steels EN 1.4301 and 1.4401/1.4404 are normally considered corrosion resistant in low chloride natural waters like drinking water. However, a number of corrosion failures have been observed in e.g. fire extinguisher systems and drinking water installations, where stagnant conditions or periods of low water consumption have occurred prior to the failure. Typically the corrosion attacks appear within 2-3 years in weld nuggets, heat affected zones or in crevices like e.g. press fitting pipe connections. The failure mode is pitting and crevice corrosion leading to leaks and rust stains on the outside of the installation. Corrosion may occur in water qualities with rather low chloride contents and fairly low conductivity, which would usually not be considered especially corrosive towards stainless steel.

One key parameter is the ennoblement documented on stainless steel in drinking water qualities, due to the formation of a biofilm. In itself, this is not enough to initiate pitting in these water qualities, but combined with a geometrically or metallurgically vulnerable area, corrosion may accelerate. The mechanism is linked to the naturally occurring microbial activity, where the localisation and growth of specific bacteria depend on the environment. Inside a crevice the oxygen content will decrease and anaerobic, stagnant conditions will form leading to growth of e.g. sulphate-reducing bacteria, whereas the heat tint on a heat affected zone with its high content of iron facilitates the growth of iron oxidising bacteria. A number of failure cases from Danish and Finnish stainless steel installations are discussed with the objective to identify key parameters, suggest possible mechanisms and discuss whether prediction is possible.

The paper includes a short literature review, practical experience with corrosion in connections in stainless steel installations - either welded connections or press fittings - and suggested mechanisms for the microbiologically influenced corrosion of stainless steel in low chloride water. This cooperation was facilitated by COST D33 “Nanoscale electrochemical and bio-processes at solid-aqueous interfaces of industrial materials”.

Keywords: “stainless steel”, “press fittings”, “microbially influenced corrosion”, “drinking water”, “crevice corrosion”

Introduction

Stainless steels EN 1.4301 and 1.4401/1.4404 are normally considered corrosion resistant in low chloride natural waters like drinking water [1]. However, for Danish and Finnish stainless steel installations a number of corrosion failures have been observed in e.g. fire protection systems and drinking water installations, where stagnant conditions or periods of low water consumption have occurred prior to the failure. Corrosion attacks are found in weld areas or in press fitting connections. These cases are discussed with the objective of identifying key parameters, suggest possible mechanisms and discuss whether prediction is possible.

In an expert consensus on microbially influenced corrosion (MIC) by NACE International TG 304 [2], an overview of likely places for MIC to occur is given. This includes water distributions systems, cooling water, fire protection systems etc. and stresses the critical conditions of stagnant areas. It furthermore links a number of organisms as being responsible for the enhanced corrosion. For anaerobic systems like dead ends in fire protection systems the interesting bacteria are anaerobic and sulphate reducing bacteria (SRB), whereas in water distribution aerobic and anaerobic acid producers, SRB, manganese and iron oxidising bacteria (MOB, IOB) could be involved.

Industrial systems are often monitored in order to obtain good process control, and fire protection systems must be checked for safety reasons. For drinking water installations in public or private buildings control is generally limited to an external visual control, if this at all is possible. Furthermore the water quality is usually only monitored by periodical general analyses of specific chemical and microbiological parameters at the waterworks.

In Finland stainless steel is rarely applied for drinking water installations, but in a number of water distribution systems and fire protection systems stainless steel is being used replacing older installations of carbon steel or cast iron. Corrosion resistance of stainless steel in cold, flowing, low-chloride containing water is excellent, but diminishes with increasing temperature, chloride content or stagnant conditions. In welded structures, corrosion is often concentrated in the weld nugget itself or in the heat-affected zone [3, 4]. On-site welds are often welded from the outside of the pipe using shielding gas inside. Normally, it is difficult to clean the root of the weld after welding properly and heat tint layers (coloured oxides) will be formed close to the weld, if the shielding gas is not optimum. These heat tint layers promote initiation and growth of corrosion pits in seemingly harmless environments and the pitting resistance is reduced in both the heat affected zone and in the weld itself. The pitting resistance in chloride media with sulphide produced by microorganism has also been shown to be lowered for the specific microstructure formed in the heat affected zone, which is also affecting the morphology of pitting attacks [5, 6].

The use of stainless steel EN 1.4401 type for drinking water installations has been rapidly increasing in Denmark over the last decade. Stainless steel rarely causes corrosion problems and furthermore the consumers get better water quality at the tap due to lower metal release than in systems of hot dip galvanised steel, copper and copper alloys, which are the materials traditionally used for installations in Denmark [7]. Polymer materials are also used widely and recommended in more corrosive water types. In general chlorination is not applied in Danish drinking water, and the overall intention is to treat the water as little as possible to avoid disturbing the natural biofilm in the water supply system. However a few waterworks are forced to disinfect the water by chloramines because of too high numbers of vibrio. Stainless steel installations are commonly chosen for critical water distribution systems as in hospitals, where the development of biofilm and pathogenic bacteria in the system must be limited, and in some of these cases welded connections are preferred.

A small number of failures in stainless steel press fittings occurring within 2 years from installation seem to be the primary problem with the Danish stainless steel installations. The water quality is not considered aggressive towards stainless steel, and the chloride content is often low, but still crevice corrosion develops in the connection between pipe and fitting causing rust stains and small leaks at the outside of the connection. The Fe^{2+} ions from the crevice are mixed with the oxygen containing water in the pipes forming Fe_2O_3 on the inside of the pipe surface and at the crevice Often the failure is more of a visual problem than severe leakage, but it may still be unacceptable for the consumer for several reasons, including the metal release of iron, nickel, and chromium. The failures discovered are typically in larger public buildings.

Laboratory testing of the susceptibility to crevice corrosion for pipe/connection systems based on break-through potentials in simulated drinking water (demineralised water + chloride) indicates that it is safe to use 1.4401 connections in the temperature range 20-65 °C [8]. However, these data were not obtained in natural drinking water and test duration is usually short. The corrosion attacks in low chloride water have been linked to microbial activity, and it does cause concern regarding the wide application of stainless steel and the general recommendation for Danish water systems. If we were able to understand the mechanism and the conditions needed for MIC to develop in these systems, these corrosion attacks might be predicted and prevented. For the industry this will mean a higher success rate in choosing the right material for an installation and less costs and disturbance for the consumer.

