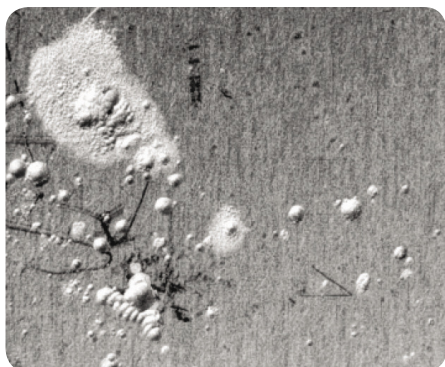


Microbiologically Influenced Corrosion



Contents

MIC on Stainless Steels in Wastewater Treatment Plants... 2

Field Tests and a Risk Assessment.

Service Experience with High Performance Stainless Steels in Aggressive Fresh Waters 12

Dear Reader

"Water, the essence of life" has been used as a slogan within the desalination industry for many years and the truth of this short sentence could not be overestimated. Water is next to oxygen the most important compound for human life and we cannot be without any of them. However, despite the large amounts of water around the world, the availability for human consumption is by different reasons limited.

Desalination is one way to solve this problem in areas where climatic conditions govern the supply of fresh water, but lack of clean water is also an issue in several industrialised countries due to pollution of the water resources that actually are available. However, proper water management can handle that problem as well and efforts to clean industrial wastewater and municipal sewage are important tasks for communities nowadays, applying tight demands on effluents disposed in rivers and lakes.

One key element when designing sewage treatment plants is the use of correct construction materials, not only for the plant itself, but also for the collectors or ducts transporting the sewage from different parts of the city to the treatment plant. Such collectors are often buried under major streets where heavy traffic can cause ground settlements and cracking of the collectors if not made of a tough enough construction material. Stainless steel is a natural construction material for a variety of components in sewage treatment plants and also for the collectors. The grade of stainless steel to be used depends on process stage in the plant and also of the composition of the feed.

This issue of Acom contains two papers covering materials selection in municipal sewage treatment plants. The first describes testing of stainless steels in six Scandinavian sewage treatment plants and some guidelines for selection of the correct grade; the second describes service experience of stainless steel when used in water and some of the case stories are directly linked to sewage treatment.

Yours sincerely

Jan Olsson

Technical editor of Acom

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MIC on Stainless Steels in Wastewater Treatment Plants

Field Tests and a Risk Assessment

Abstract

Field tests of stainless steels were carried out in six wastewater treatment plants. Welded coupons were tested in the final settling tanks in the plants. Ennoblement of the OCP, similar to that reported from investigations in seawater, was observed at two plants. Pitting corrosion was observed under deposits after the field test on steel grade AISI 304 (UNS S30400) and on AISI 316 (UNS S31600) in one plant. No corrosion was found on 2205 (UNS S31803) after the field tests. Laboratory measurements were also carried out to predict MIC in the final stages of aerobic wastewater treatment systems. The breakdown potential was measured in distilled waters with various amounts of chlorides, nitrates and sulfates according to a factorial design from maximum and minimum values in two levels measured in six plants. A risk window for MIC in wastewater treatment plants was designed, which was in good agreement with the field tests.

Introduction

Microbiologically influenced corrosion (MIC) on stainless steels in fresh water is commonly related to an attached biofilm on a stainless steel surface. If the condition favors microbial activity in the water, one of the effects of the adhesion of a biofilm to the stainless steel surface is ennoblement of the potential. The increase in the potential may cause localized corrosion on stainless steel if it reaches a value exceeding the breakdown potential of the steel grade. Cases of MIC on stainless steels have been reported for alloys with relatively low molybdenum content as localized corrosion and deposits were often found at or close to the corrosion sites [1].

New biological purification treatments have been introduced in wastewater treatment plants world-wide, which efficiently reduce nitrates from the water. However, after the introduction of these new biological treatments, a number of unpredicted cases of increased corrosion damage have been reported [2–4]. In this study, an attempt was made to evaluate major risk factors for MIC in new systems using new biological treatment that reduces the nitrate content in the water.

Biofilms and Ennoblement

From early investigations in seawater the effect on the open circuit potential (OCP), of an active biofilm attached to a stainless steel surface was reported as ennoblement to high values about 350–450 mV_{SCE}[5].

These values were found independent of geographical locations and hydrological properties in a European exposure program but sensitive to temperature increase [6]. Mollica and Trevis attributed the ennoblement to an increased rate of the cathodic reaction, which has an effect on the corrosion rate in the propagating stage [5].

The authors proposed an enzymatic oxygen reduction mechanism. Scotto et al. stated that the ennoblement was caused by the respiratory metabolism of bacteria living in the biofilm and observed that a biofilm could be present on a stainless steel surface without involving any ennoblement [7].

The exact mechanism of the ennoblement is still not clear but several proposed mechanisms are described in the literature. Mollica and Trevis proposed a relationship

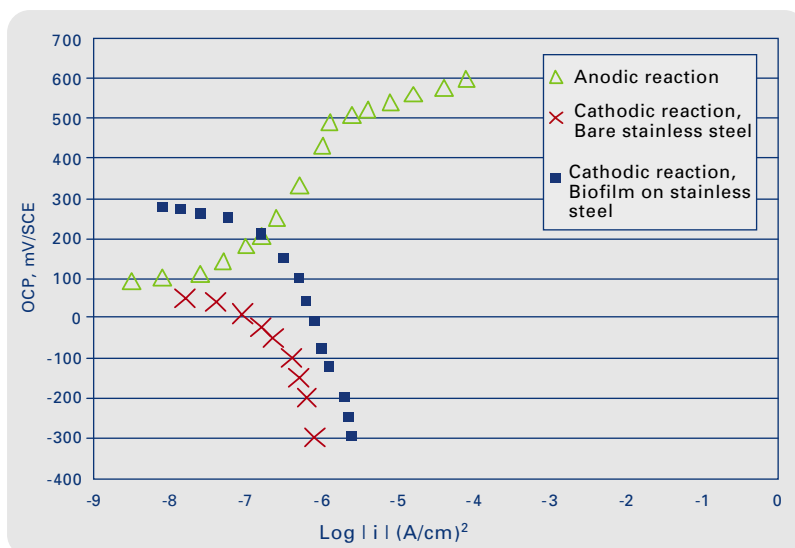


Fig. 1 Schematic view of the cathodic reaction, which is influenced by biofilm activity.

linking oxygen reduction depolarization, biofilm growth and potential for stainless steels exposed to natural seawater [8]. They concluded that oxygen depolarisation of a stainless steel surface was due to the formation of localized active sites. These sites were attributed to the covering or adsorption of bacteria or bacteria-produced catalysts, on the metal surface, which reduced oxygen with fast kinetics. Figure 1 shows schematically how the overall cathodic reaction is influenced by the activity of the biofilm.

A decrease in pH has been proposed to be the reason for ennoblement [9,10]. Chandrasekaran measured with micro-electrodes a pH-gradient in marine

biofilms and noted the accumulation of iron and manganese in biofilms [11]. Millimolar concentration of peroxide was also measured in biofilms on stainless steel and the author assumed that the concentration of peroxide was regulated by enzymes present in biofilms. However, Mollica et al established that a decrease in pH is not the complete reason for ennoblement of stainless steels [12]. Indeed, they attributed the ennoblement to the fact that the microbial activity in the biofilm plays a role in the catalysis of the oxygen reduction. Scotto and Lai confirmed a hypothesis of enzyme catalysis by extracellular enzymes present in the EPS matrix of biofilms [13]. The presence of organic acids and hydrogen peroxide as a result of an enzymatic reaction between oxygen and, for example, catalase was also reported by Dupont et al [14].

Another aspect to the mechanism of ennoblement is the action of manganese oxidizing bacteria. Several authors have reported manganese-rich deposits in combination with corrosion on standard stainless steel grades [15–17]. Little and Wagner state that bacteria have been recognized for a long time for their ability to deposit manganese dioxide in structures outside their cells [18]. The bacteria oxidize Mn^{2+} to manganese dioxide MnO_2 and it is claimed that the dissolution of the oxide is responsible for ennoblement. The mechanism is based on the theory that MnO_2 is not stable in the environment and that the bacteria provide the energy needed for the oxidation. Nevertheless, Dickinson et al showed that a paste of MnO_2 on a stainless steel surface corresponded to an increased cathodic reaction and potentials in the same range as ennoblement [16]. The authors analyzed manganese in deposits on stainless steels exposed to river water using SEM/EDS.

