



## **UNUSUAL CORROSION FAILURES OF STAINLESS STEEL IN LOW CHLORIDE WATERS**

Troels Mathiesen, Jan Elkjaer Frantsen  
FORCE Technology  
Park Alle 345  
DK-2605 Brøndby, Denmark  
trm@force.dk

### **ABSTRACT**

Rare corrosion failures of stainless steel are reviewed in the paper. The cases originate from low chloride waters like potable water or fresh water in the temperature range of 15-25°C. Under such conditions full resistance of austenitic stainless steel like AISI 316 is usually expected. In all cases corrosion was associated with the build-up of dense corrosion products (tubercles), which suggests microbial influence on corrosion. This is further supported by ennobled potentials in most cases. Based on the observations collected through failure investigations, possible theories for the cause of corrosion are discussed. Precautions to avoid corrosion e.g. when doing hydrostatic testing are also discussed.

Keywords: stainless steel, AISI 316, pitting, MIC, fresh water, corrosion potential

## INTRODUCTION

Use of conventional stainless steel types like AISI 304 and AISI 316 does normally not present a risk of corrosion when used in fresh water having low chloride content. For use at ambient temperature the “rule of thumb” chloride tolerances are commonly mentioned as 200 mg/l and 1000 mg/l, for AISI 304 and AISI 316 respectively [1]. Consequently, only AISI 316 or better, may be used in Danish drinking water, which may contain up to 250 mg/l chloride [2,3]. A more differentiated view on the limits for localised corrosion can be obtained by evaluating design diagrams like the one shown in Figure 1. Besides from temperature, this diagram also takes the oxidizing force of the water (i.e. redox potential) into account.

Several cases of corrosion have been observed lately in such waters despite the fact that the stainless steel was within the safe range as concerns chloride content and temperature. As a materials testing institute, FORCE Technology undertakes failure analysis in a wide range of industrial systems. Consequently, we often see the worst cases when it comes to corrosion of stainless steel. Luckily (from a scientific view) most of such cases can be explained by obvious errors in relation to welding, selection of steel grade or material fabrication. However, a few rare cases remain harder to explain.

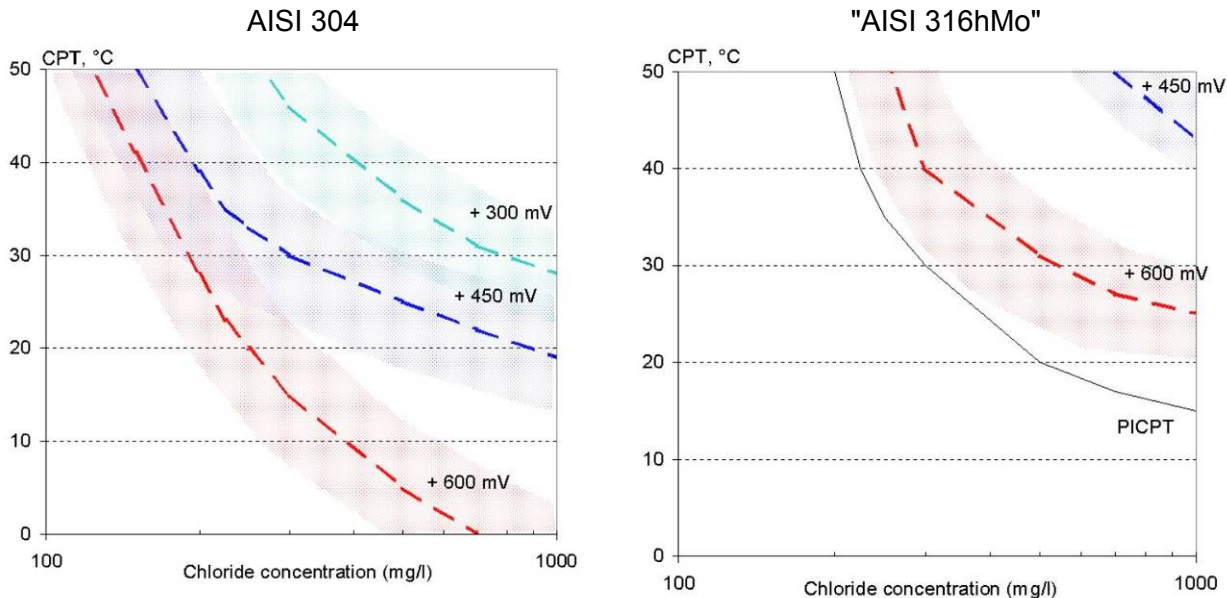


FIGURE 1 - Critical pitting temperature (CPT) of AISI 304 and "AISI 316hMo" (1.4435) in welded and pickled condition. PICPT represents the borderline of the potential independent CPT. Potentials are relative to SCE [4].

