

1. Introduction

Stainless steel is widely used in the brewery industry because of its resistance to corrosion. In addition, well-chosen high-alloy steel allows for easier maintenance of hygienic conditions inside the tank [1]. An analysis of possible technological solutions indicates that 1.4301 steel is one of the most popular and cost-effective materials [2]. Corrosion problems in beer manufacturing are frequently reported. Both the beer manufacturing lines and the auxiliary infrastructure are at risk [3]. The data concerning problems with stainless steel resistance to corrosion depending on the surface treatment are also presented [4].

This paper presents the causes and a diagnosis of the corrosion types in a tank used to store warm water in a brewery house. Corrosion of the installation made of austenitic stainless steel in conditions of hot water containing chloride ions can be considered as a very common problem [5]. Detailed researches had been performed in order to solve this problem after it was found that corrosion phenomenon also concerns cold water installations in nuclear power plants [6,7]. It was recognised that it would be demanded to perform a very detailed selection of construction materials on the basis of chemical composition of water and its temperature [8,9]. Corrosion in hot water installations occurs mainly in the form of stress-corrosion cracking or pitting corrosion [10]. Nevertheless, the stress-corrosion cracking process can be initiated by the pitting corrosion, precisely by the increase in stresses in the pits' bottom [11,12]. Data available in scientific literature indicate that appearance of localised corrosion processes in hot water installations (static stresses) does not demand high concentration of chloride ions. Studies carried out by Turnbull et al. [11] point out the critical concentration of chloride ions at the level of 1.6 pp. [11].

The tank in question is made of 1.4301 (304 AISI) steel and has been in operation for 12 years. The investigated tank was made of 12 welded cylindrical elements of 1.4301 stainless steel of thickness from 2.5 mm at the upper part of the tank to 5 mm at the bottom part. The altitude of the tank was 18.6 m and cubic capacity was 200 m³. The water under hydrostatic pressure resulting from the actual level of water in conditions of 80 °C was stored in the examined tank. Walls of the bottom

cylindrical part of the tank were subjected to circumferential stresses, longitudinal stresses resulting from the interactions of hydrostatic pressure of water, and to the buckling forces resulting from the high altitude of the tank and the low thickness of the walls. In the case of stresses analysis, one should also consider changes of water temperature. Permissible stresses for 1.4301 stainless steel are decreasing by about 25% in the case of hot water storage as compared to the strength in conditions of cold water. It served as a storage tank for utility water used in beer mashing. The water temperature inside the tank was in a range of 70–80 °C. The water level in the tank was variable, and the water supply was connected to the upper part of the tank. The tank was not supervised during operation. As a result of its 11-year operation, a traverse crack occurred in the tank, causing a spill of utility water. Less than a year after that event, another crack appeared. Due to the extensive corrosion of other system components, there was the need to explain the causes of corrosion damage that threatens the safety of the manufacturing process.

2. Destruction of water storage tank

After a downtime and submitting the tank for inspection, the inner stainless steel surface was covered with dark brown deposit consisting mainly of the products of corrosion. The deposit was not very adhesive and could be easily removed with a paper towel. No changes in the steel below the deposit were found, so it can be concluded that the deposit was driven in by the water due to the corrosion in the water supply installation. The condition of the tank surface is shown in Fig. 1.

A corroded area was found in an approx. 1.5 m-wide cylindrical fragment of the tank (Fig. 2), located in the zone of mechanical impact of the pipeline outside the tank (See Fig. 3).

The locations of tank repairs correspond precisely to the zones of intense stress caused by the pipeline. This allows for associating the corrosion with the mechanical and corrosive impact. Corrosion attack visible in the form of branched lines and local centres is shown in Fig. 4.



Fig. 1. View of the inner surface of the container with partially removed deposit.

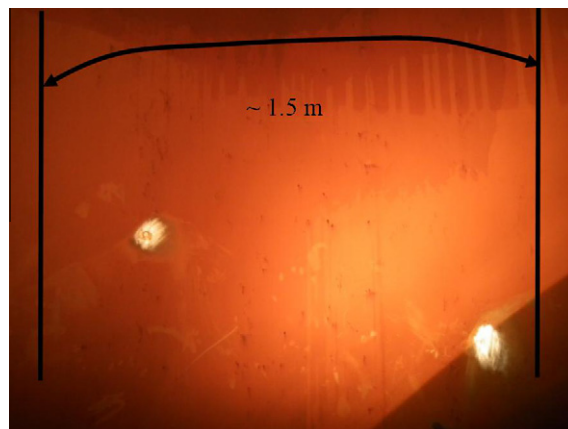


Fig. 2. A corroded part of the stainless steel tank.