In addition, the action of manganese oxidizing bacteria depositing MnO_2 on stainless steel surfaces in the presence of chlorides creates conditions for under deposit corrosion. These conditions increase the risk of localized corrosion on stainless steels.

MIC and Requirements for Localized Corrosion on Stainless Steels

Biofilm attached to a steel surface is not enough to cause corrosion on stainless steel in a chloride-free environment, even if ennoblement were to occur on a stainless steel grade with low resistance to corrosion (e.g. AISI 304). For localized corrosion to occur as the result of biological factors, certain criteria have to be fulfilled for the breakdown of the passive layer. Factors such as the environment, biological activity and steel grade have to be considered in combination. Localized corrosion on stainless steel is dependent on the breakdown of the passive layer and the breakdown potential. This potential can be referred to as a transition potential between the two regimes of metastability and stable corrosion [19]. Szklarska-Smialowska reviewed the complexity of the breakdown potential, which is dependent on many variables such as temperature, surface conditions, set potentials, the induction time and the amount of alloying elements in the steel

grade [20]. The solution environment is of major importance and it is well known that chlorides have an adverse effect on stainless steels in terms of corrosion, On the other hand, nitrates and sulfates are effective corrosion inhibitors due to their properties of competitive adsorption, which help to replace the aggressive chlorides and thereby increasing the breakdown potential [21].

Ennoblement from microbial activity provides a high potential closer to, or in the vicinity of, the breakdown potential for standard stainless steel grades (AISI 304, 316) under certain conditions such as in the presence of chlorides, crevices and deposits. In these environments, localized corrosion can be initiated and propagated with an increased corrosion rate due to the enhanced cathodic reaction caused by the microbial activity.

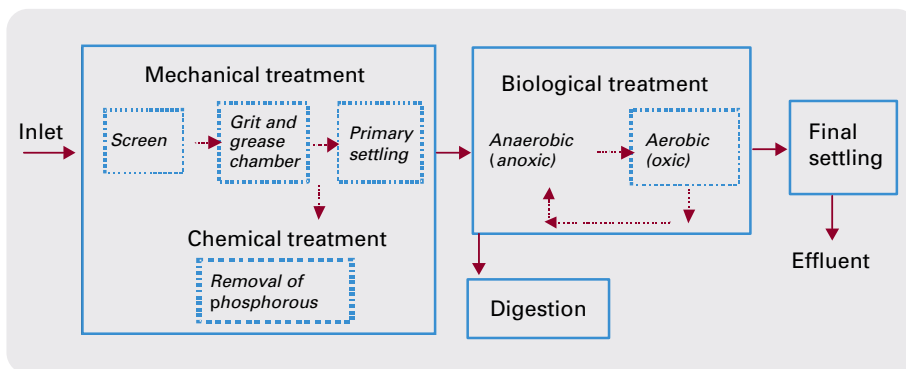


Fig 2. Schematic view of the main processes in a wastewater treatment plant.

Exposure Environment in a Wastewater Treatment Plant

At present, municipal wastewater treatment serves mainly to diminish the amount of phosphorus and nitrogen compounds in the wastewater. Wastewater treatment plants can be built in several stages according to a number of designs depending on the purification demands involved. Figure 2 shows a schematic representation of the main stages in a wastewater treatment plant.

Experimental

Material

The test materials were standard austenitic stainless steel grades (AISI 304, AISI 316) and a duplex stainless steel grade (2205). The chemical compositions are shown in Table 1. Chromium, molybdenum and nitrogen are the most essential elements for the resistance to localized corrosion of stainless steels. The pitting resistance equivalent (PRE) and the critical pitting temperature (CPT) are shown in Table 1. PRE is calculated on the basis of the composition of the alloy and gives information on the corrosion resistance of the stainless steel grade according to:

$$\text{PRE} = \%Cr + 3.3\%Mo + 16\%N \quad \text{Equation 1}$$

Alfonsson and Qvarfort investigated several formulas to calculate PRE values and compared the PRE values with critical pitting temperatures (CPT) [22]. They found an acceptable linearity between the CPT and PRE values for any of the PRE formulas investigated and the stainless steel grades used in this investigation. CPT values measured according to ASTM G150 using the Avesta cell of the tested stainless steel grades are shown in Table 1.

Steel grades used in field and laboratory tests.

Table 1.

Material	UNS	EN	SS	CPT, °C	PRE	Nominal composition, (%)					
						Mn	Cu	Cr	Ni	Mo	N
AISI 304	S30400	1.4301	2333	–	19	1.79	0.26	18	8.7	–	0.06
AISI 316	S31600	1.4436	2343	27	27	1.39	0.46	17	11	2.7	0.06
2205	S31803	1.4462	2377	52	35	1.47	0.19	22	5.5	3	0.17

This investigation includes previously presented results from five plants [23] and new results from plant 6. The test materials were produced from cold rolled sheet as coupons with longitudinal welds. The filler composition in the welds corresponded to the base material. The welding method used was automatic Tungsten Inert Gas (TIG) welding, a method commonly used for thin stainless steels. The samples exposed in five plants, were pickled after welding while the samples exposed in the sixth plant were pickled on one side but with residual weld oxides on the other side. The purpose of exposing the one-sided pickled samples was to simulate tube conditions where the weld oxides usually remain inside the tube. All the coupons were 30 cm long, exposed longitudinally in the plants and half-immersed so that the electrical contacts were protected from the water line.

The width of the samples varied between 3 cm and 4 cm depending on the width of the weld.

Laboratory Tests

The stainless steel grades shown in Table 1 were also investigated in the laboratory, however, no welds were exposed in the laboratory tests. Anodic polarization curves were recorded using an electrochemical cell, as shown in Figure 3, chosen for its capability to provide conditions similar to deposits on a stainless steel surface or in shallow crevices. The electrochemical cell was used to simulate two kinds of deposits on the surface, (one kind using the o-ring as more dense deposits and the other masking the o-ring with gelatin for simulating less dense deposits). The breakdown potential was measured for all steel grades in the cell with the two kinds of deposits. For both events the breakdown potential was noted from anodic polarization curves when the localized corrosion current density exceeded $10 \mu\text{A}/\text{cm}^2$ for more than one minute. A factorial design was carried out at maximum and minimum values for various amounts of chlorides, sulfates and nitrates based on the values found in six wastewater treatment plants. The design was carried out to find a risk assessment for stainless steel grades used in Swedish wastewater treatment plants. Table 2 shows the minimum and maximum values of chlorides, nitrates and sulfates used in the factorial design [24].

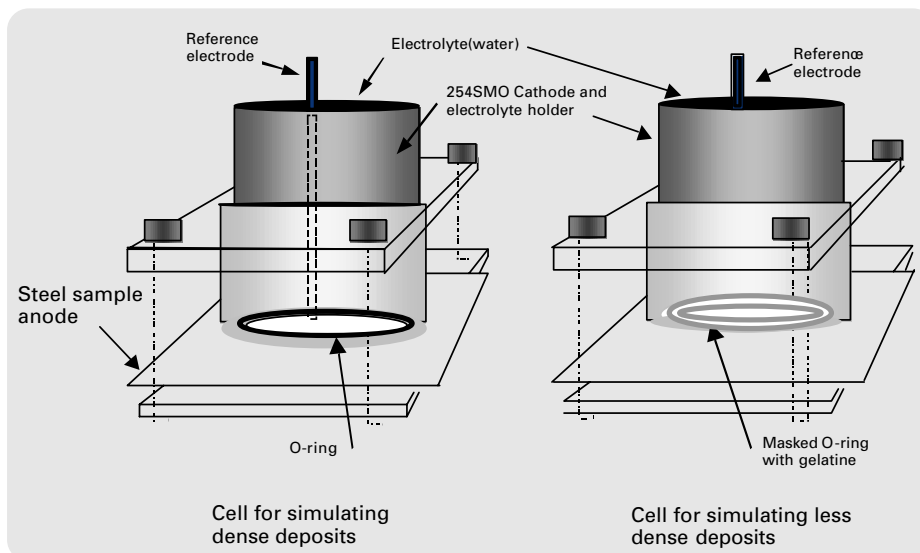


Fig. 3 Electrochemical cell used to simulate deposits on the steel surface.