The intention of this paper is to present and discuss possible causes for corrosion of such unusual cases. Microbial corrosion (MIC) is often suspected when all other obvious causes have been excluded. This type of corrosion is very far-reaching and still vaguely documented, giving a wide range of possible mechanisms. Basically, the fundamental (inorganic) corrosion reactions are still valid and prevailing, but they are now influenced by the complex of micro environments created by micro organisms.

However, for seawater use of stainless steel the mechanism is well-described and understood [5]. In this type of water it has been shown that stainless steel develops a relatively high

corrosion potential, often referred to as ennoblement. The main cause for this ennoblement especially known from marine environment is biofilms that produce peroxidase enzymes. By this oxygen is transformed to highly oxidising peroxy compounds that cause a corrosion potential in the range of 350-450 mV SCE on the stainless steel surface. The mechanisms of MIC in fresh water systems have not yet been documented as thoroughly as for seawater although some well-accepted theories exist. For instance, manganese oxidising bacteria have been shown to cause ennoblement in treated waste water and some fresh water types [3,6,7,8]. The resulting deposition of manganese dioxide ( $MnO_2$ ) causes highly oxidising conditions of the steel surface, often in the range of 450-500 mV SCE.

TABLE 1  
Specified composition of discussed stainless steel types.

| AISI     | EN equiv. | C     | Si    | Mn    | P      | S      | Cr        | Mo      | Ni        |
|----------|-----------|-------|-------|-------|--------|--------|-----------|---------|-----------|
| 304      | 1.4301    | ≤0.08 | ≤1.00 | ≤2.00 | ≤0.045 | ≤0.030 | 18.0-20.0 |         | 8.0-10.5  |
| 316      | 1.4401    | ≤0.08 | ≤1.00 | ≤2.00 | ≤0.045 | ≤0.030 | 16.0-18.0 | 2.0-3.0 | 10.0-14.0 |
| 316L     | 1.4404    | ≤0.03 | ≤1.00 | ≤2.00 | ≤0.045 | ≤0.030 | 16.0-18.0 | 2.0-3.0 | 10.0-14.0 |
| “316hMo” | 1.4435    | ≤0.03 | ≤1.00 | ≤2.00 | ≤0.045 | ≤0.015 | 17.0-19.0 | 2.5-3.0 | 12.5-15.0 |

### CASE 1 - PIPING FOR TREATED WASTE WATER

In the 1990's a great number of corrosion failures were observed in stainless steel installations handling treated water in Danish municipal sewage treatment plants. The corrosion was unexpected when considering water chemistry and steel grades, which were either AISI 304 or AISI 316L type [3].

A survey that included 62 Danish sewage treatment plants showed that 60% had experienced corrosion failures with stainless steel, and most failures (80%) were located in installations near the final stage, i.e. secondary clarification, sand filter or piping for discharging and recycling treated water. Inspections of 18 sewage plants showed that most failures occurring in the treated waste water were associated with extensive deposits of manganese dioxide on the internal surface of the stainless parts, Figure 2.

It was further shown that the deposition of manganese dioxide was an extremely selective process that took place even in waters where the dissolved manganese was less than 6 µg/l. Several groups of bacteria enable oxidation and precipitation of manganese and iron oxides. These bacteria are generally characterized as ferro/manganese oxidizers and include *Galionella* as the best-known example in relation to corrosion.

As a result of this, highly oxidizing conditions were generated by the manganese dioxide deposits on the steel surface. Measurements of the corrosion potential in the waste water showed a steady level of 450-500 mV SCE that was typically reached within 30-60 days after exposing fresh samples. Bacterial analysis of several water samples from the affected installation did not provide a clear correlation between the test results and the observed manganese deposition.



a.

b.

FIGURE 2 - Pits in AISI 304 base material at the outlet flow meter in sewage treatment plant H. a) overview showing two penetrations, b) extensive attack surrounded by  $\text{MnO}_2$  deposits on the inside.

Given the extreme oxidising conditions, failures were quite frequent in the AISI 304 type installations. For parts made from AISI 316, strict precautions should be taken regarding weld quality and surface treatment in order to avoid localised corrosion.

