Crevice corrosion at welded spacers of stainless steel double pipeline. Case study

Korozja szczelinowa rurociągu i płaszcza ze stali nierdzewnej przy przyspawanych elementach dystansowych. Studium przypadku

JAN MARJANOWSKI

DOI 10.36119/15.2022.5.3

Pipe in pipe (PIP) constructed from DIN 1.4301/1.4307 stainless steel was used for neutral product (chocolate) transport at 58°C in a food plant. Stainless steel spacers were welded along the internal pipeline. Corrosion rate increased because iron ions dissolved and dispersed in water were introduced to the outer stainless steel pipeline from carbon steel installation and carbon steel buffer tank. Rust patches were formed in all pockets present in the pipeline jacket because of iron ions content in water. Local chlorides concentration increased due to adsorption in rust so that crevice and pitting effects were very high. Heating water circulating between external and internal pipeline effected high number perforations of both lines in 20 days after production started. Perforations were localised mainly in crevices present between stainless steel spacers and both pipelines. Preventive measures against corrosion were suggested.

Keywords: stainless steel corrosion, crevice corrosion, pitting corrosion, stainless steel pipe in pipe, welded stainless steel spacers, depolarization with Fe^{3+} *ions.*

Instalacja rura w rurze (PIP) wykonana ze stali nierdzewnej wg DIN 1.4301/1.4307 służyła do transportu wewnętrzną rurą neutralnego produktu (czekolady), który był podgrzewany do temperatury 58°C przez wodę płynącą rurą zewnętrzną. Wzdłuż rurociągu wewnętrznego przyspawano elementy dystansowe ze stali nierdzewnej. Szybkość korozji takiej konstrukcji wzrosła wskutek wprowadzania do wody jonów żelaza z instalacji rurowej i zbiornika retencyjnego wykonanych ze stali węglowej. Zwiększona zawartość jonów żelaza w wodzie spowodowała powstawanie i gromadzenie rdzy we wszystkich kieszeniach przyspawanych elementów dystansowych. Adsorpcja chlorków w rdzawych osadach spowodowała lokalne zwiększenie ich stężenia, co sprawiało formowanie szczelin i wżerów korozyjnych. W rezultacie powstała duża liczba perforacji obu rurociągów w ciągu zaledwie 20 dni od rozpoczęcia produkcji. Perforacje były zlokalizowane głównie w szczelinach pomiędzy przekładkami dystansowymi i miejscami ich kontaktu z powierzchniami rurociągów. Zaproponowano środki zapobiegawcze dla przeciwdziałania korozji istniejącego układu rury w rurze.

Słowa kluczowe: korozja stali nierdzewnej, korozja szczelinowa, korozja wżerowa, rura w rurze ze stali nierdzewnej, przyspawane przekładki dystansowe, depolaryzacja z udziałem jonu Fe^{+3}.

Introduction

Stainless steel crevice corrosion can cause a complete failure with very little material loss. Narrow openings between metal-metal or metal with nonmetal components are prone to localized corrosion. It also occurs under deposit having limited access to the surrounding environment. It is not possible for oxygen to gain access to the stainless steel surface within very tight crevices where water state is close to stagnant. Oxygen is used in corrosion reaction within a crevice so that its level depletes. The crevice interior becomes an anode with a very small area ratio compared to surrounding cathode which have much higher oxygen access. A surplus of metal positively charged ions (mainly iron, but also chromium) relieved within a crevice due to corrosion is balanced by negatively charged chloride ions by migration into the crevice. The environment inside the crevice becomes enriched in chloride salts. Interior of the crevice becomes more and more acidic due to salt hydrolysis decreasing pH value. Strong acid within the crevice results fast anodic dissolution and removes passive film, increasing enormously the corrosion rate. Usually pits are formed first before conditions are set for the onset of crevice corrosion **[1]**. Around a crevice takes place cathodic depolarization reaction with participation of free iron ions and oxygen dissolved in water. Rust is deposited as a result. It is to remember that crevice geometry decides on the metal loss. Narrower the crevice the higher metal dissolution **[2].** Openings between 0.1 and 100 μm have been typically found to cause crevice corrosion **[3].** Stainless steel crevice corrosion of welded spacers located in between internal and external pipe was described here for the first time in the literature. The photos of spacers and views of the surface after the spacers removal show very well pickled stainless steel under spacers (anodes) and rust patches around them (cathodes).

Operating conditions

The spacers serve to even position of the inside pipe within the outer pipe. Despite the fact that different kinds of centralizers are applied for jacketed pipe systems (PIP) made from stainless steels no effective solution that protects against crevice corrosion

Jan Marjanowski – Marcor Co. , Gdansk, Poland j_marjanowski@marcor.com.pl

failures has been proposed. Corrosion problem is quite difficult to solve because it requires preventing formation of free spaces between the spacers and the pipes. High number of commercial spacers is non-metallic bands having shape of half cylinders fixed to the outside of the inner pipe. Each spacer has a series of longitudinal ribs fitting tight inside the outer pipe. Another type of spacers have plastic clamps over an inner pipe, four plastic blocks that fit inside of the outer pipe with all plastic parts in the stainless steel holders. There may be more types of the centralizers used.