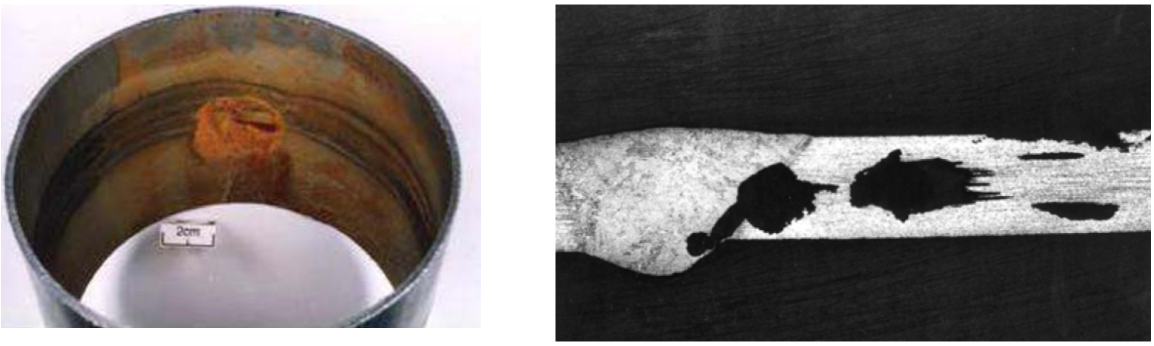
Schmitt et al [9] have reported of similar corrosion failures of press fittings of 1.4401, flange joints and pitting at welds in German tap waters within short term exposure of < 2 years. In their study ennoblement was shown to occur for different surface qualities of 1.4401 in tap water and corrosion potentials up to 550-650 mV vs. SHE were measured. In a field test rig study with press fittings it was shown that chlorination lowered the corrosion potential and thereby reduced the risk of corrosion. For non-chlorinated water microbially influenced crevice corrosion could initiate in some water types, but not others, and it seems that the water treatment is of large importance for the tendency to ennoblement and for the subsequent development of crevice corrosion. It is especially interesting that a water quality with low degree of ennoblement can be changed by active charcoal filtration after which corrosion potential increases and redox potential decreases. Chlorination removes the effect and brings the corrosion potential back down and the redox potential up. Schmitt et al furthermore studied the effect of assembling aids for o-ring lubrication. In the case of chlorinated water there is no effect of the assembling aid, but in the non chlorinated water the electrochemical activity (corrosion) is higher, and the difference between the protectiveness of the aids become visible within a few months exposure. The authors furthermore suggest the use of 1.4435 with 2.5-3.0 mass % Mo to mitigate crevice corrosion. Ennoblement may also occur on this material, but corrosion will not initiate as easily as in 1.4401.

Cases

A number of practical experiences from failures in Finland and Denmark [10-12] have been collected to give an insight into the phenomena. In all the cases given here the material quality was as specified and the press fittings were correctly assembled. In some cases with welded connections, however, these were not of good quality. The microbiological data available are very limited, as these cases are often a matter of controlling whether the material quality and the installations were correct according to specifications. In the expert consensus on MIC by NACE International TG 304 in 2004 [13], good advice is given on the failure analysis and diagnosis stating a variety of techniques. To thoroughly evaluate the failure both metallurgical and microbiological data must be combined and ideally trends in chemical and microbiological data included. In these cases the specific mechanism has not been documented, but a number of parameters common in the cases can be acknowledged.

Case 1. Fire protection system

In a fire protection system in a power plant perforating pits were found in stainless steel (EN 1.4401) pipes ø140 mm of 3 mm wall thickness after two years of service [10, 11]. The system included both older parts of carbon steel and cast iron and newer, replaced parts of stainless steel 1.4401 and 1.4301. The water was tap water (drinking water) with low chloride content of 20-30 mg/l and the system was at ambient temperature. The water was chloramine treated when the system was filled, and water was exchanged typically once a year. The pits were situated in the welds or in the heat affected zones. Pipes of EN 1.4301 were also attacked and leaks detected after two years of service. Typically the pits were very small having large subsurface cavities. In general the pits were situated close to or in the transversal on-site welds. There were clear indications of oxidation of the heat affected zone (heat tints) but no other signs for welding defects were found. Reddish brown deposits were found and the pits were 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 a yellowish brown deposit.



a) *b)*

Fig. 1 a) Reddish brow deposit on the inner surface of a stainless steel type 1.4401 pipe section removed from the fire protection system. b) Optical micrograph of a wall-through, mainly subsurface corrosion pit in 1.4401 pipe after two years of service in the system.

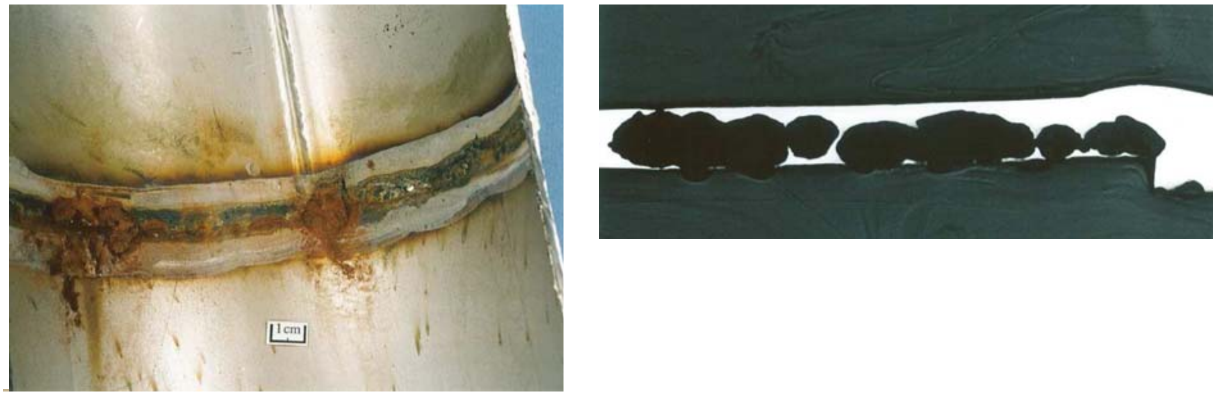
Sulphur and occasionally also high amounts of manganese as well as small amounts of phosphorous were detected in the deposits in or around the pits by energy dispersive spectroscopy (EDS). This indicates that manganese probably exist as MnO_2 (a compound formed by aerobic bacteria) and S as a sulphide formed by the reduction SO_4^{--}. SRB and a high amount of aerobic bacteria ($4.3 *10^6$ cfu/ml) could be detected in a sample that was delivered moist to the laboratory and cultivated in microbiological assays. The samples for microbiological analysis had wall-through pits. The presence of IOB was verified in one pipe sample and in the water, but the presence of MOB was not checked.