Maximum and minimum values of chlorides, nitrates and sulfates used in the factorial design. Table 2

Ion	Max amount (mg/l)	Min amount (mg/l)
Chloride	600	50
Nitrate	10	1
Sulfate	150	50

Test Locations in the Wastewater Treatment Plants

Coupons were exposed in six different wastewater treatment plants for two time periods. The first field test was carried out at five plants (plant 1–5) for one year at each site, starting in November 1996 and ending 11–14 months later. In the second field test, coupons were exposed at one plant (plant 6), from June 2000 to November 2000. The chemical compositions of the water from the plants are shown in Table 3. The field test coupons were exposed in the final settling tank at each wastewater treatment plant. In plants 1-5, a single coupon of each steel grade was exposed while in plant 6, two replicates of each steel grade was exposed.

The water temperature at the exposure sites varied between 10°C and 15°C.

Chemical compositions of treated wastewater from the field-test locations.

Table 3

Compound	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5 (anaerobic)	Plant 6
Nitrate-N (mg/L)	10.2	3.6	1.5	2.8	4.1	<0.5
Sulfate (mg/L)	129	92	150	82	69	110
Chloride (mg/l)	515	225	585	58	78	410
Iron (mg/L)	0.16	0.32	0.083	0.38	0.98	0.17
Manganese (mg/L)	0.18	0.068	0.045	0.060	0.069	0.18
Aluminium (mg/L)	<0.01	0.02	<0.01	0.05	0.06	<0.02
pH	6.8	7.8	7.1	6.5	7.6	7.1
Conductivity (mS/m)	208	147	263	58.7	60.2	194
COD* (mg/L)	4.3	8.4	6.6	6.8	16	250

* Chemical oxygen demand

During the field tests at the wastewater treatment plants, the OCP was measured with a multimeter HY14. The measurements of the OCP were carried out manually. All measurements of potential used a saturated calomel electrode (SCE) as the reference electrode.

Results and Discussion

Biofilms and Ennoblement

It is well known that the grow rate of aerobic biofilms largely depends on the concentration of nutrients, (such as nitrate, sulfate, phosphate and potassium), on the presence of a carbon source and on the concentration of oxygen in the water [1]. Measurements of the OCP performed in the final stages of wastewater treatment plants have shown that the OCP reached, during exposure, was largely dependent on the composition of the water and the oxygen concentrations, (see Table 4).

Chemical composition, oxygen supply and maximum measured OCP in the final stages of wastewater treatment of the different plants.

Table 4

	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5 (anaerobic)	Plant 6
Nitrate-N (mg/L)	10.2	3.6	1.5	2.8	4.1	<0.5
Sulfate (mg/L)	129	92	150	82	69	250
COD* (mg/L)	4.3	8.4	6.6	6.8	16	
Max OCP (mV/SCE)	337	28	219	194	50	0

*Oxygen consumption measured as chemical oxygen demand, COD.

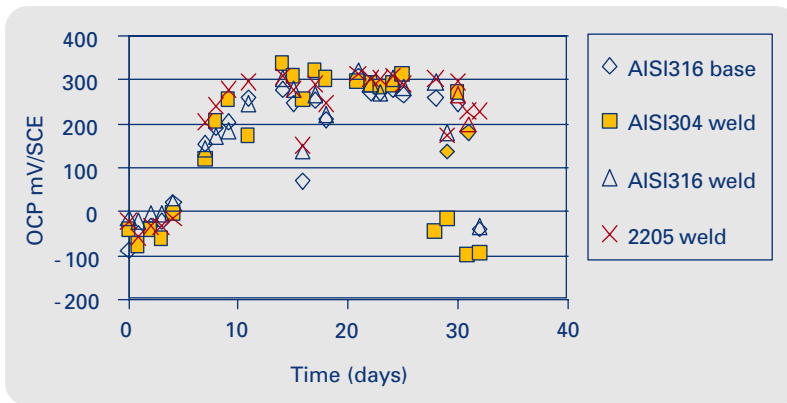


Fig. 4 Time dependence of OCP during exposure of AISI 304, AISI 316 and 2205 coupons in the final stage of wastewater treatment plant 1 (aerobic biodegradation of wastes).

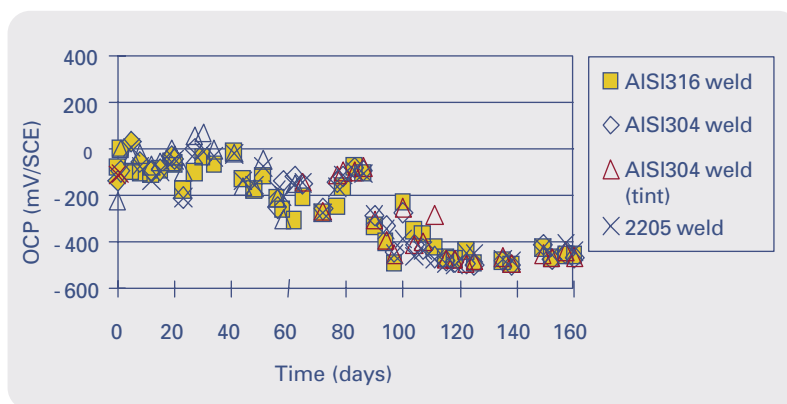


Fig. 5 Time dependence of OCP during exposure of AISI 304, AISI 316 and 2205 coupons in the final stage of wastewater treatment in plant 5 (anaerobic biodegradation of wastes).

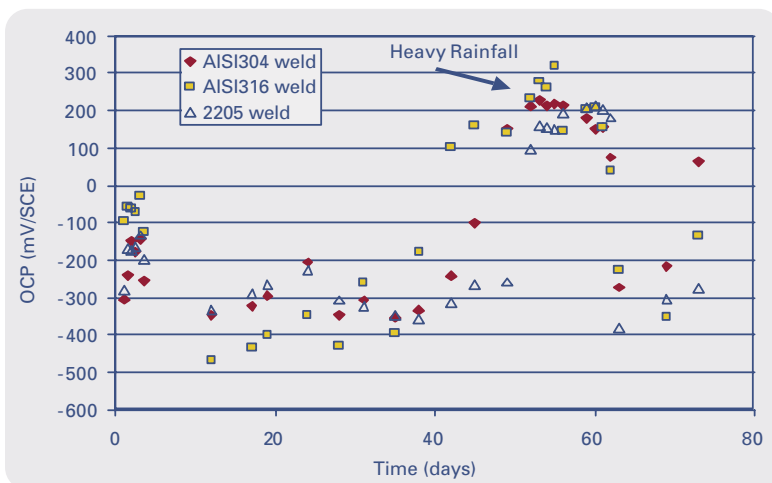


Fig. 6 Time dependence of OCP during exposure of AISI 304, AISI 316 and 2205 coupons in the final stage at wastewater treatment plant 6.

In aerobic conditions (e.g., COD values ranging from 4–7), the potential increased between 190 mV/SCE to 340 mV/SCE, whereas, in more anaerobic conditions (e.g. COD values higher than 7), the OCP increase was low and even decreased at higher COD values. The increase or decrease in OCP of stainless steel was independent of parameters such as the composition of the stainless steel grade, on the surface oxide composition, weld or unwelded conditions, with or without pickling the weld oxides, and on the microstructure of the steel, (i.e. austenitic or duplex stainless steel) as shown in Figures 4 and 5. The large oscillations in the OCP measured after 15 and 30 days exposure in the final stage of the wastewater treatment of plant 1, (Figure 4), are probably due to the initiation and the repassivation of pits.

These results are in good agreement with results obtained in natural seawater [6], [25–27]. It also confirms the importance of oxygen in the respiration process of aerobic biofilms and the ennoblement of the OCP on stainless steel in natural or industrial waters. Further evidence of this is shown in Figure 6. The OCP measured in plant 6 first decreased due to the high COD value, (i.e., anaerobic conditions) and thereafter increased during a heavy rain fall which may have affected the supply of oxygen that corresponded to a large decrease in the COD value.