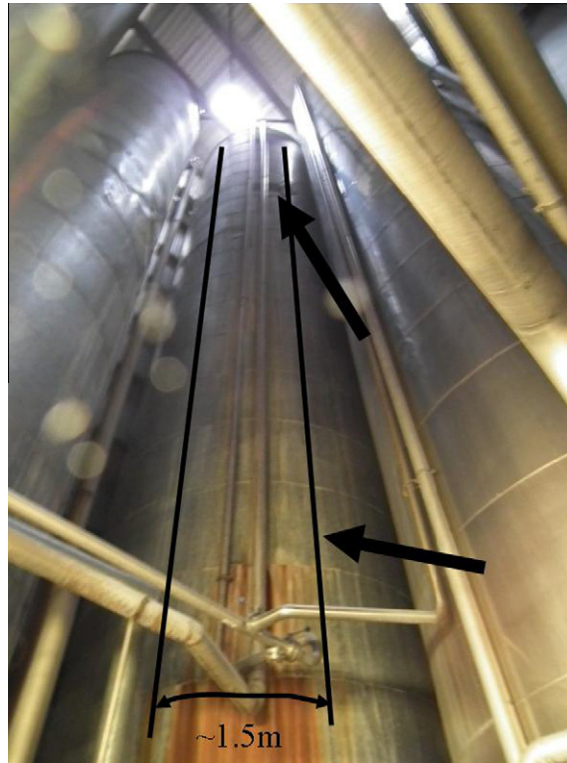


Fig. 3. Outside view of the tank with the corroded zone inside the tank marked.

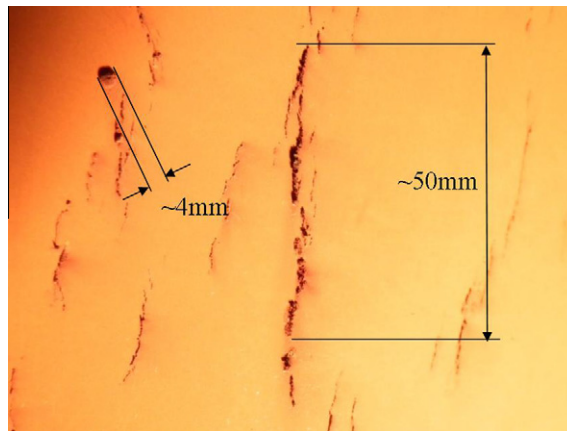


Fig. 4. Examples of corrosive attack of the cylindrical part of the tank.

After the products of corrosion were removed, clear corrosive attacks could be seen as cracks, pits and etchings (the result of deposit corrosion) (Fig. 5).

In some places, the cracks extended across the thickness of the tank. Fig. 6 shows the location of the total tank rupture (perforation).

Due to the presence of cracks visible on the tank surface, the stresses resulting from the interactions of hydrostatic pressure were calculated at the levels of 63% and 85% of the permissible tensile stresses for cold and hot water, respectively.

3. Experimental methods

Electrochemical investigations were carried out on 1.4301 stainless steel, from which the examined tank was constructed. The chemical composition of 1.4301 austenitic stainless steel is given in Table 1.



Fig. 5. Corrosive attacks in a stainless steel tank.



Fig. 6. Corrosion cracking of the mantle as the cause of perforation.

Table 1

Chemical composition of the austenitic stainless steel (AISI 304).

C	Si	Mn	P	S	Cr	Ni	Nb	Cu	Co	N
0.020	0.34	1.68	0.027	0.001	18.17	8.03	0.002	0.28	0.20	0.062

Cyclic polarisation tests were performed with the use of Gamry Instruments electrochemical measurement set-up. The tests were used for the determination of the susceptibility of the examined alloy to pitting corrosion and they were carried out in a three-electrode system. The scan rate of the potential was 0.5 mV/s. The examined electrode was the investigated stainless steel, the auxiliary electrode was made of platinum net and the reference electrode was a silver wire covered with silver chloride and placed directly in the solution used for tests. The susceptibility to pitting corrosion was determined in water before and after treatment. Comparative studies were also carried out for 1.4436 and 1.4462 stainless steels. The first type of steel is the potential material for the new tank, while the 1.4462 steel seems to be the most suitable material when considering the corrosion resistance and mechanical strength for applications involving water treatment.