### **CASE 2 - STORAGE TANK CONTAINING DRINKING WATER**

Another example of unusual corrosion is the feed tank for a water treatment plant. The tank was made from AISI 316 type stainless steel and contained drinking water with a chloride content of 56 mg/l. Due to delayed start-up of the water treatment plant, the tank had unintentionally remained water-filled at ambient temperature for two years. During an inspection just before start-up, several rust formations were observed along the welds, Figure 3. Small penetrations could also be seen on the outside.

At close hand, it was noticed that large rust tubercles had been built up in association with the corrosion. Moreover, clouds of microbial growth were floating in water. The measurement of the corrosion potential showed +400 mV SCE.

The weld quality was not poor, but could on the other hand have been better. Although the measured potential was higher than expected, it was still surprising that the AISI 316 welds were attacked by corrosion in water with just 56 mg/l chloride at 20°C.

The tank was repaired immediately and no further investigations were requested to analyse the exact cause of corrosion.



a.



b.

FIGURE 3 - a) Vertical lines of rust products from welds inside the storage tank containing stagnant water. b) Close-up of rust tubercle, approx. 30 mm in diameter.

### CASE 3 - PIPE CONNECTIONS FOR DRINKING WATER

Stainless steel type AISI 316 is increasingly being used for drinking water installations all over the world. The pipes are mostly connected by pressed fittings or, in fewer cases, by threaded joints. Both connection types generate crevices within the installation as opposed to e.g. welded joints. In drinking water the crevices do not usually present a problem since AISI 316 type stainless steel provides a good tolerance against crevice corrosion in waters with 250 mg/l chloride or more. This has been proved by long-term tests under well-controlled conditions in the laboratory [9]. Generally, the determined critical crevice corrosion potential of AISI 316 was above 500 mV in water with 300 mg/l chloride at 20-40°C, Figure 4. Despite this, crevice corrosion of fittings has been observed in certain geographical areas.

As shown in Figure 5, the corrosion is associated with build-up of large rust tubercles. There is no evident deposition of manganese dioxide or other products that generate highly oxidizing conditions. When potential measurements could be performed, the recorded level was 250 to 350 mV SCE. This level should not cause crevice corrosion of stainless steel why other potential mechanisms were evaluated. Chemical analysis of the products inside the crevice performed by SEM-EDS showed, in some cases, an increased content of sulphur. However, this determination was complicated by the overlap of molybdenum in the spectra.

In some cases the iodine azide showed a positive response, which indicates presence of sulphide in the crevice.