The water contained high amounts of precipitated iron (0.44 mg/l measured after two years service) which can facilitate iron oxidizing bacteria but could also in itself affect the risk of localized corrosion of stainless steel.

Case 2. Condenser pipe

In the condenser pipe of an air conditioning system designed in stainless steel 1.4301, the first leak was observed after just a couple of months service [11]. The water was a mixture of ground water and drinking water with 120 mg/l chloride. Apart from some short stagnant periods of operation the system had been generally flowing continuously with 1 m/s. The maximum temperature was 30 ºC.

The attacked areas were all in the weld or in close vicinity of the welds. These were covered with reddish brown deposits, and the investigations showed that the weld quality was poor. Remains of root paste could be seen, which has been used to form a slag layer on the root side of the weld to protect the weld root from oxidation. The weld itself was partly corroded, but pits were also present in the heat affected zone. High amounts of manganese, chromium, iron, and smaller amounts of sulphur, phosphorus, and chlorine were found by EDS in deposits covering the pits. Bacteria were detected in the failure area with a total aerobic count of $7.8*10^3$-$1.4*10^4$ cfu/ml and SRB 54 cfu/ml.



a) b)

Fig. 2. a) Reddish brown deposits on the inner surface of a stainless steel type 1.4301 condenser pipe section removed from the air conditioning system b) Optical micrograph of severe wall-through corrosion pits in 1.4301 pipe after few months of service in the system.

Case 3. Public swimming bath

In the stainless steel (1.4404) installation in a public swimming bath providing a mixture of warm and cold water to 40 showers, fittings were leaking after less than a year. The corrosion attacks were concentrated in the circumferential welds in the large dimension fittings of ø 108 mm. Water temperature was 37-38 °C, and the water was circulated, but during night time temperature increased to 47 °C. The particular local Danish drinking water quality was neutral, hard, of average conductivity and chloride content (70-110 mg/l), and with some organic matter.

a) *b)*

Fig. 3. a) Press fitting for large dimension pipes perforated after less than 1 year service with lukewarm drinking water. b) Inside of fitting showing red brown tubercles at welds.

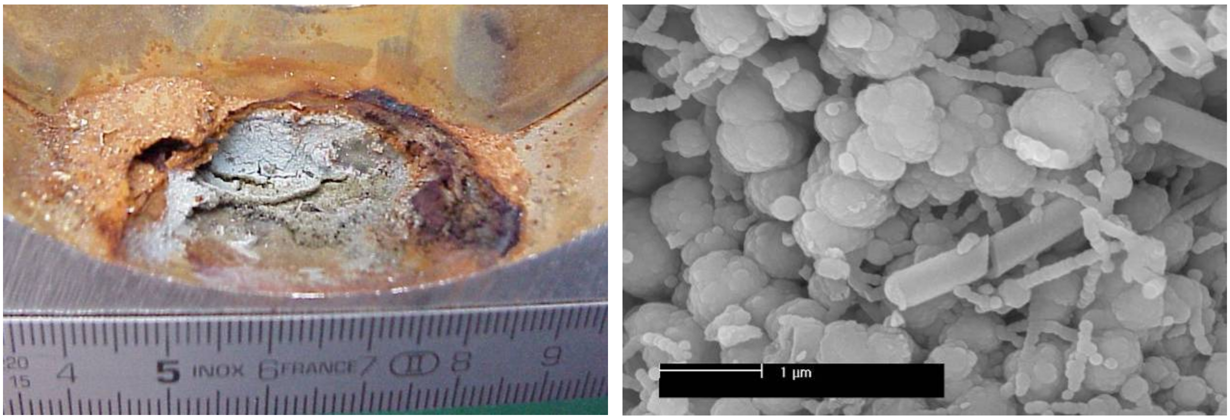
As shown in fig. 3 the corrosion attacks were covered by tubercles. Sulphide was qualitatively detected in the crevices at corrosion attacks by an iodazide test, but not directly in the tubercles. The sulphide could originate from the presence of SRB, but no microbiological analysis was performed.

In this case the primary critical parameter was defects in welds, which were found by metallographical examinations. To avoid this type of failure better weld quality must be specified (root defects, crater pores, lack of fusion) and then the normal pickling procedure will ensure resistant fittings without sensitive areas. However, it is likely that a high degree of microbiological activity has enhanced the critical situation and helped build tubercles under which corrosion attacks continued. According to the Danish Code of Practice for domestic water installations [14] no place in the system should the hot water temperature be lower than 50°C, and 45 °C at peak load. This is to reduce the risk of bacterial growth of especially pathogen bacteria such as *Legionella*, but it would also help to reduce the risk of MIC. Furthermore the use of circulating lukewarm water is unwise from both a hygienic and a corrosion point of view.

Case 4. Fire protection system

Another case [12] is from a fire protection system in stainless steel, EN 1.4401/1.4404. The system was filled with drinking water containing 100-130 mg/l chloride, which resided in the system at about 10°C. Two years after installation several small leakages were observed in the system. Corrosion was observed in association with heat tints and crevices (i.e. weak areas). Indicative potential measurements in the system showed a level of up to 560 mV vs. SHE (~320 mV SCE), indicating that ennoblement had occurred. There were no signs of manganese deposits, but voluminous rust tubercles, Fig. 4a, were found.

Chemical analyses of the products in the tubercle showed high amounts of the steel elements, i.e. iron, chromium, nickel and a surprisingly high concentration of molybdenum. Moreover, a wide variety of organic deposits expected to be of microbiological origin were observed, Fig. 4b, which were taken as remnants of bacteria, e.g. sheets of rod shaped bacteria.