The importance of nutrients and oxygen content on the ennoblement of the OCP of stainless steel can be seen in Figure 7. An empirical function representing the influence of the amount of nutrients and the oxygen content has been defined using data from this investigation:

$$F(\text{nutrient, oxygen}) = (C_{\text{nitrate}} + C_{\text{sulfate}}) \times \frac{1}{\text{COD}} \quad \text{Equation 2}$$

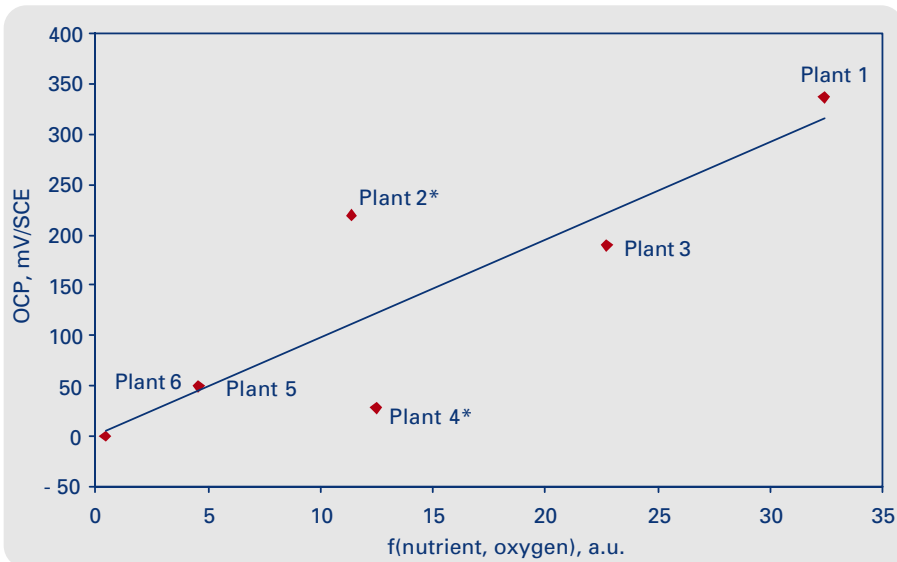
Where C_{nitrate} and C_{sulfate} are the concentration of nitrate and sulfate in the final stage of the wastewater plant and COD is the chemical oxygen demand.

From the results, it is obvious that there is a relationship between the nutrient and oxygen content in the water and the ennoblement of the OCP of stainless steel. However, it should be noted that the function defined in equation 2 is empirical and other parameters such as the temperature, carbon, potassium and phosphorus content may play an important role in the development of the biofilm [1].

The deposits remaining on the samples exposed at plant 1, after washing with water where tightly adhered to the steel surfaces. Under the slimy, easily removed deposits, there were black brownish deposits that were analyzed by SEM/EDS, (Figure 8). Both manganese and sulfur were detected. The origin of the presence of manganese and sulfur in the deposits is not clear.

MIC on Stainless Steel From the Field Tests

At plant 1, corrosion was found on stainless steel grades AISI 304 and AISI 316 in combination with heavy deposits, a high chloride content and ennoblement. Figure 9 shows the extent of corrosion on the base material and on the welds of steel grade AISI 316 after removal of the deposits.



*Unreliable reference electrode.

Fig. 7 Maximum OCP measured on stainless steel in the final stage of wastewater treatment plants as a function of nutrients and oxygen content in the water (see equation 2.)

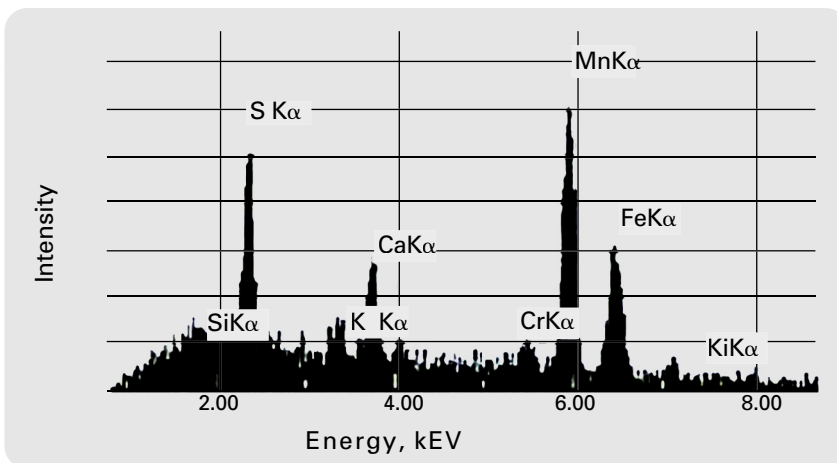


Fig. 8 SEM/EDS analysis of the deposits found on AISI 316 after a year field test at plant 1.

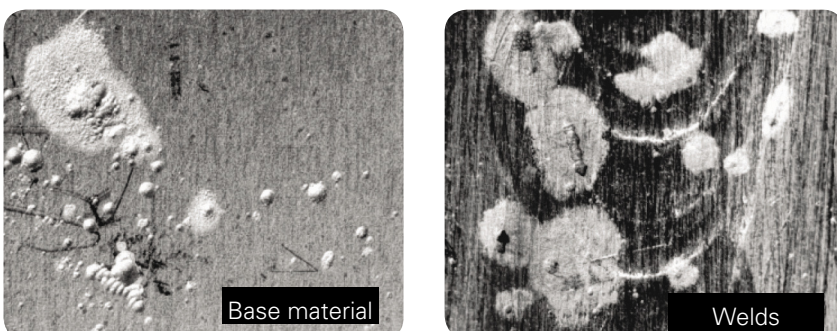


Fig. 9 Localized corrosion found on AISI 316 under heavy deposits after a field test at plant [1]. (magnification x3)

Results from the visual inspections made after field tests in the final stages of six treated wastewater treatment plants.

Table 5

Plant	AISI 304 (EN 1.4301) weld	AISI 316 (EN 1.4436) base	AISI 316 (EN 1.4436) weld	2205 (EN 1.4462) weld	Max OCP, mV/SCE	Chloride content mg/L
1	Corrosion	Corrosion	Corrosion	No corrosion	337	515
2	Corrosion	No corrosion	No corrosion	No corrosion	(28)*	225
3	Corrosion	No corrosion	No corrosion	No corrosion	219	585
4	No corrosion	No corrosion	No corrosion	No corrosion	(194)*	58
5	No corrosion	No corrosion	No corrosion	No corrosion	50	78
6	Corrosion (weld oxides)	No corrosion	No corrosion	No corrosion	0 or 321**	340

*Unreliable value due to unreliable reference electrode.

** The later value corresponds to a heavy rainfall.

Table 5 shows the potential values obtained in the field tests in combination with the chloride content and visual observations after the field tests. Biofilms or biological deposits were observed on all samples after the exposure at the plants, but ennoblement was only observed at some plants.

It is well known that the combination of a high OCP value generated by microbial activity in a biofilm and a high chloride content will lead to a higher susceptibility of localized corrosion for AISI 304 and AISI 316. The results shown in Table 5 are in good agreement with this observation. Localized corrosion was observed in plant 1 for AISI 304 and 316 because of a high OCP and high chloride content. On the other hand, for plants with a low chloride content in the water, no corrosion was observed (e.g. plants 4 and 5).

From the data, it is obvious that the likelihood of localized corrosion on AISI 304 and 316 will be governed by the combination of the OCP value and the chloride content in the water. A high OCP value may increase the potential above the critical potential for pitting and/or crevice corrosion, whereas the role of chloride ions will be to increase the susceptibility to localized corrosion.

Risk Assessment for Stainless Steels in Wastewater Treatment Plants

The results from the field tests were used to design a laboratory method to estimate the risk of corrosion in freshwater systems such as the final stages of wastewater treatment plants. The risk assessment was based on parameters in the systems that are considered either detrimental or inhibitive for localized corrosion on stainless steel.