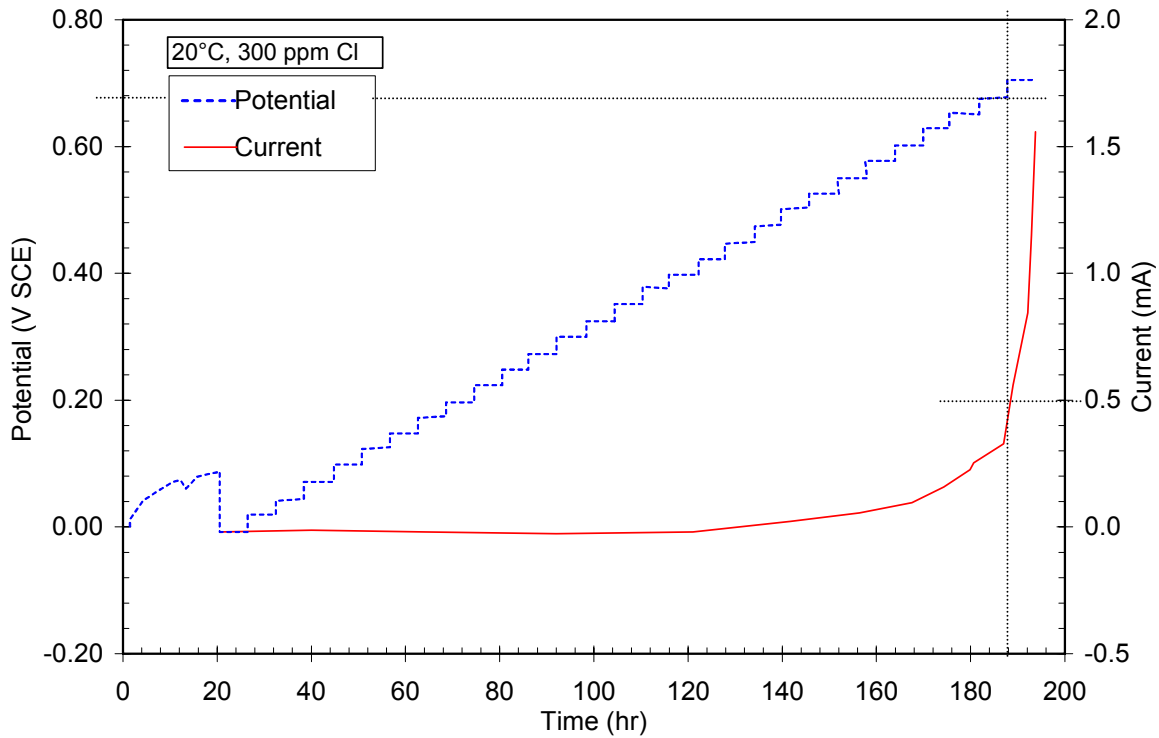


FIGURE 4 - Stainless steel connection tested at 20°C in water containing 300 mg/l chloride. The specimen shows extremely slow initiation of crevice corrosion. The break-through potential is read at 0.5 mA ( $\geq 10 \mu\text{A}/\text{cm}^2$ ), which in this case corresponds to 675 mV SCE [9].

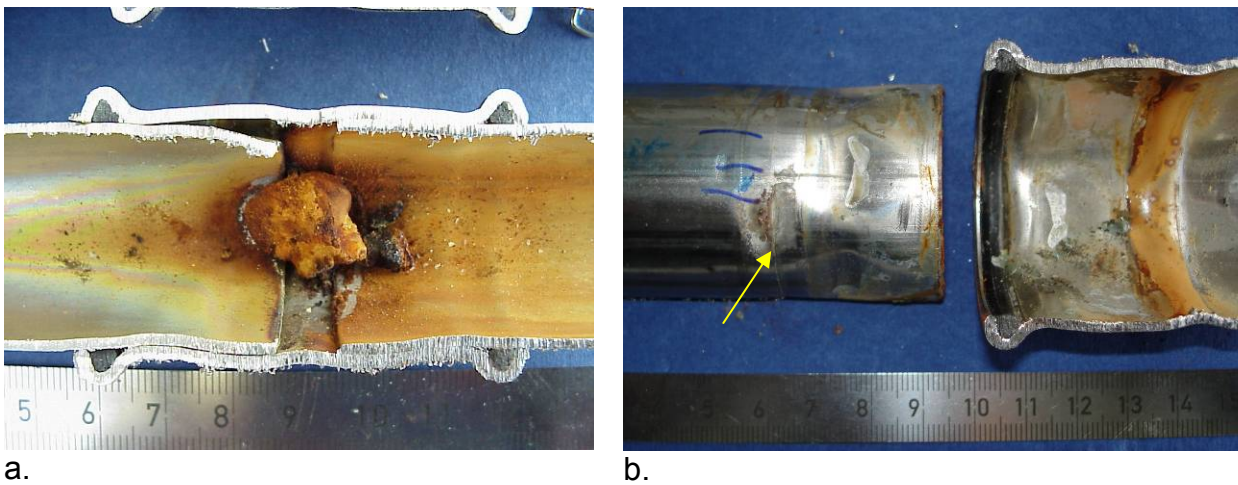


FIGURE 5 - a) Rust tubercle in press fitting of a drinking water system. b) Corroded area causing leakage between O-ring and pipe at the bottom of the crevice.

## CASE 4 - FIRE WATER SYSTEM CONTAINING DRINKING WATER

The last example of “rare” corrosion cases originates from a fire water system that was built entirely from stainless steel, type AISI 316 or AISI 316L. 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. Although, corrosion was observed in association with heat tints and crevices (i.e. weak areas) it was still somewhat surprising that penetrating corrosion had developed. Indicative potential measurements in the system showed a level up to 320 mV SCE. Moreover, there were no signs of manganese deposits. Otherwise, the corrosion had the same features as the above examples, i.e. voluminous rust tubercles, Figure 6a.

Chemical analysis of the products in the tubercle showed high amounts of the steel elements, i.e. iron, chromium, nickel and molybdenum. Moreover, a wide variety of organic compounds were observed, Figure 6b.