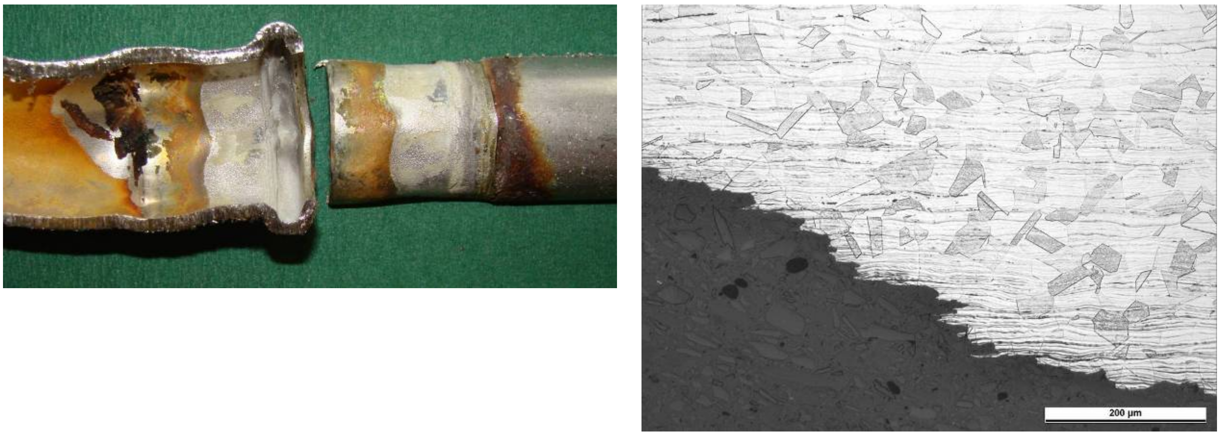


a) *b)*

Fig. 4 a) Voluminous rust tubercle at crevice inside a stainless steel junction (1.4404) of fire water system. b) Scanning electron micrograph of the products in the rust tubercle expected to be of microbiological origin, e.g. bacteria sheets.

Case 5. Student house in major city 1.

In the drinking water installations of EN 1.4404 in the student house in a major Danish city, rust stains were detected at cold water press fittings after 1 year in service, but no leaks were apparent. The failure analysis was conducted after 2½ years service, when the fittings and pipe sections were cut out. The hot water installations did not seem affected by corrosion. A water analysis performed on water from the basement revealed high manganese (0.11 mg/l) and iron (1.2 mg/l) contents in the water, which exceeded the allowed values of Mn 0.05 mg/l and Fe 0.2 in drinking water as delivered from the water works. The origin of Mn and Fe were not identified, but could be related to corrosion in the system. Corrosion attacks were severe crevice corrosion attacks in fittings and pipe, preferably under the o-rings. At the crevice opening voluminous tubercles were found, and inside the pipes reddish brown deposits covered larger areas. Qualitative iodazide tests indicated sulphide in deposits close to the corrosion attacks. Some of the press fitting connections had an oily appearance as if some organic substance had been leaking from the o-ring or was applied for lubrication during installation.



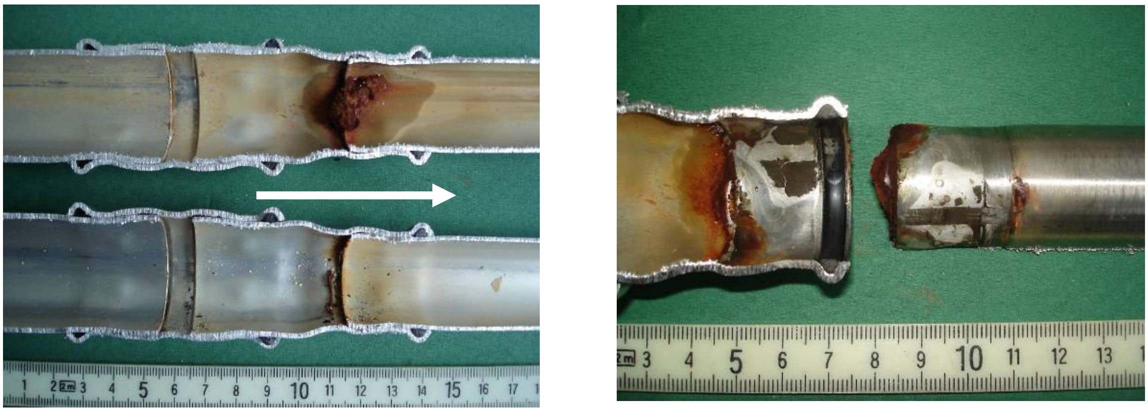
a) *b)*

Fig. 5. a) Crevice corrosion in press fittings of drinking water installations of EN 1.4404 after 2½ years in service. b) Optical micrograph of edge along the corrosion front. The microstructure appears normal for 1.4404.

Case 6. University building in a major city 1.

In the drinking water system in a university building in the same city as case 5, a very fast development of crevice corrosion was found. In less than 4 months rust stains developed at press fittings of EN 1.4404 and minor leaks occurred. In this case the cold water pipes were hardly affected but corrosion occurred in the warm water installations of maximum temperature 55 °C, and primarily on pipes of smaller diameter ø35 mm. After installation the system was filled with water that was circulated at 55 °C for an unknown period of time, until the building was taken into use. The water quality was considered acceptable being neutral, of medium hardness, medium conductivity, medium chloride, and with some organic matter and acceptable cell counts.

As in case 5 crevice corrosion attacks were found in fittings and pipe, especially under o-ring, and the corrosion attacks were characterized by voluminous tubercles and brown surface deposits. In the dark brown deposits in the corroded zone, sulphide was qualitatively detected by iodazide test. From the distribution of corrosion products and deposits (fig. 6b) there are indications that standstill and half filled pipes have been occurring. It was reported that water was circulated until the system was taken into use, but if this has not been the case or the system has not been full of water, this could explain the very fast corrosion attacks combined with the growth of bacteria occurring in stagnating and perhaps oxygen depleted warm water.