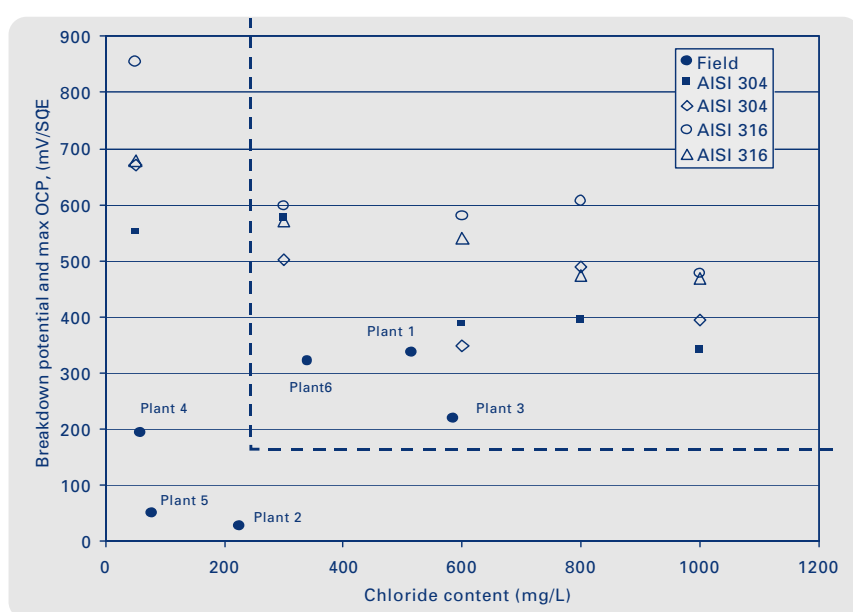


Fig. 10 Breakdown potentials of AISI 304 and AISI 316 providing a risk window in wastewater treatment plants, where a microbiologically active biofilm causing ennoblement is attached to the stainless steel surface. The results from field tests are indicated.

Using statistical methods, it was shown that the chloride content was the major parameter influencing the initiation of localized corrosion on AISI 304 and 316. Based on these calculations, experiments were carried out excluding sulfates and nitrates for a risk assessment design to cover the worst case scenario. A risk window for MIC in wastewater treatment was designed for clean water and with the addition of chloride ions. Figure 10 shows the risk window for standard steel grades AISI 304 and AISI 316 as a function of the chloride content. The figure shows the breakdown potentials for parallel samples of the two steel grades. For potential above the breakdown potential, the risk of localized corrosion increased. The upper limit of the window is not defined since it is based on the probable potentials received with addition of oxidative chemicals.

The lower limit of the window has been defined from real plants in order to be below the risk of initiation of localized corrosion. Hence, the role of the biofilm may be to raise the potential at values within the window. This was the case for coupons exposed to treated wastewater at plant 1. It should be noted that the exact definition of this window depends on the temperature and whereas the material is used as base or welded conditions.

Conclusions

In order to explore the conditions for MIC in wastewater treatment plants, a number of field and laboratory tests were carried out.

The following conclusions were drawn from the field tests:

- No corrosion was found on SS 2205 after field tests in the final stages at six wastewater treatment plants in Sweden and Denmark.
- Ennoblement of the OCP of stainless steel occurred at two plants to high values as previously found in natural seawater (300-350 mV/SCE).
- The ennoblement of the OCP was independent of the composition of the stainless steel, of the microstructure and the presence of remaining weld oxide after TIG welding using root gas protection.
- The ennoblement depended on the presence of nutrients and on the oxygen content in the water.
- AISI 304 under welded conditions suffered from localized corrosion at four plants where the chloride concentration was above 200 mg/L.
- AISI 316 was attacked at one plant where ennoblement was obtained in combination with chloride concentration above 500 mg/L and the coupons were covered with tightly adherent deposits.
- Biofilms growing in an anaerobic biodegradation stage induced negative potentials around -500 mV_{SCE}.
- MIC on stainless steel in aerobic environments was a result of ennoblement induced by an active biofilm in combination with sufficient chloride contents, deposits and the steel grade.

The following conclusions were drawn from the laboratory tests:

- The risk of MIC on steel grade AISI 304 was most pronounced during the combined action of ennoblement, high chloride concentration and deposits on the surface.
- A risk window for predicting MIC on stainless steel in aerobic wastewater treatment plants was designed, and found to be in good agreement with obtained field results.

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Service Experience with High Performance Stainless Steels in Aggressive Fresh Waters

Abstract

Five case histories are described where standard Types 304 or 316 stainless failed prematurely by localized corrosion in fresh waters that nominally would be considered to be non-aggressive. These waters were, however, very aggressive because of the effects of microbes, manganese or chlorination, depending on the particular case. In each of these cases the standard stainless steel was replaced with one of the high performance stainless steels with good results.

Introduction

The standard Types 304 and 316 stainless steels (S30400 and S31600) are widely used as vessels, piping and heat exchanger tubing for handling fresh waters of all kinds. There are, however, certain situations involving fresh water where localized pitting or crevice corrosion is a possibility and where failure can occur. For example, corrosion can occur where certain microbial populations exist under stagnate or low flow rate conditions, or in the presence of a combination of the manganese ion and a strong oxidant.

Another class of stainless steels, the high performance stainless steels (HPSS), is intended primarily for service in more aggressive saline waters sometimes made more aggressive by the presence of an oxidant or high temperature as might be encountered in such applications as paper bleaching, in steam condensers operating on chlorinated cooling water, and in evaporators. Experience is showing that the HPSS can be used in some of these fresh water situations where an unusually aggressive condition exists. The purpose of this paper is to describe some of these situations, providing some examples from field experience where substitution or replacement with a HPSS has taken place.

Background

When one speaks of the serviceability of Types 304 and 316 stainless in fresh waters, one is usually thinking of four primary environmental parameters that must also be defined. These are the chloride content of the water, the presence of oxygen or other strong oxidant, the temperature, and the presence of crevices. For example, Type 304 is thought to be suitable for use as steam condenser tubing at water chloride levels up to about 250 ppm, chlorine levels less than about 1 ppm, temperatures up to 110°F and at water flow velocities fast enough to avoid sediment build-up, and thereby the creation of crevices, in the tubes (about 3 ft/second) [1]. However, if one or more of these environmental parameters exceeds these empirical limits, the possibility of localized corrosion is introduced.

The HPSS are a group of stainless steels that are resistant to localized attack not only at higher chloride levels but also resistant to attack at higher levels of oxidants, higher temperatures, and the presence of crevices. This superior resistance is achieved primarily through the use of large amounts of chromium, molybdenum and nitrogen as alloying

elements, and these raise the resistance to pitting and crevice corrosion significantly in most aqueous environments. The chemical compositions of some representative HPSS alloys discussed in this paper are given in Table 1 and compared to those of Types 304 and 316. The relative localized corrosion resistance of these alloys can be estimated by their pitting resistance number (PRE) where: $PRE = \%Cr + 3.3\%Mo + 16\%N$. In this relationship %Cr, %Mo and %Ni are the weight percent of that alloying element in the steel. This relationship is based on statistical regression analysis of critical corrosion temperatures, pitting or crevice, for many stainless steels as determined in standard laboratory corrosion tests. The three independent variables are not truly independent of one another and they are not metallurgical substitutes. Nevertheless, the PRE has proven to be a highly useful benchmark for resistance to localized attack in aqueous chloride solutions. A high PRE number indicates high resistance to localized corrosion. The PRE numbers for the HPSS cover the range of about 30 to 55, well above the values of 18 to 25 typical for Types 304 and 316. A detailed discussion of all of the HPSS is given in the recent Nickel Development Institute publication No 11021 [2].

It is no surprise that the higher alloy contents of the HPSS increase their resistance to

corrosion. The use of the PRE parameter demonstrates a remarkably consistent relationship of these alloy elements in dramatically increasing the resistance of HPSS to localized corrosion. As shown in Figure 1, this increased resistance to localized corrosion is achieved over widely different chloride contents, oxidant contents, temperatures, and the presence or absence of crevices. The high critical pitting/crevice temperatures for these stainless steels demonstrate their ability to maintain passivity under severe environmental conditions.

A body of field experience is now accumulating which confirms the anticipated good performance of these stainless steels in aggressive waters. Examples demonstrating this behavior are provided in the following case histories.