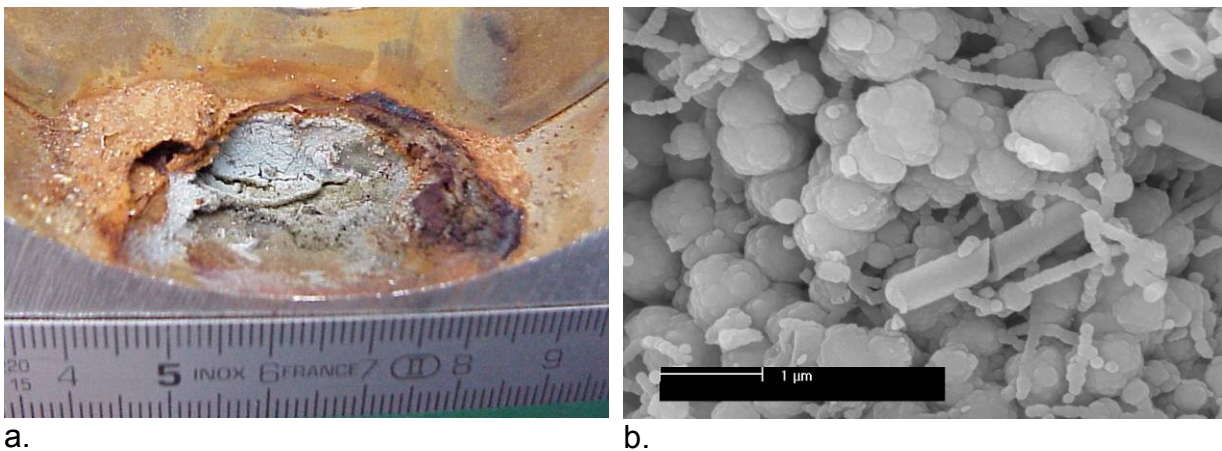


FIGURE 6 - a) Voluminous rust tubercle at crevice inside a stainless steel junction (AISI 316L) of fire water system. b) Scanning electron micrograph of the products in the rust tubercle.

## DISCUSSION

The presented cases demonstrate that fresh water can sometimes be corrosive to conventional stainless steels like AISI 304 and AISI 316 although the materials were used within a range of temperature and chloride concentration where full resistance is expected. Severe ennoblement has been observed in waste water due to extensive bacterial deposition of manganese dioxide, which pushes the materials to and above the limit of localised corrosion. Otherwise, the observed corrosion could not be explained from ordinary design criteria like CPT diagrams or obvious material defects.

In three cases corrosion of AISI 316 type stainless steel has been observed in drinking water with less than 150 mg/l at low temperature (< 25°C). Potential measurements in the installations showed only slight ennoblement given by the level of 300-350 mV SCE. This view is further supported by long-term exposure tests performed in stagnant drinking water in the laboratory. In most cases the corrosion potential reached a level of 300 mV SCE after 60 days, which indicates biofilm formation, Figure 7. Moreover, laboratory tests of creviced samples have shown that the critical crevice corrosion potential of AISI 316 is 500 mV or more in water

with 300 mg/l chloride at 20-40°C [9]. Consequently, it is surprising that corrosion was able to penetrate the materials. Another mechanism must also take part aside from simple pit initiation due to oxidizing conditions that exceed the critical pitting potential limit.