a) *b)*

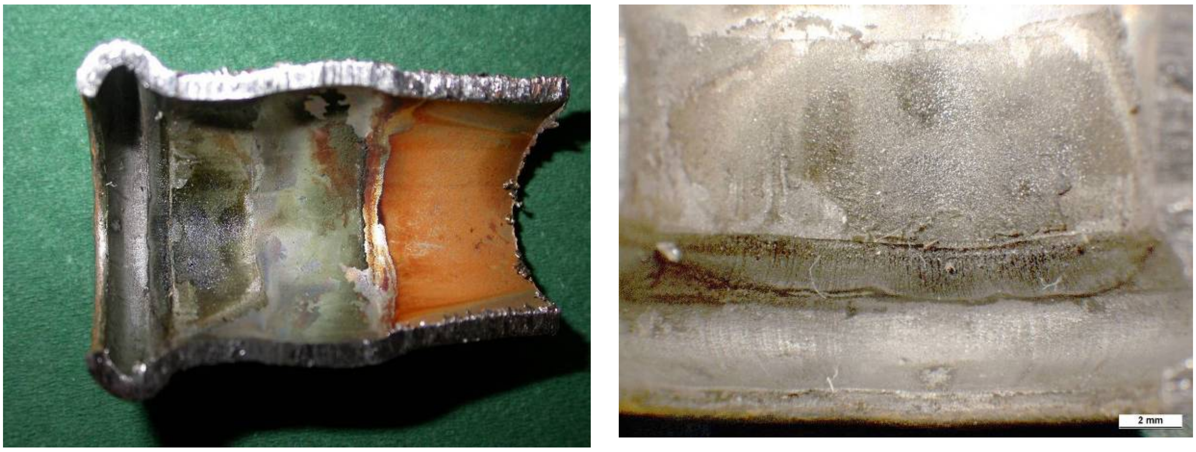
Fig. 6. a) Crevice corrosion in press fittings of drinking water installations of EN 1.4404 after 4 months in service. Note tubercles and lack of deposits in one of the pipe halves. Flow direction is marked by arrow b) Corrosion attacks are both on pipe and fitting. Deposits inside crevice are dark gray, brown to green.

Case 7. Apartment house, major city 2.
The last case of press fitting corrosion is from another major Danish city and from an apartment house. After only 9 months of service small leaks were detected and rust stains were visible at press fitting connections. In this case the water quality was questionable, although still accepted as drinking water in Denmark. The water was neutral, of high hardness, high conductivity, high chloride content, and both some organic matter and quite high cell counts were found.

a) *b)*

Fig. 7. Crevice corrosion in press fittings of cold drinking water installations of EN 1.4404 after 9 months in service. b) The area close to the o-ring is severely attacked and appears bright and etched.

The material used was EN 1.4404 and crevice corrosion was found in the fittings and pipes, especially under the o-ring. The warm water installations were severely affected, but attacks were also found in the cold water installations. The corrosion attacks were primarily in the horizontal pipes, but attacks were also encountered in vertical pipes. As for the previously described case voluminous tubercles were found at the crevice mouth and outside the crevice red brown surface deposits were present. Inside the crevice deposits were darker, grey to green and sulphide was confirmed qualitatively in deposits by iodazide test. The o-rings appeared greasy and sticky, and remains of pale yellow grease was observed, which might have been used during assembly or has leaked from the o-ring. IRS analysis indicated that the grease was mineral oil based.



a) *b)*

Fig. 8. Crevice corrosion in press fittings of hot drinking water installations of EN 1.4404 after 9 months in service. Note green to dark grey deposits in the crevice. b) The area close to the o-ring is severely attacked and appears bright and etched.

General features for press fitting crevice corrosion (case 5-7)

A number of general impressions obtained by FORCE Technology through failure analyses on the fairly rare cases of crevice corrosion in press fittings in drinking water installations are summarized below:

- Failures are often not detrimental, as the stainless steel surface repassivates after a small leakage event, when the corrosive environment is removed. Air entering the pit through the leakage facilitates the change and corrosion products keep the connection from leaking afterwards.
- The consequences are rust stains and minor leaks, but major water spills are rare.
- Attacks appear in large installations in public/apartment/office buildings and typically in big cities.
- The rust stains typically appear less than 1-2 years from installation, and failures are often in relation to renovations in existing systems. For systems older than 3 years appearance of new failures are rare.
- In general good manufacturing practice characterizes installation and material quality and this type of corrosion has been seen in several different brands of press fittings.
- Corrosion appears in different water types, with no direct link to cell counts or chloride concentration, but often the cold water temperature has been too high, or the warm water temperature too low.
- Often the water use pattern has been unstable with possible stagnant conditions, or a low degree of exchange and circulation.

- In some cases contamination with organic matter or hydrostatic testing with prolonged exposure can be documented.

Mechanistic suggestions

Typically the corrosion attacks appear within 2-3 years in weld nuggets, heat affected zones or in crevices like e.g. press fitting pipe connections. The failure mode is pitting and crevice corrosion discovered by leaks and rust stains on the outside of the installation.

One key parameter generally accepted in the mechanism is ennoblement due to the formation of a biofilm. This is well known in sea water but has also been documented on stainless steel in drinking water qualities. Fig. 9 [15] shows the potential development in four different Danish water types under stagnant conditions, and all favour ennoblement with time, although corrosion attacks were not developed during this experimental time. Potential values reach up to 550 mV vs. SHE (307 mV vs. SCE) which is in accordance with the values found by Schmitt et al [9] and in the fire protection system of case 4.

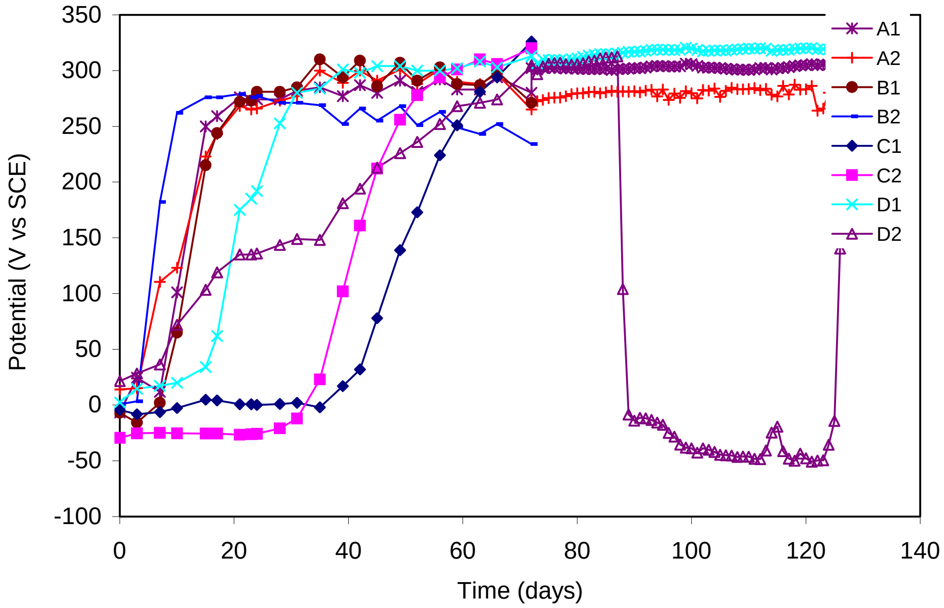


Fig. 9. EN 1.4401 stainless steel fittings exposed under stagnant conditions in four Danish drinking water types (A-D) at 22°C. Ennoblement occurs for all after 5 to 60 days up to the range of 275-310 mV vs. SCE (518-553 mV vs. SHE). Temporary activation is seen for one sample after 85 days, but no penetrations were detected [12, 15].