Potential measurements of the inner surface of the tank were performed under field conditions. The value of the corrosion potential measured using a specially constructed reference electrode shows the quality of the passive layer covering the steel. The lower the value of the potential is, the greater the risk of corrosion. After it is emptied, the tank undergoes self-passivation due to the presence of air and moisture, which makes it possible to use the potential measurement to determine the locations, where the passivation conditions are hampered.

Additionally, SEM research of the examined steel surface was conducted. Steel specimens were taken from the places, where the corrosion products were detected on the tank. SEM images were obtained by using S-3400N Hitachi VP-SEM (with THERMO Scientific EDS unit attached). Results of this analysis are presented in Fig. 7.

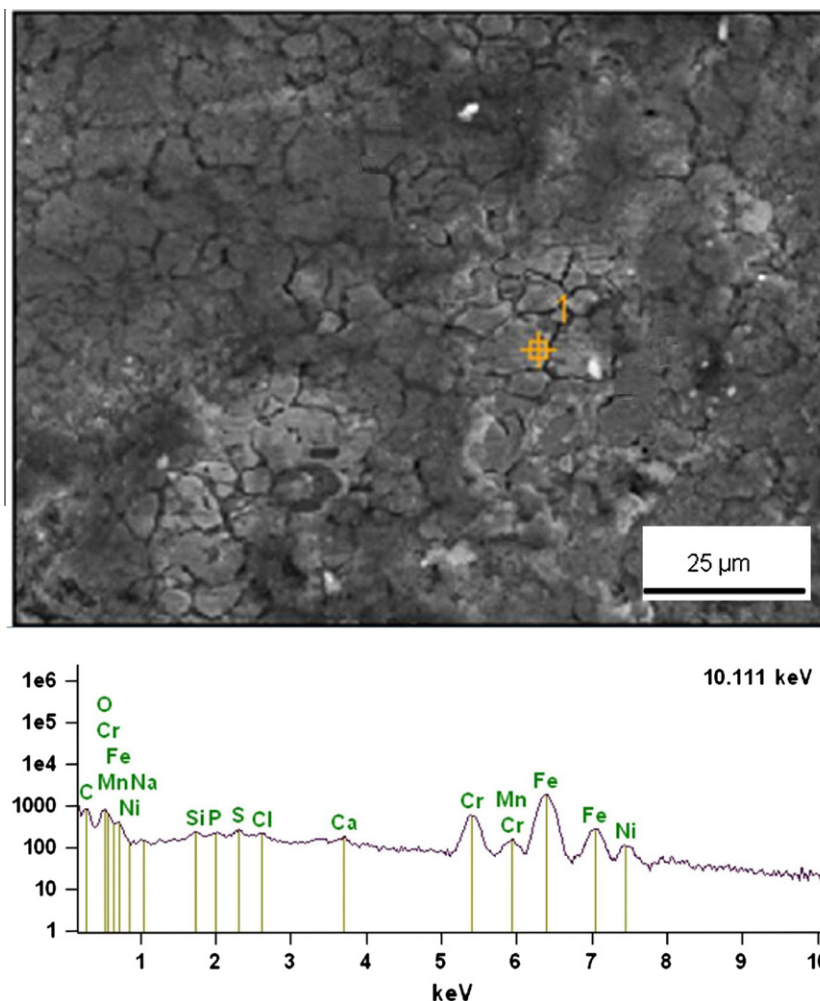


Fig. 7. SEM and EDS images of the corroded surface of the tank.

During the study of the buffer tanks, water samples were taken in order to conduct rudimentary analytical studies that would allow for the determination of the threat of corrosion associated with the influence of the water environment.

The water samples were taken from the following locations:

- Raw water taken before the water treatment system.
- Water taken from the water installation of the brewery house after treatment.
- Circulating water taken from a tank made of unalloyed constructional steel.

Aggressive ion contents in the raw water and in the treated water (after pH correction) are gathered in [Table 2](#).

In order to determine the corrosivity of water at the each stage of the beer production, corrosivity indexes for the investigated solutions were calculated in various temperatures. Temperature of raw water was about 7 °C. The Langelier index in such conditions was 0.08. As a result, the cold water could be determined as one of weak corrosivity with low tendency to form carbonate layers. Extrapolation of the calculated Langelier indexes to higher temperature improves their value.