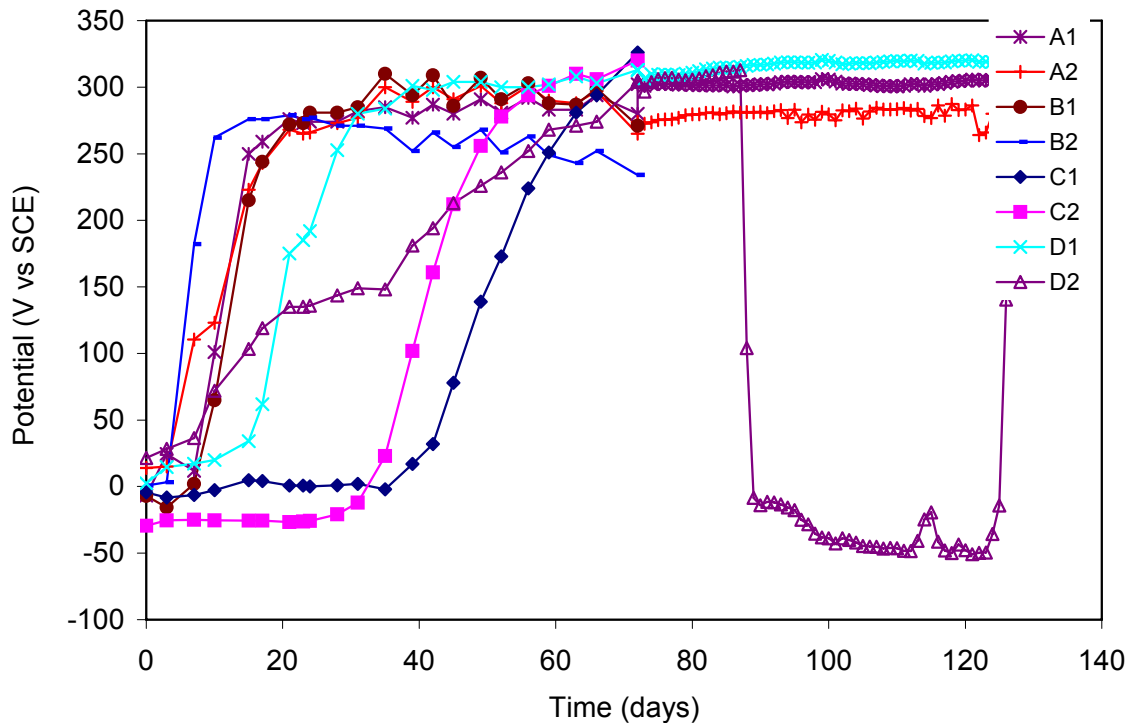


FIGURE 7 - Type AISI 316 stainless steel fittings exposed in four types of drinking water (A-D) at 22°C. Temporary activation is seen for one sample after 85 days but no penetrations were detected [10].

A common feature in the described cases is the formation of voluminous tubercles measuring 2-4 centimetres in diameter. The products within the tubercles consisted mostly of stainless steel corrosion products that were organised in an organic structure, which indicates bacterial activity. Sulphur was also detected in some cases, but not always. More suitable techniques than the applied SEM-EDS or iodine azide test for detecting sulphur should possibly be evaluated for this purpose in future.

The penetrations due to corrosion occurred from few months to two years after installation. However, the subsequent development of corrosion always appeared to stop and/or be clogged by corrosion products. Severe water spills were hardly ever associated with the corrosion. Apparently, the access of air through the leakage to the bottom of the pit or crevice brought corrosion to an end.

The overall experience is also that initiation of corrosion is most crucial in the period just after installation. This means that it is very unlikely that corrosion will develop in an installation where no corrosion has been observed within the first 1-2 years. To our knowledge no cases

are known where corrosion suddenly develops after several years of service unless the conditions were changed.

The build-up of the tubercle most likely influences the initiation of corrosion that should not otherwise appear at such low potentials. It is still unknown exactly which bacteria facilitate the tubercle formation. Besides from the "oxygen concentration cell" due to the tubercle, the bacteria must also be able to form aggressive components that tend to corrode stainless steel. The formation of the oxygen concentration cell alone cannot explain corrosion. Up-concentration of chloride by bacteria seems unlikely since this element does not take part in any known metabolism. It seems more likely that sulphurous compounds are involved, such as sulphide or thiosulphate. Both compounds are known to destabilise stainless steel and may be produced by sulphate reducing bacteria (SRB) at anaerobic conditions within the crevice or rust tubercle, Figure 8 [11-14].

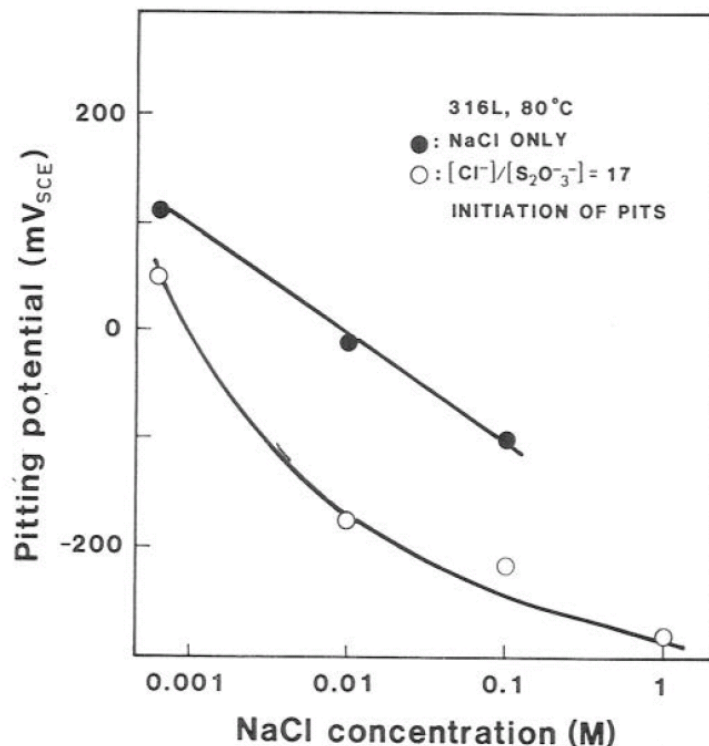


FIGURE 8 - Pitting potential of 316L as function of chloride and thiosulphate concentration [11].