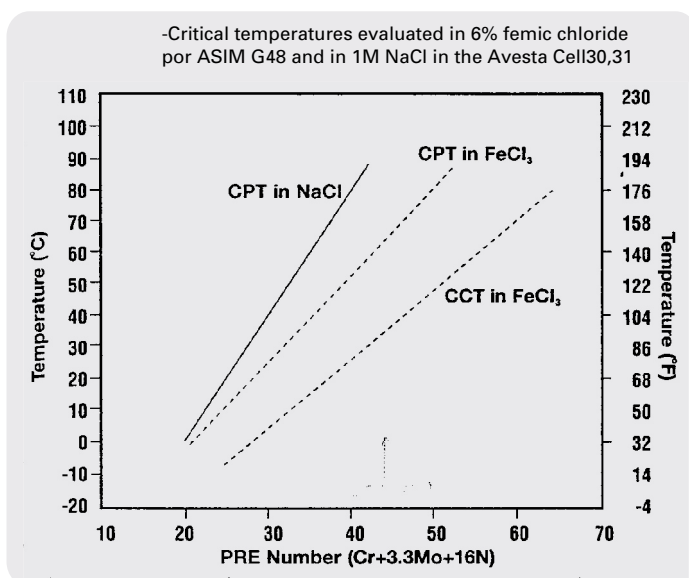


Fig. 1 Critical pitting and crevice corrosion temperatures for austenitic stainless steel related to PRE numbers

Description of the High Performance Stainless Steels Cited in the Case Histories

Table 1

UNS Number	Alloy Structure	C	N	Ni	Cr	Mo	PRE* Number
S30403	Austenitic	0.015	0.06	8.5	18.2	0.2	20
S31603	Austenitic	0.015	0.06	10.5	17.5	2.2	26
S44660	Ferritic	0.010	0.004	2.0	27.5	3.5	39
S32205	Duplex	0.010	0.18	5.5	22.5	3.3	36
N08367	Austenitic	0.02	0.22	0.24	20.5	6.2	44.5
S31254	Austenitic	0.010	0.22	18.0	20.0	6.3	45
S32654	Austenitic	0.010	0.50	22.0	25.0	7.5	58

*Pitting Resistant Equivalent (PRE) = % Cr + 3.3 % Mo + 16 % N

Presentation of Case Histories

Case 1: S44660 Condenser Tubing Replacing Type 304 Stainless

This case history involves a nuclear power station main steam surface condenser. The station is located on the Ohio River in southwest Pennsylvania and uses river water for make-up to a closed loop evaporative tower main cooling system. The condenser was originally tubed with Type 304 stainless tubes when the plant began operation in 1976. Condenser tube leaks became a reoccurring problem shortly after startup and continued through a refueling outage in 1983 at which time the tubes were thoroughly inspected and significant tube degradation noted. Based on this inspection the Type 304 tubes were replaced with HPSS SEA-CURE^{®(1)} (S44660) tubes during the next refueling outage in 1984.

Some design and nominal operating conditions for this condenser are listed in Table 2.

The tube wall thickness, at 22 BWG (0.028 inches/0.7mm), is normal for most condensers of this kind. The maximum circulating water temperatures range from 81°F (27°C) inlet to 107° (42°C) outlet, and thus are not unusual, nor is the nominal water flow velocity of 6.0 fps (1.8 mps) unusual. From a salinity standpoint, Ohio River water is quite low in chloride having a typical value of 20 ppm. Even with a cooling tower concentration factor of 10 to 1, a rule of-thumb chloride limit of 250 ppm would not be exceeded. The Ohio River, of course, carries significant pollutants as well as a quite high manganese loading compared to most fresh waters. Manganese has previously been associated with unusual pitting corrosion of brass and stainless condenser tubes at other locations on the Ohio River [3]. Chlorination is used to minimize waterside fouling at a 2 ppm limit which might be considered somewhat above a normal range considered satisfactory for Type 304 stainless steel.

Representative samples of the Type 304 tubes were removed and examined during the 1983 outage after they had been in service about seven years [4]. The tube I.D. surfaces contained a loose black deposit that consisted primarily of manganese dioxide (Table 3). A thin very tenacious reddish layer existed directly on the tube surface and this layer required a nitric acid soak and wire brushing for complete removal. A detailed microbial assay was not conducted on the water or deposits at the time these tubes were removed and examined. However, in relation to another corrosion problem with the service water system in 1994, a microbial analysis was made and showed that pits in carbon steel pipe contained sulfur-reducing bacteria, the anaerobic bacteria *Clostridium*, and the iron-oxidizing bacteria *Gallionella* in turbercles. The cleaned tube I.D. surfaces displayed numerous corrosion pits that opened into large cavities beneath the surface upon probing with a needle. This pitting displayed no preference for grain boundary or heat affected zones.

Nominal Design and Operating Conditions for the Steam Surface Condenser

Table 2

Condenser Surface Area	720,000 sq. ft.
Tube size	0.750 in. dia. x 0.028 in. wall (19 x 0.7 mm)
Max. cooling water temp.	81 °F to 107°F (27–42°C) inlet/outlet
Water velocity	6 fps (1.8 mps)
River water chloride	16–30 ppm
River water pH	6.7–7.9
River water Mn	0.05–1.0 ppm
Chlorination	2hrs/24hrs (2 ppm max.)

*Pitting Resistant Equivalent (PRE) = % Cr + 3.3% Mo + 16 % N

Tube I.D. Surface Black Deposit Composition by EDS Analysis (wt. Percent)

Table 3

Mg	Al	(Si)	K	Ca	Mn	Fe	Ni	Cu	Zn
1.10	6.51	8.09	1.35	3.89	54.42	15.52	1.19	3.45	4.49

¹ SEA-CURE is a registered trademark of Crucible Materials Corp

Performance Comparison of Type 304 and S44660 Tubes After Service in the Same Condenser

Table 4

	1976	1983-84	1987	1992	1996	2002
Type 304	Start-up	35% tubes pitted – 25% with > 50% penetration	–	–	–	–
S44660	–	Start-up	No pits	No pits	No pits	No pits

An evaluation of the performance of the new HPSS S44660 tubes has been made based on condenser leak experience and eddy current testing conducted over seventeen years since their installation in 1984.

This experience is compared in Table 4 to the detailed eddy current testing conducted on the previous Type 304 tubes in 1983 after seven years service. With thirty-five percent of the Type 304 tubes affected and more than half of these having more than half the tube wall penetrated, it is obvious that the original tubes had not given satisfactory service. Normally, thirty years service is expected for installations of this kind. In contrast, there has been no indication of any pitting corrosion taking place on the replacement S44660 tubes after seventeen years of service. The S44660 tubes have obviously fully resisted pitting corrosion that affects the Type 304 tubes.

Case 2: S31254 Pipe Replacing Type 304 Stainless Chiller Coils

Chiller coils are used to cool product in a vessel operating in a batch-type mode. The original installation utilized coils constructed of 2-inch schedule 10 Type 304 stainless steel pipe. The coils handle chilled treated water that enters the coils at 45°F (7°C) and exits at 60°F (16°C). Once a week the coils are drained and the entire unit is subjected to sterilization procedure where the coils are heated to 250°F (121°C) for four hours.

After successful operation for about fifteen years without any difficulties the chiller coils began to experience failures from I.D. pitting corrosion. Replacement coils made from Type 304 stainless then displayed rapid failure rates about every two years. At this time chlorination was implemented to help control product purity as it might be affected by the leak ingress of microbially contaminated chilled water. Thus this case history represents a situation where some unknown change in the raw water chemistry, or some other variable, introduced rapid pitting corrosion failures in Type 304 stainless; and chlorination did not improve the situation and possibly added another dimension to the diagnosis of the corrosion problem.

The site of this case is a plant located near the Ohio River in western West Virginia. The raw water source is from nearby deep wells. Some aquifers in this region are known to carry high manganese. The treated water analysis is given in Table 5. The water would not be considered aggressive from the standpoint of pH, chloride or microbial population. It does, however carry very high manganese and is highly chlorinated. The nominal water chloride and operating temperature range would not represent conditions that would be considered aggressive to Type 304 stainless from the standpoint of pitting corrosion. Although the coils are heated to a high temperature for a short time each week, stress corrosion cracking was not observed, and so it is unlikely that this sterilization procedure played a role in the pitting corrosion.