The case presented here shows very high corrosion rates leading to fast perforations of the stainless steel pipeline by hot water containing moderate chloride content. Pipeline constructed as PIP from DIN 1.4301/1.4307 (AISI 304L) austenite stainless steel had length around 2000 m. The diameter of the internal pipeline was mostly equal to DN80. That of the external pipeline was mostly equal to DN100. Hot water containing around 60 mg/dm^3 chlorides was flowing between the internal and external stainless steel pipeline from a collector made from carbon steel. Also a hot water circulation buffer tank was made from carbon steel. Rust deposit was found on both pipelines. Much rust was collected at the bottom part of the outer pipeline. Liquid chocolate flowing within internal pipeline got required temperature of 58°C from water that flows in an external coat. According to Thomas & Betts 304 Stainless Steel Corrosion Compatibility Chart: chocolate syrup has excellent compatibility to the stainless steel 304L.

Temperature of heating water flowing into the stainless steel pipeline from the hot water circuit was up to 70°C. The flow rate of water was equal to 4 dm^3/min.

When the prefabrication of the pipeline was finished the pressure tests at 5 – 6 bars using demineralised water were carried out. This operation lasted a short time and could not be a reason of fast PIP perforation.

Twenty days after the production started around 40 perforations were found. Perforations of the product pipeline appeared under the spacers. Perforations of the external pipeline were over the spacers. Some perforations occurred under the rust patches at weld sensitive regions.

Stainless steel composition and structure

The stainless steel samples were taken from the leaking piping. The steel composition is given in the Table.1.

Tab. 1. Composition of stainless steel 1.4301/1.4307 used for pipeline construction
Tab.1 Skład stali nierdzewnej 1.4301/1.4307 użytej do budowy instalacji rurowej

C	Cr	Ni	Mn	S	P	N	Si
0.02	18.02	8	1.4	0.001	0.035	0.045	0.44

The micro-structure of the stainless steel used to construct the pipelines show high content of linear δ-ferrite in the structure (Fig. 1-2). The existing structure was probably the result of improper cooling rate of stainless steel treatment in the mill. Austenite mixed with δ-ferrite inclusion does not have such good corrosion resistance like pure austenitic structure [4].

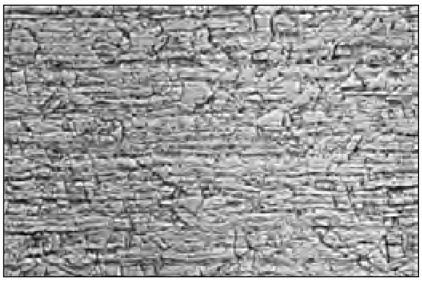

Fig. 1.
Stainless steel austenite structure with δ-ferrite inclusions
Rys.1. Struktura austenityczna stali nierdzewnej z wtrąceniami δ-ferrytu

Fig. 2.
Stainless steel austenite structure with high number of δ-ferrite inclusions7
Rys.1. Struktura austenityczna stali nierdzewnej z dużą ilością wtrąceń δ-ferrytu

Water parameters

Hot water was the only one corrosive medium effecting PIP system perforation so that its properties were fundamental to evaluate the reasons of the damages.

Water analysis results showed also that water entering the stainless steel pipeline from the carbon steel installation, introduced high number of iron ions. Fe^{+3} ions, being cathodic depolarizers, offer in water environment increased stainless steel corrosion rate (steel oxidation). Chosen analysis results of water samples taken from different places of the installation are presented in the Table 2.

The calculated indexes showed that water outflowing from carbon steel collector did not form a corrosion protective film on carbon steel surfaces. Water was corrosive against carbon steel installations. Water circulating within pipeline coats contained fewer chlorides compared to the feeding one. Water conductance diminishing, that means less salinity, chlorides and sulphates within stainless steel installation, was the result of adsorption and precipitation of water components, but also a buffer action.