Table 2

The results of chemical analyses of water samples.

	pH	Ca ²⁺	Mg ²⁺	Fe-total	SO ₄ ²⁻	Cl ⁻	O ₂	Cond.
Raw water	7.11	76	10	0.098	58	12.05	0.46	40.80
Treated water	5.86	61	8	0.04	45	66.72	0.55	32.50
Tank water	5.94	60	8	0.41	42	72.31	0.57	34.20

4. Experimental results and discussions

4.1. The study of the susceptibility of stainless steels to pitting corrosion in water prior to pH adjustment

The water in the brewery was subjected to the technology of changing its chemical composition in order to obtain the optimal parameters for beer-manufacturing purposes. It underwent water treatment and pH adjustment. Apart from the steel used to build the tank, the study also included the 1.4436 steel to be used as an alternative material for the future tank and the recommended 1.4462 steel with good mechanical properties and better corrosion resistance.

Tests of susceptibility to pitting corrosion in water before treatment were performed at 75 °C. This is a typical temperature of the water stored in the tank. Fig. 8 shows example curves of the cyclic polarisation of stainless steels in water.

The studied steels remained in the passive state in these conditions. The increase of the current in the polarisation curves occurs at a potential of about 0.9 V and it is linked to the emission of gaseous oxygen on the surface of the working electrode. The polarisation curve after the reversal of polarisation clearly indicates the lack of pitting corrosion. Based on these results, it can be concluded that pre-treatment water is not aggressive. The probability of pitting corrosion occurring is nearing zero in all types of steel studied.

4.2. The study of the susceptibility of stainless steels to pitting corrosion in treated water

The cyclic polarisation measurements were also performed at 75 °C. Fig. 9 presents the results of these tests.

In a pH-adjusted water, only duplex 1.4462 steel does not show any susceptibility to pitting corrosion. Microscopic evaluation of the steel surface has also not shown the presence of pitting. Therefore, it can be concluded that the steel is resistant to corrosion in treated water within the whole temperature range. 1.4301 and 1.4436 steel types are subject to pitting corrosion. The pitting nucleation potentials are:

- 1.4301 steel = + 0.30 V in Ag/AgCl.
- 1.4436 steel = + 0.45 V in Ag/AgCl.

The pitting nucleation potential for 1.4436 steel is higher than that for 1.4301 steel, which indicates a higher resistance to pitting corrosion and a lower probability of occurrence of this type of corrosion in treated water at 75 °C, but does not exclude the occurrence of such destruction.

After completing the electrochemical measurements, a photo of a 1.4301 steel sample was taken after studying it in water at 75 °C, which is shown in Fig. 10.

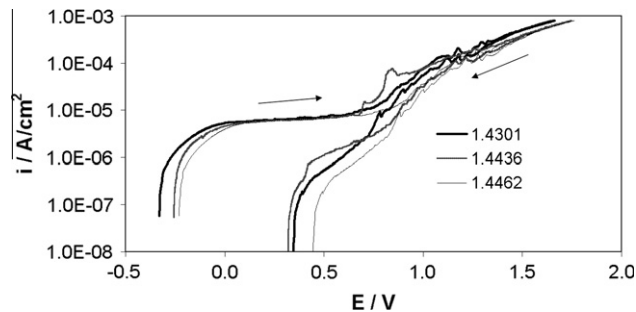


Fig. 8. Cyclic polarisation curves in raw water at a temperature of 75 °C for investigated steel.

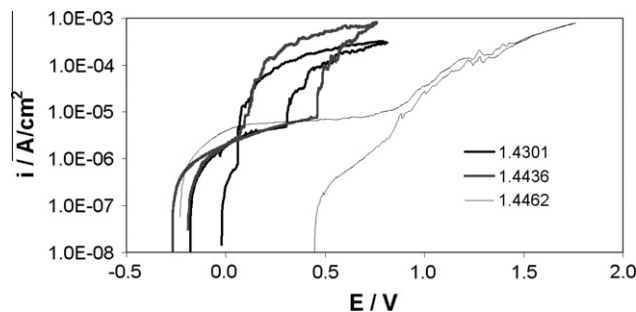


Fig. 9. Cyclic polarisation curves in treated water at a temperature of 75 °C.