The mechanism of crevice corrosion in press fittings can be described as a line of events starting with ennoblement of the pipe due to aerobic biofilm formation. This increases the risk of crevice corrosion, but the pitting potential for the pipe surface is not exceeded. In the crevice media is changed with time, and probably effects of iron-oxidizing bacteria that may thrive under microaerobic (low-oxygen) conditions using Fe(II) as a sole energy source are involved. The iron oxidising bacteria produce ferric iron, which in combination with chloride ions produces aggressive ferric chloride. Mn oxidizers (Mn^{2+} to Mn^{4+} forming MnO_2) are important in fresh water and waste water MIC introducing a strong oxidant causing potential increase, but is probably not as important in drinking water, where manganese concentration is often low, except if a source of Mn like corroding steel is present.

If anaerobic conditions are formed in the crevice production of sulphide may occur e.g. by growth of SRB. The effect is a lowering of the redox potential in deposits on the surface by producing sulphides and formation of metal sulphides that may act as efficient cathodes. The number of SRB is usually low in drinking water, but given the right conditions they grow. In presence of air, sulphide may be oxidized to thiosulphate generally accepted to enhance the corrosion of stainless steel, especially if conditions are alternating anaerobic/aerobic. Furthermore the reduction of pitting potential as a function of the ratio between chloride and thiosulphate concentration was presented more than 30 years ago [16].

The o-ring material and possible assembly aids are important in the respect that they may leak organic material/chemicals that can be utilized by the bacteria and change the microenvironment. Corrosion attacks in the press fittings appear mostly in areas next to sulphides and under the o-rings. The crevice is often found to be closed by corrosion products limiting the contact to the rest of the pipe surfaces and limiting the exchange of media. In many of the Danish experiences a small leak has appeared and the corrosion attack seems to stop by this event. The leak gives the possibility of air ingress and loss of aggressive media thereby possibly seizing the growth of specific bacteria, as well as facilitating oxidation of sulphides. Furthermore the corrosion products have isolated the crevice from the rest of the pipe. This last observation is controversial in the respect that a minor leakage can then actually be considered a positive event, after which the corrosion attack will seize and long lifetime of the connection is expected.

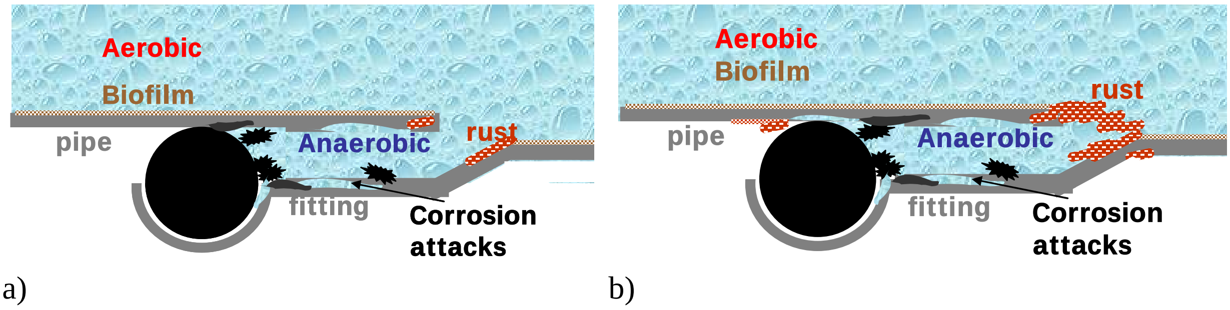


Fig. 10. Suggested mechanism for crevice corrosion in press fitting. a) Formation of aerobic biofilm on pipe surface, depletion of oxygen in crevice leading to initiation of crevice corrosion attack in combination with IOB and SRB activity. b) Leakage due to penetration leads to oxygen ingress and loss of corrosive media –corrosion attack seizes and corrosion products close the crevice.

Ennoblement in itself is not enough to initiate pitting or crevice corrosion in these water qualities, but combined with a geometrically or metallurgical vulnerable area, corrosion can be accelerated. The mechanism is linked to the naturally occurring microbial activity, where the localisation and growth of specific bacteria depend on the environment. Inside a crevice the oxygen content will decrease and anaerobic, stagnant conditions form leading to growth of e.g. sulphate-reducing bacteria, whereas the heat tint on a heat affected zone with its high content of iron facilitates the growth of iron oxidising bacteria. The driving force is initially the difference between the media inside and outside the crevice, but the morphology of the attacks indicates that the primary anodic site is under the o-ring.

A new contribution to the mechanistic explanation is the findings in a similar case with press fitting corrosion examined by P. Møller. These data are from an apartment building from the major city described in cases 1-3 and occurred in the same time frame. In this case rust stains appear after < 2 years of service and crevice corrosion was observed. Corrosion products inside the crevice under the o-ring revealed high concentrations of Mo and S in the same areas as illustrated in fig 11.