Water samples taken were analysed for microorganisms content using Schülke

Tab. 2. Results of physical-chemical water analysis
Tab.2 Wyniki fizykochemicznej analizy wody

Water parameter	Inlet to stainless steel installation from carbon steel collector 4	Return collector from the stainless steel installation
pH	7,14	6,15
Hardness [°dH]	14,9	1,11
Calcium [mg/dm^3]	71,6	1,60
Alkalinity [mmol/dm^3]	2,0	1,0
Salinity [mg/dm^3]	272,1	67,7
Conductance [μS/cm]	634	157,8
Chlorides [mg/ dm^3]	59	24
Sulphates [mg/dm^3]	85	22
Iron [mg/dm^3]	up to 7.25	0.42
Silicates [mg/ dm^3]	-	13.7
*Langelier Index LSI preference – 0,5 < LSI < +0,5; allowance LSI < 2,0	-0,43	-3,53
*Ryznar Index RSI preference 6,0 < RSI < 7,0; allowance RSI > 5,0	8,00	13,21
*Larson-Skold Index ILS preference ILS < 0,8; allowance ILS < 1,2	1,28	0,88
Saturation level $CaCO_3$ CSI (used for carbon steel)	0,21	0,00

*Remark: preferred and allowed index values do not influence much stainless steel.

& Mayr GmbH Mikrocount Combi test. The test result was negative, what means that no bacteria were present within the measurement limit (>10^2).

Photographic documentation of pipelines failures connected with the spacers

Complete photographic documentation showed perforations and conditions having influence on pipeline corrosion. The perforations were results of the presence of crevices.

In most corrosion cases the stainless steel perforations happen mainly because of chloride presence in water **[5]**. Chlorides effected perforations of 304L stainless steel used for PIP construction. Chlorides w4ere adsorbed at the stainless steel surfaces and punch the passive film at corrosion active places. Places that were sensitive to the attack were crevices at spacers (Fig.3), heat affected zones, segregated δ-ferrite structures (less resistant against corrosion compared to austenite) and inclusions in the steel.

Fig. 3.
The spacer at the side rusted at its bottom and its upper surface
Rys. 3 . Boczny element dystansowy pokryty rdzą pomiędzy spoinami oraz na całej powierzchni

Additional corrosion factors were iron ions transported in water from joined installations made of carbon steel. These ions entered the stainless steel installation from pipelines, pumps, buffer tank and other constructions made from carbon steel. The steel local damage increased due to the presence of iron Fe^{3+} ions. Precipitated iron hydroxides ions were deposited over adsorption supporting surfaces, especially at weld regions. Other salts were also adsorbed from the circulating water. A corrosion reaction rate was higher when crevices were filled with rust. With rust deposition pitting corrosion rates were higher especially in crevices between the spacers and the pipelines, because the existing conditions promoted chloride ions and other salts adsorption. Narrow distances between the spacers and the pipelines activated crevice corrosion because of lower steel oxidation due to lower flow rate of water with dissolved air in such geometries. Chlorides were adsorbed in the rust layers and in existing pockets at such increased quantities that pitting could be initiated **[6]**. Aggressive deposits were dangerous when they fulfill crevices between spacers and pipeline because they contained high chloride concentration that was enough for crevice and pitting corrosion of 304L stainless steel. Corrosion reaction initiated by chlorides after punching of a passive film was directed into bulk steel leaving an intact passive layer around a pit. Large difference in the surface ratio between the anode and cathode areas favored increased corrosion rate **[7]**. Corrosion products ($Fe(OH)_3$) formed around the pit resulted in further separation of the electrolyte **[8]**. In this way perforation of a wall or a weld happened in a very short time.

Fig. 4.
Rusted and clean spacers after 20 days of hot water flow in the installation
Rys. 4. Zardzewiały oraz czysty, metaliczny element dystansowy po 20 dniach przepływu gorącej wody w instalacji

Fig. 5.
The spacer filled with rust at its bottom within the crevice
Rys. 5. Element dystansowy wypełniony rdzą w szczelinie pomiędzy spoinami spawalniczymi

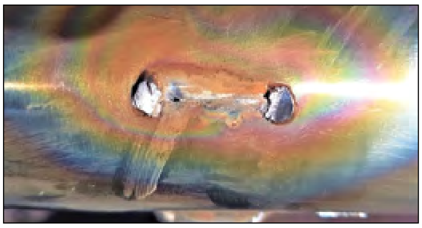

Fig. 6

Fig. 7

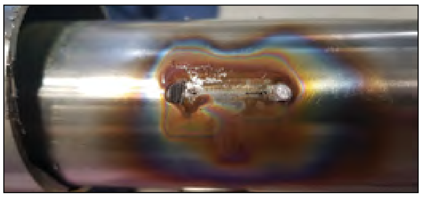

Fig. 8.
Fig. 6-8. Stainless steel pipeline surface after removal of the spacers. Pits or crevice were present within bright surface (corrosion couple anode)
Rys. 6-8. Powierzchnia rurociągu ze stali nierdzewnej po usunięciu elementu dystansowego

Wżery lub szczelina obecne na niemal metalicznej jasnej powierzchni (anoda ogniwa korozyjnego)