While the above mechanism involving SRB seems plausible, it still remains difficult to predict the required conditions that facilitate it. It is a fact that the described form of corrosion only occurs in few cases while most applications under similar conditions resist corrosion. Stagnant conditions, surface cavities or crevices as well as slightly elevated temperatures may very well promote the mechanism, but were not present in all cases. Thus, we believe that other factors are equally decisive, such as water chemistry (NVOC<sup>1</sup>), surface contaminants and decomposition products from polymers as well as run-in of the installation.

<sup>1</sup> NVOC Non Volatile Organic Compounds

Corrosion failures similar to the examples above have often been reported in connection with hydrostatic testing. Again the main cause for such failures is the combination of stagnant water, possibility of growth and up-concentration due to evaporation. In some cases the addition of biocide may be considered to prevent corrosion when the environmental concerns allow this. In this context, tests performed with the biocide, THPS (tetrakis(hydroxymethyl) phosphonium sulphate), have shown promising results. The effect on corrosion potential was studied in the laboratory. It appeared that the potential immediately dropped several hundred millivolts when THPS was added, Figure 9. The potential remained in this region, where localised corrosion of stainless steel is highly unlikely. In a full-scale stainless steel system containing stagnant drinking water, the contents of oxygen and LNB (low nutrient bacteria) were monitored over a period of two years. By adding THPS, the LNB count dropped from 100-1000 #/ml to 0 and remained at this level for at least a year. The oxygen-scavenging effect of THPS was lower than anticipated at the low temperature (approx. 15°C). However, given the beneficial effects on potential and bacteria control, it was still possible to prevent new corrosion.

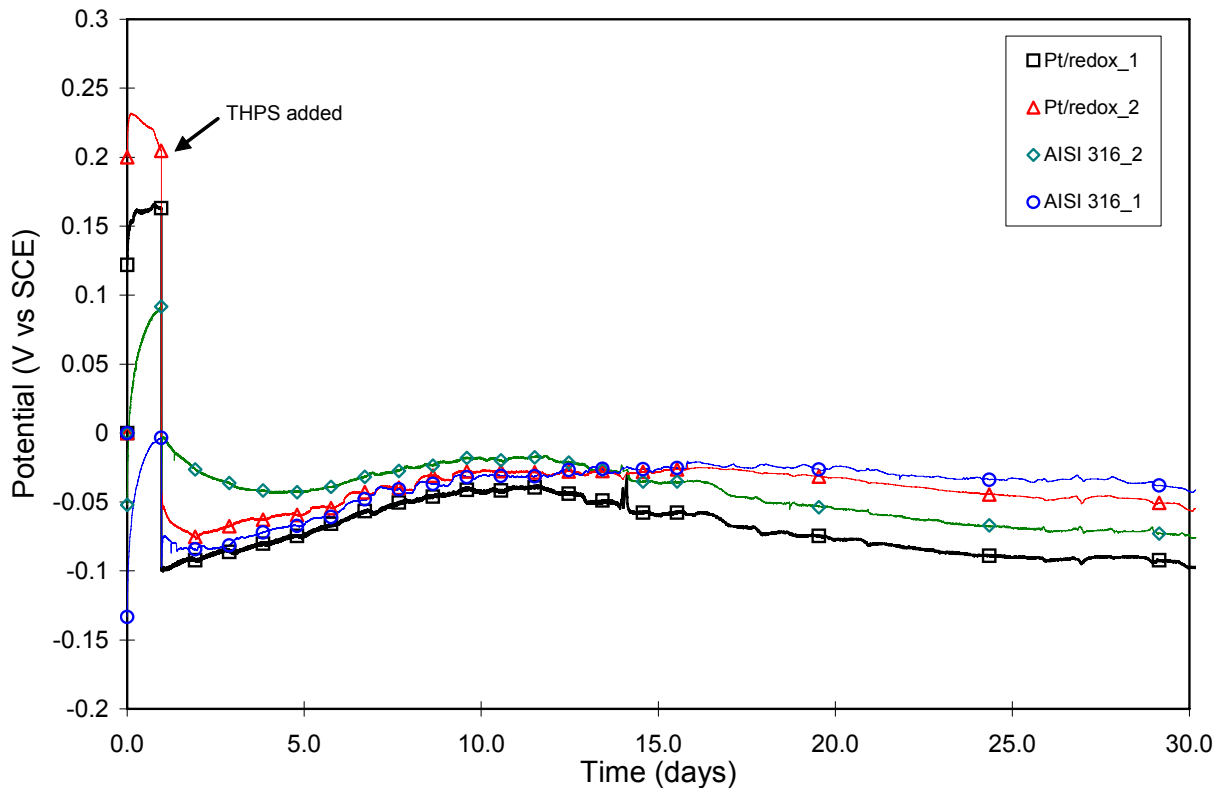


FIGURE 8 - Corrosion potential of AISI 316 and platinum (i.e. redox potential) in drinking water at ambient temperature. THPS was added to a concentration of 300 ppm after one day.