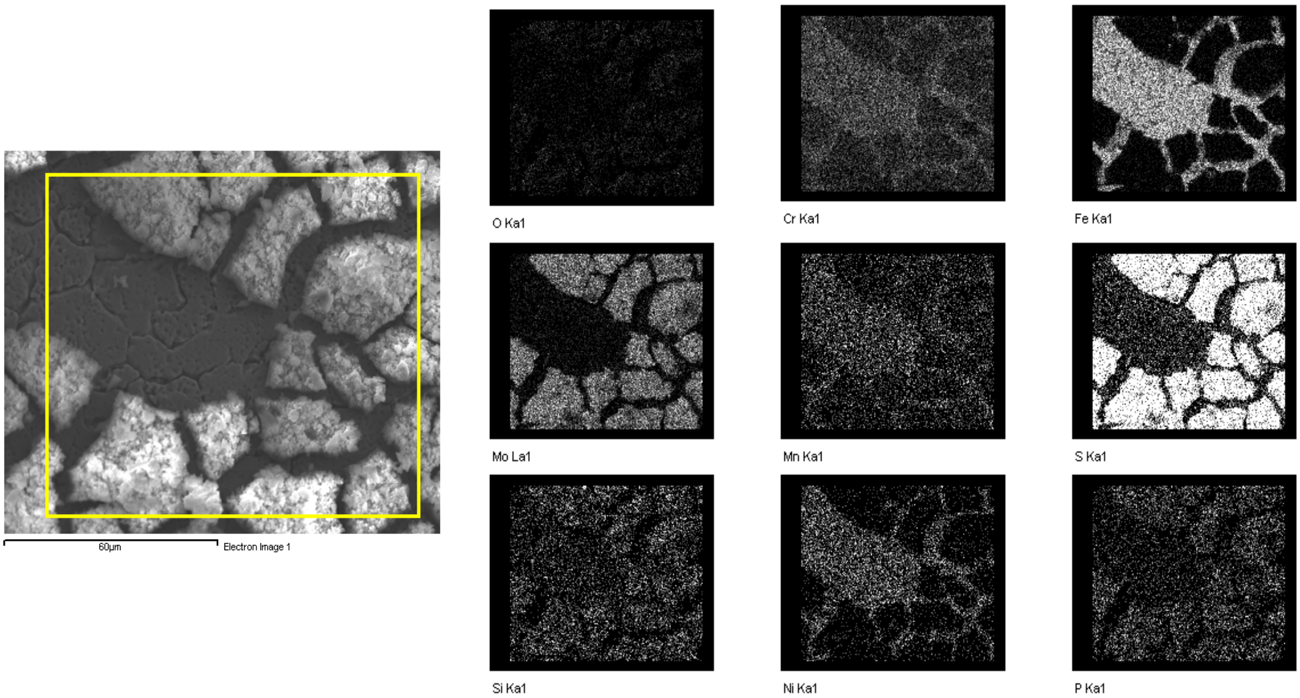


Fig 11. Scanning electron micrograph showing corrosion products in the crevice of a corroded press fitting. Mapping of elements indicated presence of molybdenum sulphides and EDS analysis showed 4 S and 9 Mo atomic % (3.4 and 23 % by weight).

This corresponds to the findings of Duan et al [17], who reported that after 7 weeks exposure of type AISI 316L (EN 1.4404) in natural sea water, a number of inorganic and organic sulphides were found on the surface by XPS. This included molybdenite MoS_2 and organic Mo sulphides even present in the passive film. The mechanism suggested by P. Møller is that the presence of MoS_2 inside the crevice, from a thermodynamical point of view, could push the reduction of oxygen and act as an efficient cathode. MoS_2 is a very catalytic surface. Focus is also on the o-ring material on which MoS_2 can sometimes be used for lubrication, but this is not the case here.

On the specific stainless steel samples XPS was not used for documentation, but only EDS, which unfortunately is less reliable due to overlapping of the S and Mo signals. This especially is a problem for the presence of small amounts of the two elements. In other cases the appearance of high amounts of Mo and S in the same area has been detected by EDS, but generally not taken as more than indications. Chemical analysis by e.g. ICP or XPS should therefore be applied for better documentation and it would be interesting to follow this line of thought and examine whether MoS_2 is really a part of the mechanism for stainless steel press fittings.

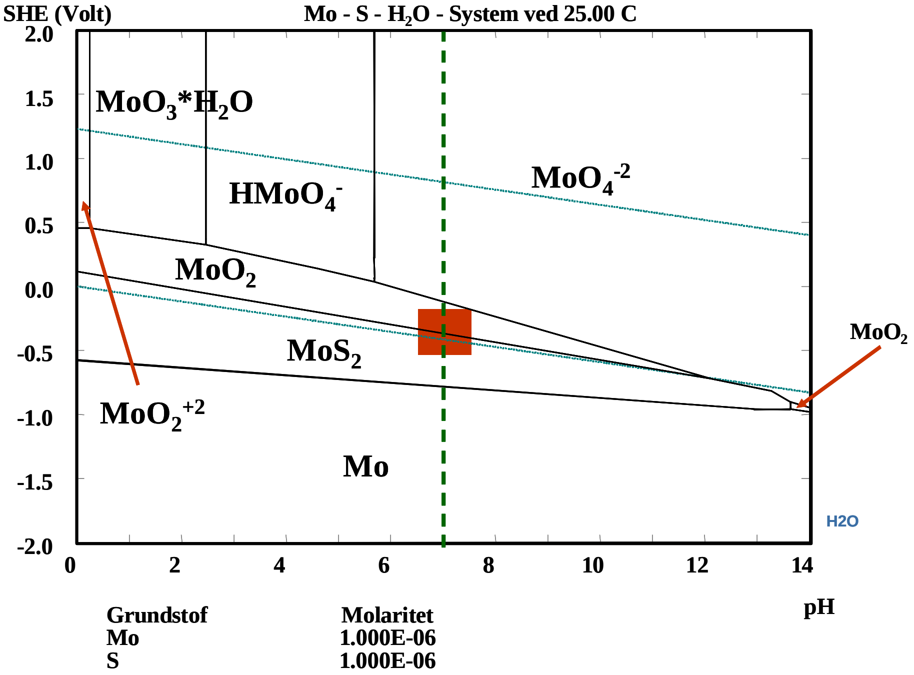


*Fig.12. Pourbaix diagramme for Mo and S at 25°C and 1*10*$^{-6}$ *mol/l of Mo and S species. The stability area of* MoS_2 *is at lower redox potentials.*

Discussion

The corrosion of stainless steel 1.4301 and 1.4401 in low chloride drinking water is unexpected as from a chemical point of view the water quality would normally not cause corrosion. However, natural waters give rise to ennoblement due to biological activity and this in combination with a metallurgical/geometrically sensitive area increase the risk of corrosion. And finally under specific process parameters (standstill, low exchange rate, contaminations e.g. due to repair work) the critical conditions can occur that leads to crevice corrosion in press fittings or pitting in the vicinity of welds. So which of these parameters – biological activity, material sensitivity, and process conditions - can be controlled or predicted?