**Typical Chemistry of Water Handled
by the Type 304 Chiller Coils**

Table 5

pH	Chloride (ppm)	Mn (ppm)	Chlorine (ppm)	Total HPC
7.5	47	3.4	5.0 limit	"no growth"

As already mentioned the cause of failure in these coils was determined to be I.D. initiated pitting corrosion. The pitting typically took the form of large cavities beneath the I.D. surface. There were no metallurgical abnormalities in the coils themselves. The coils did contain I.D. deposits, and the pitting was associated with tubercles and showed some preference for field fabricated pipe butt welds. The general I.D. deposit appeared brown when dry and contained iron, manganese, sulfur and chlorine.

The analysis of the Type 304 coil failures, which took place in 1997, pointed to the possibility that high water manganese content acting in combination with a microbial or chlorine oxidant was the cause of the problem. A decision was made at that time to gradually replace the coils with alloy 254SMO^{®(2)} (S31254), one of the 6% Mo austenitic high performance stainless steels. This decision was based on the anticipated high resistance of this steel to permanganate-chloride pitting corrosion and because it has the necessary formability and field weldability to be fabricated into large chiller coils. The first installations were made early in 1998. It is now more than four years since the first of these coils went into service and so far they have showed no signs of pitting in this environment.

Case 3: N08367 6% Molybdenum Stainless Steel Replacing Type 304 in a Hot Water Line

A food processing plant uses water from its own well as a food ingredient. The water is pre-chlorinated and passed through a green sand/carbon filter and pumped into a reservoir outside the plant. All piping outside the plant is made from carbon steel or cast iron. From there the water is chlorinated again and brought into the plant. A Type 316 stainless steel heat exchanger heats the water to 150°F. The water is carried into the food processing area by an overhead “hot water line”. The insulated line is about 2,000 feet long and was originally built in Type 304 stainless steel. It has a main header of Type 304, 4-inch diameter schedule 10 pipe (0.12 inch wall thickness). At the far end of the insulated water line, the water temperature decreases to 80 – 120°F. After less than two years of service, the smaller diameter piping of the hot water line began to leak. Within five years, leaking was evident along the entire line. Figure 2 shows a picture of the pipe that has been temporarily repaired with patches.

² 254SMO is a registered trademark of Outokumpu Stainless

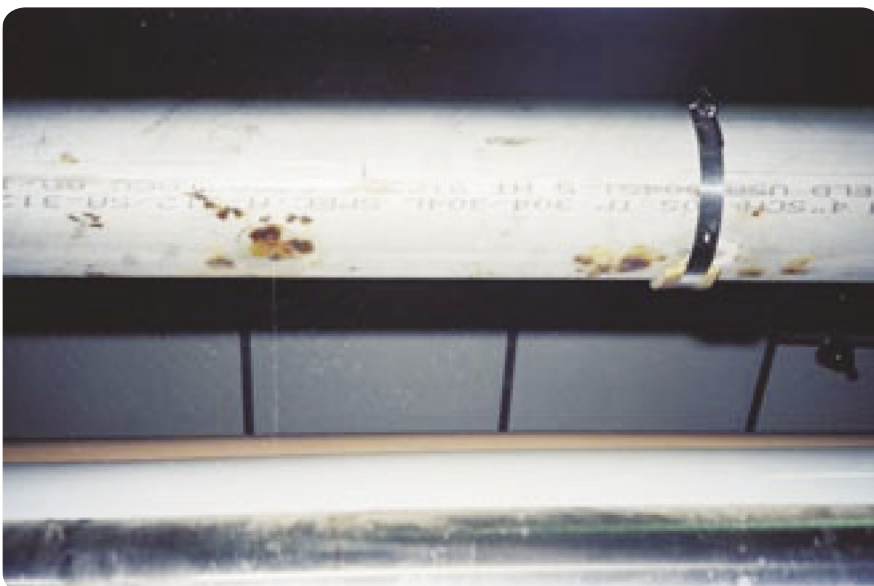


Fig. 2 Insulation removed from hot water pipe. A patch intended to temporarily fix a leak is visible on the right.

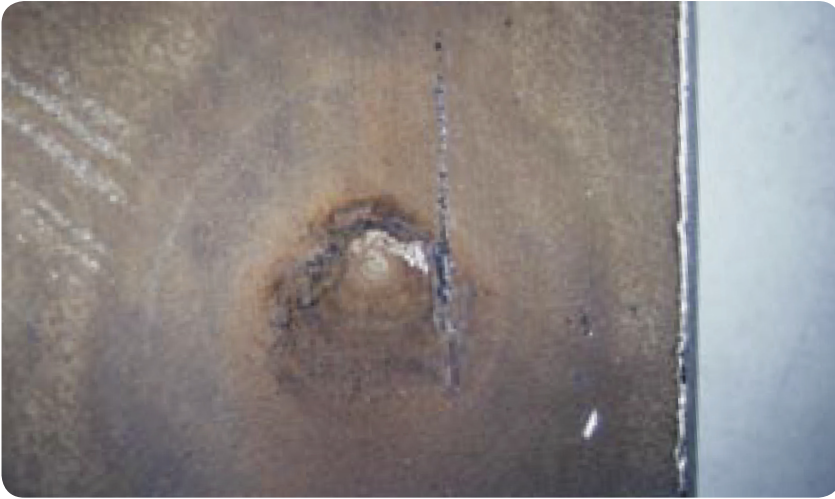


Fig. 3 A through-wall pit. The area directly at the pit mouth is blank metal surrounded by a dark stain.

Chemistry of water in food plant

Table 6

pH	Chloride (ppm)	Chlorine (ppm)	Manganese (ppm)	Total HPC	Metal Oxidizing Bacteria+
7.5	59	< 0.5	358	340,000/ml	35,000 units/ml

+As iron bacteria per method SMEW 9240D

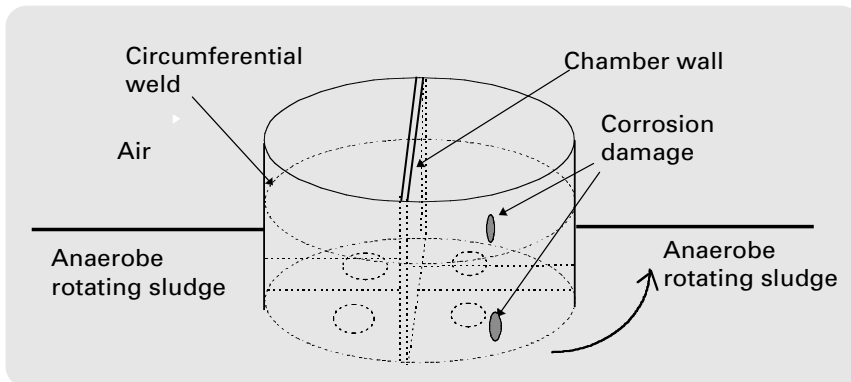


Fig 4. Schematic View of Corrosion Damage on the Outside of a Gas Seal on the Top of a Digester at a Wastewater Treatment Plant.

ID of the pipe. The pits were usually surrounded by a dark stain aligned with the flow direction of the water and a clean-etched area immediately at the mouth of the pits (Figure 3). SEM-EDAX analysis of the material within the mouth of a pit showed very high manganese contents compared to the manganese content of the deposit and in the stainless steel.

Table 6 shows the chemical analysis of the well water. The chloride and chlorine content of the water are relatively low. The pH is neutral. While the water temperature is slightly high, Type 304 is usually expected to withstand pitting corrosion under these circumstances. However, in this case the water analysis also shows high manganese content and a high population of bacteria, some of which are metal oxidizing.

CASE 4: Corroded Water/Gas Seal Placed on Top of a Digester in a Wastewater Treatment Plant.