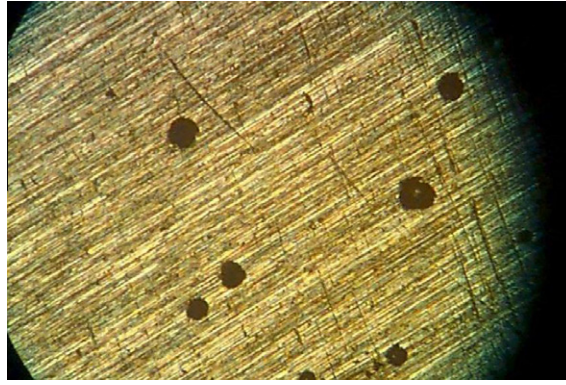


Fig. 10. The surface of a 1.4301 steel sample after cyclical polarisation test in water at 75 °C.

Fig. 11 shows a curve of pitting nucleation potentials as a function of the temperature of the treated water.

As shown in Fig. 11, the 1.4462 steel does not undergo pitting corrosion throughout the whole temperature range, and the probability of pitting corrosion occurring in 1.4436 steel is smaller than in 1.4301 steel.

4.3. Analysis of the chemical composition of water

After sampling the water before and after treatment process, basic analytical tests were made, that may be useful to determine the causes of corrosion problems in the installation. The results of the analyses are presented in table 2.

The chemical analyses of the treated water show a change in the pH value of approximately 7 to 5–5.5. This is caused by the dosing of concentrated hydrochloric acid. This results in a simultaneous increase in the Cl^- ion content in the water from 15–35 mg/dm^3 to 55–100 mg/dm^3 . The pH change and the increase in the chloride ion content impact the corrosive aggressiveness of water. It should be noted that there is an additional increase of chloride ion content in the water that is circulating in the circuit (Table 2). The pH drop also accelerates corrosion in the installation, thus increasing by 10-fold the concentration of iron ions. The high chloride ion content increases the susceptibility of 1.4301 steel to pitting corrosion. Chloride ions weaken the passive film on stainless steel and cause the intensification of corrosion processes on non-alloyed steels. The stainless steels undergo pitting corrosion, while the low-alloy steels are subject to uneven general corrosion. The high level of chloride ions and the temperature of 75 °C create the conditions for initiation of both pitting and corrosive cracking.

4.4. The study of the potential of the inner part of the stack

The measurement results show that the tank is well-fitted. However, areas with a significantly lower potential (by as much as 0.3 V) can be found on the surface. These are probably places, where pitting corrosion develops. The potential studies have shown that the passive condition of the tank is much better in the upper parts. The potential measurement results are summarised in Table 3.

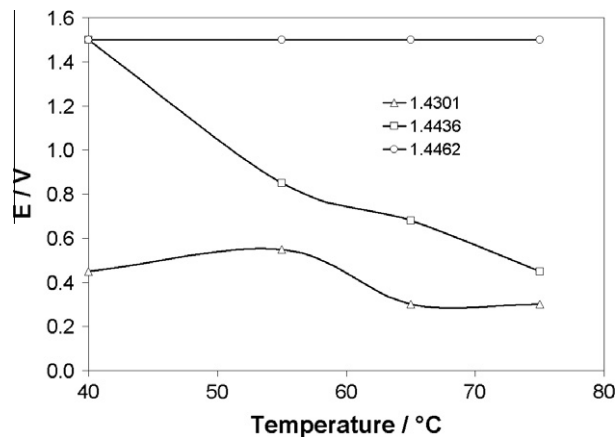


Fig. 11. Changes of pitting nucleation potentials vs. the temperature of the treated water.

Table 3

The results of potential measurements of the tank walls a Zn/ZnSO₄ electrode.

Location of measurement	<i>E</i> /V
The area around the welded joint between the first and second sheet in the cylindrical part of the tank	1.340, 1.330, 1.281, 1.256, 1.237, 1.244, 1.329
The sheet of the second cylindrical part of the tank	1.257, 1.190, 1.197, 1.181, 1.175, 1.179
Polished area on the sheet of the first cylindrical part of the tank	1.215, 1.217, 1.237
The sheet of the first cylindrical part of the tank	1.200, 1.228, 1.218, 1.206, 1.171
The area around the weld joining the bottom with the cylindrical part of the tank	1.167, 1.202, 0.865 , 1.184, 1.279, 1.191, 1.193
The area around the weld of the two bottom parts	0.979 , 1.278, 1.015, 1.217, 1.057
Tank bottom	1.198, 1.171, 1.030, 1.050, 0.985

Bold values indicate places where passive layer is especially weak.