It is important that water as clean as possible is used with low amounts of solids, chlorides, manganese, iron and organic substances. Ennoblement will occur in time in all water types, except if water treatment like chlorination is used, which is rarely done in Denmark. Presence of a specific organism has been suspected for causing failure, but as long as this has not been identified, the only indication is that often more cases appear in the same town or area during a specific time frame thereby linking the failures to the specific feature of the water quality at that time. It seems clear that strong microbial activity is a risk, but whether in future this may lead to a prediction based on a water sample is so far not likely unless major mechanistic breakthroughs take place. Prevention of contamination of the systems with microorganism can be obtained by e.g. using ultrafiltration of pressure testing water and chlorination at commissioning of installations. Correct design and service may limit biofilm formation and growth of microorganisms (including pathogen bacteria like *Legionella*). In short this means avoiding dead ends and keeping hot and cold water separated as well as sufficiently hot and cold. Furthermore, organic compounds that can be utilized as nutrients must be limited and focus must be on ensuring that O-rings are inert and are not leaking possible nutrients.

The welds can be optimised and quality control can help avoid corrosion sensitive surfaces. From the good practice applied in e.g. the food or pharmaceutical industries the quality control systems are available and it is well known how to produce corrosion resistant welds. Removing oxygen from the piping by shielding gas flushing prior to welding and using backing gas during and for some time after the welding process will reduce the detrimental heat tints. Pickling after welding is also an option, but not always applicable.

To avoid the problem with crevice corrosion, pressfittings of gun metal are available which from a theoretical point of view can provide cathodic protection of the stainless steel. The gun metal would release copper ions in the process, but crevice corrosion can be avoided even in higher chloride waters for which these connections are approved. More corrosion resistant alloys like 1.4435 might be applied but the mechanism suggested by P. Møller indicates that stainless steel qualities with lower Mo content would actually be more resistant, if molybdenum sulphides are a part of the mechanism. Another option is to continue to work on optimisation of the o-ring material and assembly aids, as suggested by G. Schmitt et al [9].

The third important option is to avoid the critical process conditions like standstill or periods of low water consumption, or at least to be aware that these operations should be avoided and include a risk. If not avoided, some action could be necessary to prevent development of localised corrosion after pressure testing with water, conditions beneficial for microbial growth, or repair work. Most cases occur within 2 years from installation or major changes in operation before e.g. calcareous deposits have formed. If continuous flow is not possible, the water should be changed regularly and the amount of bacteria checked. Information is the key parameter to a higher degree of awareness during installation and use.

Conclusion

In general, the stainless steel alloys are resistant in drinking water qualities excelling by a low metal release and long lifetime. A number of cases from fire protection systems and drinking water installations have been described in order to document how metallurgical (welds, heat affected zones) or geometrically (crevice in press fitting connections) sensitive areas of EN 1.4301/1.4401/1.4404 can corrode in low chloride drinking water types. The mechanisms are still not fully understood, but a number of parameters have been highlighted, including ennoblement and stagnant conditions, indicating that microbially influenced corrosion is taking part in these corrosion failures occurring within less than 2 years service. The failure mode is pitting and crevice corrosion leading to leaks and rust stains on the outside of the installation.

To predict and prevent these corrosion failures better understanding of the mechanism would help, however, dedicated studies are rarely conducted in connection with industrial failure analysis. Application of relevant microbiological techniques could be included for better documentation and in order to investigate the possible effect of the microorganism. Cooperation between research groups and exchange of experience is necessary, if the understanding should improve. Presently the best tools available for prevention therefore are awareness of the risk, combined good practice regarding water quality, installation, and process conditions.

This cooperation was facilitated by COST D33 “Nanoscale electrochemical and bio-processes at solid-aqueous interfaces of industrial materials”.

References

1. EN 12502-4:2004 , Protection of metallic materials against corrosion – Guidance on the assessment of corrosion likelihood in water distribution and storage systems – Part 4: Influencing factors for stainless steel.

2. P.J. Scott, Expert consensus on MIC: prevention and monitoring, Materials Performance, March 2004, (2004), 50

3. L. Carpén, L. Raaska, K. Kujanpää, K. Mattila, P. Uuetela, M- Salkinoja-Salonen, T. Hakkarainen, "Simulation of MIC at splash zone areas of the paper industry", CORROSION 2001, (2001), Paper no. 245, Houston, Texas, Nace International 2001.

4. T. Hakkarainen, L. Carpén, "Effects of heat tints on pitting susceptibility of stainless steel", (2000), Paper no. 061, 7th International Symposium on Electrochemical Methods in Corrosion Research, EMCR2000, Budapest 2000

5. D.A. Moreno, J.R. Ibars, C. Ranninger, Revista de Metallurgia (Madrid), **36**, no 4, (2000), 266

6. D.A. Moreno, J.R. Ibars, C. Ranninger, "Forms of the localised corrosion on UNS S30400 Austenitic stainless steel in the presence of chloride plus biogenic sulphide solution", in: Biodeterioration and Biodegradation 9, Eds. A. Bouscher, M. Chandra, R. Edyvean, International Biodeterioration Association and Institution of Chemical Engineers, U.K., (1995), p. 520

7. Nielsen, K., A. Andersen and F. Fontenay, Miljøprojekt 110 2006, "Metalafgivelse til drikkevand, del 3", Miljøstyrelsen (2006).

8. T. Mathiesen, K. Nielsen, F. Fontenay, Evaluation of susceptibility to crevice corrosion in drinking water of stainless steel pipes with connections, CEOCOR Malmö Meeting 2005, (2005)

9. G. Schmitt, H. Schlerkmann, W. Sand, H. Klemp, MIC in Stainless Steel Plumbing Systems for Drinking Water, (2007), EUROCORR'2007, Freiburg-Germany

10. L. Carpén, T. Ohligschläger, A case study on corrosion of stainless steel in firewater mains, (2008), 6th European stainless steel conference - Science and market. Helsinki, Finland, June 10 - 13, 2008. Jernkontoret

11. L. Carpén, "MIC Cases of Stainless Steel in Systems using Drinking Water", (2008), presentation given at COST D33 2nd Workshop, Obernai-France 14.-15.5. 2008

12. T. Mathiesen, J. E. Frantsen, "Unusual corrosion failures of stainless steel in low chloride waters", NACE Corrosion 2008, (2008), Paper 08174

13. P.J. Scott, Expert consensus on MIC: failure analysis and control, Materials Performance, April 2004, (2004), 46

14. Code of Practice for domestic water supply installations, DS 439 (Danish Standard), 3rd Edition, 2000

15. N. Rasmussen, B.Sc. thesis, Technical University of Denmark, January 2007

16. R. C. Newman, N.P, Wong, H. Ezuber, A. Garner, Corrosion **45**, (1989), 282-287

17. J. Duan, B. Hou, Z.Yu , Materials Science and Engineering, C **26**, (2006), 624 – 629