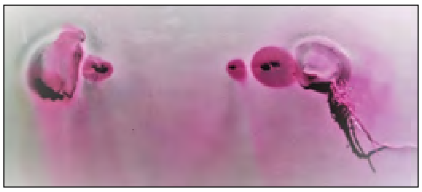

Fig. 9.
Stainless steel pipeline surface after spacer removal and application of a penetrant test. Pits were located under the spacer in the line within the crevice
Rys. 9. Powierzchnia rurociągu ze stali nierdzewnej po usunięciu elementu dystansowego i zastosowaniu preparatu penetrującego. Wżery powstały w szczelinie pod elementem dystansowym

Rehabilitation recovery of the installation

Stainless steel is corrosion resistant due to the passive film over its surface. Each stainless steel installation, especially so complicated like PIP, should be treated with pickling passivation after assembling and after pressure tests. Pickling/passivation process could be performed after removing the transported product (chocolate), mixed with water after latest breakdown, after thorough cleaning. Pickling and passivation should be carried out to remove chlorides, other salts and contaminants, hit tints rust layers from pockets, crevices and pits. This means that normal exploitation condition would be recovered with chromium content increase in the surface film that is in contact with water. Extremal differences in electrochemical corrosion potential which could initiate damage would be reduced after the process. When a proper passive film is created, stainless steel gains increased chromium content, electrochemical potential at the metal surface becomes more uniform and noble, resulting in higher corrosion resistance.

The important aim required for safe exploitation of the stainless steel installation is to reduce aggressivity of water entering into and circulating within the installation. As it had a low volume an application of demineralised water in the heating system would be possible and would protect the pipes against corrosion progress. If passivation could not be applied water at the primary period should be exchanged to remove chlorides and other contaminants. Cleanness of water must be analytically controlled for chlorides concentration. Conductance measurement allows indirectly evaluate this concentration, but chloride straight analysis would be more exact. When emptying the installation from water it would be useful to use compressed air with rapid intermittent jets to push out water (air pulse method).

Removal of iron from water with usage of side bag, filtration kidney or candle filters as a bypass at the points of water supply behind installations made form carbon steel should be installed. In this way formation of rust sediments adsorbing chlorides would be reduced.

It was also advised to use stainless steel of better quality, containing molybdenum that has repassivation properties. A good choice could be 316 or 316L types.

Water temperature in the pipeline should be lowered to 60°C. At the same time increase of flow rate and thermal insulation usage were advised. Chlorides aggressive effect would be eliminated if the demineralised water would be used as the heating medium taking an advantage of the small volume installation.

Conclusions

The reasons of the product and heating water leakages of the pipe in pipe installation were complicated. The perforations were mainly because of crevices connected with the spacers and chloride adsorption in rust patches within the crevices that effected high corrosion rate. Rust was formed due to continuous iron ions introducing from the carbon steel piping.

The spacers and contact patches made of epoxy laminate and glued to both internal surfaces of water duct at each pipe ends would stop crevice corrosion of the installation. Other corrosion preventive measures were also advised.

LITERATURE

[1] M. Raunio, Basic approaches and goals for crevice corrosion modelling, VTT Technical Research Centre of Finland, Research Report 2015.

[2] Seon-Hong Kim, Ji-Hoon Lee, Jung-Gu Kim, Woo-Cheol Kim, Effect of the Crevice Former on the Corrosion Behaviour of 316L Stainless Steel in Chloride-Containing Synthetic Tap Water, Metals and Materials International **24**, 2018, p. 516–524, DOI: 10.1007/s12540-018-0062-2.

[3] R. G. Kelly, Crevice Corrosion, ASM Handbook, Volume 13A: Corrosion: Fundamentals, Testing, and Protection, S.D. Cramer and B.S. Covino, Jr., Eds., ASM International: Metals Park, OH, 2003, pp. 242-247, DOI: 10.31399/asm.hb.v13a.a0003613.

[4] D. Jia and others, The Effects of Morphology of Ferrite and Non-Metallic Inclusions on Corrosion Behavior of As-Cast 304 Stainless Steel, Corrosion – Houston Tx- 77(10), 2021, DOI: 10.5006/3763.

[5] B. Zhang and others, Unmasking chloride attack on the passive film of metals, Nature Communications, 2018, DOI: 10.1038/s41467-018-04942-x.

[6] G. Vasyliev, I. Pylypenko, O. Kuzmenko, Y. Gerasymenko, Fouling influence on pitting corrosion of stainless steel heat exchanging surface, Thermal Science and Engineering Progress Vol. 30, 2022, p. 101278, DOI: 10.1016/j.tsep.2022.101278.

[7] M. Iannuzzi, E. Hornu, M. Salasi, Crevice Corrosion, ASTM-Books 2019, DOI: 10.31224/osf.io/fj3xq.

[8] Fong-Yuan Ma, Corrosive Effects of Chlorides on Metals, Pitting Corrosion, Nasr Bensalah (Ed.), Intechopen 2012, DOI: 10.5772/32333.

■