Corrosion damage occurred on a water/gas seal made of Type 316 stainless placed on top of a digester in a wastewater treatment plant. Figure 4 shows a schematic view of the gas seal and the damages visible from the outside of the seal. The seal was facing on one side the rotating sludge and the other side the outdoor atmosphere. The temperature in the sludge was approximately constant at 100°F (38°C) and the pH varied between 6 and 8. The chloride content was between 57 and 184 ppm. The corrosion had started from

The inside surface of the pipe was covered with a thin yellow deposit which was somewhat darker and heavier on the bottom third of the pipe where most of the leaks were found. Based on the color of the yellow-brown deposit and a SEM-EDAX analysis it was concluded that the deposit consists mainly of a hydrated form of iron with some manganese, aluminum, silicon, chloride and calcium. No tubercles or other corrosion product mounds were found on the surface.

Many pits, some of which penetrated through the wall, were found on the ID of the pipe. The pits were usually surrounded by a dark stain aligned with the flow direction of the water and a clean-etched area immediately at the mouth of the pits (Figure 3). SEM-EDAX analysis of the material within the mouth of a pit showed very high manganese contents compared to the manganese content of the deposit and in the stainless steel.

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Fig. 6 Corrosion Damages on the Gas Seal



Fig. 5 Perforated Pipe Attached to the Gas Seal

**SEM/EDS Chemical Analysis
of Deposits on the Steel
Surface of the Corroded
Water/gas Seal**

Table 7

Element	Weight %
Phosphorus	1.2
Sulfur	39
Titanium	2
Chromium	9
Manganese	0.3
Iron	29
Nickel	14
Copper	5

the inside where the water/gas seal was facing sludge under digestion under assumed anaerobic conditions. Figure 5 shows corrosion damage from the inside of the digester, on a pipe attached to the seal, and Figure 6 shows the corrosion damage on the inside of the seal. A voluminous black deposit containing a large amount of sulfur was found to cover the corroded steel surface. Table 7 shows the results from using SEM/EDS analysis on the deposits.

Due to Swedish legislation the amount of manganese in the water has to be low in the effluent. This plant had too high values for a short period of time and a common method used to reduce the manganese amount was to precipitate manganese as manganese dioxide with a dose of potassium permanganate. The potassium permanganate was added to limit the amount of manganese in the effluent water but caused oxidative conditions for the stainless steel in an anaerobic environment. This was considered to be the cause of initiation of the corrosion. Nevertheless, the extent of corrosion damages was not in proportion to the corrosive environment, and bacterial action by sulfate-reducing bacteria (SRB) was not excluded as a factor in propagating the corrosion.



Fig. 7 Corroded Type 316 Stainless Pipe with Corrosion Product from Corrosion Attack on the Circumferential Weld.

CASE 5: Corrosion of Type 316 Stainless in the Final Stages of a Wastewater Treatment Plant

A wastewater treatment plant in the south of Sweden reported corrosion damage in 1996 on welded circumferential welds and on some of the longitudinal welds on the pipes made in Type 316 stainless steel. The plant used aerobic active sludge treatment for cleaning the water. The corrosion damage was first reported to occur due to dosing with ferric chloride, FeCl_3 . However, the corroded pipe was cut out and new material was repair welded to the pipes. At an inspection a year later, 1997, the circumferential welds at several sites were corroded from the inside, through the pipe wall, leaving the corrosion products visible on the outside surfaces. The pipes were located in the exit end of the plant after the final settling tank. Figure 7 shows a corroded weld on a pipe at the later inspection. Normally, the chloride content in the water was 300–500 ppm and the temperature 50–59 °F (10–15°C), and the Type 316 would be resistant in this environment.

From the evaluation of the damage it was not possible to exclude MIC as a possible contributor to the corrosion damage. Therefore, a field test was conducted in the final stages in the plant for evaluation of whether MIC was one of the causes or if it was possible to exclude MIC as a cause. The field test showed significant potential ennoblement to take place on stainless steel in this final stage; and also heavy deposit build-up occurred on the test samples after a year of exposure. Corrosion was found on the grades Type 316 and also on Type 304. No corrosion was found on the HPSS duplex alloy 2205 (UNS S31803) [6].

Discussion of the Case Histories

In Cases 1 and 2 the cooling water carried high levels of manganese, and manganese was a major component of deposits associated with the observed pitting corrosion failures. The relatively high water flow velocity in the condenser tubes and absence of a heavy fouling deposit argue against a strong microbial involvement in the condenser tube pitting. Likewise, the use of chlorination argues against a microbial involvement in these two cases. On the other hand the pit morphology was that of large subsurface cavities which have often been associated with MIC; but this morphology is not in itself conclusive evidence of microbial involvement. In both of these cases the use of chlorination provided a strong oxidant capable of promoting permanganate formation. Thus it is most likely that chlorine assisted manganese pitting, according to the mechanism elucidated by Streicher, was the primary failure mechanism in both cases [7]. Successful replacement with HPSS demonstrates that these steels can resist this form of corrosion. This resistance is demonstrated by the now seventeen year successful performance of the condenser tubing having thin 0.028 inch (0.7mm) wall.

In Case 3 Type 304 stainless steel would usually be expected to be resistant to pitting corrosion under the nominal conditions present. However, the manganese content of the water and the presence of bacteria made the water more aggressive than expected. Metal-oxidizing bacteria can metabolize manganese to produce permanganate. This change combined with chloride can produce pitting even at relatively low chloride contents. In this case it is also possible that chlorine helped to form permanganate, but both mechanisms would lead to the same form of pitting corrosion in Type 304 stainless steel.

The company decided to upgrade the piping system with a HPSS AL 6XN^{®(3)} (N08367), one of the 6% molybdenum stainless steels. This is one of the stainless steels that has been reported in the literature as being virtually unaffected by microbiological activity [8]. At first only the parts that leaked early on were replaced. As the pitting corrosion progressed to other parts upstream and downstream of the system the company decided to also replace those areas. The first replacements occurred almost four years ago. No corrosion has been reported since that time in the new piping.

In Case 4 the environment in the sludge process is not normally considered corrosive because the pH is nearly neutral and the chloride content is low. Nevertheless, the corrosion damage was well beyond that expected in this environment and an explanation was not easily found from the literature. A possible reason for the initiation of the corrosion was the oxidizing conditions created by the use of potassium permanganate in the process in combination with deposits and sulfur-containing compounds coming from bacterial action. In anaerobic sludge treatment digestion is normally associated with the production of methane gas and some hydrogen sulfide gas. In addition, a presence of SRB in sludge from wastewater treatment is also reported in the literature [9]. Furthermore, von Rège and Sand identified a variety of compounds produced by microorganisms like sulfate reducing bacteria (SRB), for example, FeS and FeS₂ [10]. Mollica et al have also previously reported reduction in the breakdown potentials for crevices on stainless steels, when an oxidizing potential or coupling was introduced in combination with hydrogen sulfide and SRB in anaerobic seawater clay [11]. A later report showed that 654SMO^{®(4)} (S32654), was resistant in seawater environment under these circumstances [12]. Thus a HPSS like S32654 would be a material likely to resist the corrosion that occurred in the Type 316 gas seal.

In Case 5 the field test showed significant potential ennoblement of stainless steels as well as heavy deposit build-up after one year. Potential ennoblement clearly points toward a strong microbial component in the environment, the heavy deposit build-up notwithstanding. Thus a MIC contribution to the observed corrosion could more satisfactorily explain the poor performance of the Type 316 than would chloride induced corrosion alone. The corrosion resistance of S32205 in the field test points to the superiority of this HPSS under these aggressive conditions.

³ AL 6XN is a registered trademark of ATI Properties, Inc.

⁴ 654SMO is a registered trademark of Outokumpu Stainless

Conclusions

The five case histories discussed in this paper all had a common element in that Types 304 or 316 stainless steel experienced service failures by localized corrosion; and these failures occurred in systems handling waters that normally would be thought to be non-corrosive based on their nominal chloride content and temperature. In all cases some unusual element existed that could account for these failures.

These elements related to effects of microbes, manganese, and chlorination, singly or in combination.

Another common element was that in all cases one of the high performance stainless steels either replaced Type 304 or 316 in these systems and gave good service, or showed potential for doing this based on preliminary tests. In all cases the waters involved were “fresh” waters rather than the high chloride waters for which these steels were originally designed. Thus high performance stainless steels should be considered in instances where certain fresh waters could be overly aggressive to the standard stainless grades

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