New tools for predicting the corrosion risk are needed but difficult to develop, unless the exact mechanism has been proven. SRB and MIC test kits are available on the market, but their capabilities should not be overinterpreted unless thorough documentation can be provided about the correlation between the test response and the actual corrosion risk.

## CONCLUSIONS

The presented examples demonstrate that in few cases fresh water can be corrosive to conventional stainless steels like AISI 304 and AISI 316 although full resistance was expected from the combination of temperature, corrosion potential and chloride concentration. The observed corrosion was always associated with formation of voluminous tubercles that sometimes contained bacteria producing aggressive components, such as sulphide or thiosulphate. When combined with the slight ennoblement from the biofilm formation on free surfaces, pitting or crevice corrosion was enabled. It is difficult to predict the required conditions that facilitate the described form of corrosion as long as the exact mechanism remains unexplained. Based on experience from a research programme on manganese bacteria we doubt the possibility of correlating the corrosion risk with bacterial analysis of water samples, although it is clear that stagnant water containing nutrients for any type of growth should be avoided. In our view a more beneficial approach is to ensure a high degree of cleanliness and manufacturing quality during installation, and follow this by thorough flushing of the stainless steel system before use. Similarly, strict precautions should always be taken when making hydrostatic tests of a new system. Addition of the biocide THPS has shown suitable properties for preventing corrosion under such conditions where stagnant water resides in the system for long periods. Alternatively, it may be necessary to upgrade the stainless steel grade to alloys like 1.4462 or 1.4539 for critical applications, if there is a well-founded risk of MIC.

## REFERENCES

1. Avery RE, Lamb S, Powelland CA, Tuthill AH.; Stainless steel for potable water treatment plants; NIDI Technical Series No. 10087, 1999.
2. Code of Practice for domestic water supply installations, DS 439 (Danish Standard), 3rd edition, 2000.
3. The Drinking Water Directive (98/83/EC).
4. Mathiesen T, Rislund E, Nielsen TS, Frantsen JE, Tørnæs U, Pedersen HG, Nielsen P, Petersen MB; MIC of stainless steel pipes in sewage treatment plants; Proceedings of NACE Corrosion 2003, San Diego, paper 03563, 2003.
5. Féron D (editor); Marine Corrosion of Stainless Steel (EFC 33); Institute of Materials, Minerals and Mining; 320 pp; November 2001.
6. Dickinson WH, Caccavo F Jr, Lewandowski Z, The Ennoblement of Stainless Steel by Manganese Dioxide Biofouling, Corrosion Science, Vol. 38, No. 8, pp. 1407-1422 (1996).
7. Linhardt P, Nichtawitz A; MIC in hydroelectric power plants; Proceedings of NACE Corrosion 2003, San Diego, paper 03564, 2003.
8. Tverberg JC, Pinnow KE, Redmerski LS, "The Role of Manganese Fixing Bacteria on the Corrosion of Stainless Steel", NACE, CORROSION/90, Paper No. 151 Houston, Texas (1990).
9. Mathiesen T, Nielsen K, Fontenay F; Evaluation of Susceptibility to Crevice Corrosion in Drinking Water of Stainless Steel Pipes with Connections; Proceedings of CEOCOR Malmö Meeting, 2005.
10. Rasmussen N, B.Sc. thesis, Technical University of Denmark, January 2007.
11. Newman RC, Wong NP, Ezuber H, Garner A; Pitting of stainless steel by thiosulphate ions; Corrosion, pp. 282-287, 1989.
12. Hakkarainen TJ; Microbiologically influenced corrosion of stainless steels - What is required for pitting?; Materials and Corrosion, Volume 54, Issue 7, pp. 503-509; 2003.

13. Mollica A, Montini U, Lai ME, Féron D; Simulation of the effects of anaerobic or mature biofilms on the crevice corrosion behaviour of stainless steels in natural marine environment; Proceedings of EuroCorr 2003, Budapest, 2003.
14. Herbsleb G, Poepperling RK; Corrosion properties of Austenitic - Ferritic Duplex steel AF22 in Chloride and Sulphide environments; Corrosion, Vol. 36, No. 11, pp. 611-618, 1980.