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THE IMPACT OF STAGNANT WATER ON THE CORROSION PROCESSES IN A PIPELINE

VPLIV ZASTAJAJOČIH VODA V CEVOVODIH NA KOROZIJSKE PROCESE

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The occurrence of stagnant water is often the result of the incomplete or improper hydrotesting procedure of pipelines (e.g., the water installation in buildings) or improper design and construction of a pipeline with blind ends. The influence of stagnant water can also be observed in sprinkler fire-protection systems. Potable water, which is not additionally chemically treated, is commonly used for the hydrotest or as a medium in fire-protection systems. Water, therefore, contains bacteria that cause microbiologically influenced corrosion. This relatively unusual form of corrosion results from the interactions of bacteria with various metals and their alloys and can increase the corrosion rate up to 100-times above that in conventional types of corrosion. The article describes in detail the causes for the formation and progress of microbiologically influenced corrosion and its consequences for the case of galvanized water pipes. Some recommendations for a reduction of the risk concerning the microbiologically influenced corrosion in water pipes are stated in the conclusion.

Keywords: microbiologically influenced corrosion, water pipes, hydrotest

Pojav zastajajočih ali mirujočih voda je pogosto posledica neupoštevanje celotnega postopka izvedbe tlačnega preizkusa cevovodov (npr. vodovodne instalacije v zgradbah) ali nepravilnega projektiranja in izvedbe cevovoda, kjer se pojavljajo slepi odcepi. Zastajajoči vpliv vode je mogoče najti tudi v sprinklerskih sistemih protipožarne zaščite. Za izvedbo tlačnega preizkusa ali kot medij v protipožarnih sistemih se pogosto uporablja pitna voda, ki ni dodatno kemijsko obdelana in zato vsebuje tudi bakterije, ki povzročajo mikrobiološko vplivano korozijo cevovoda. Ta dokaj nenavadna oblika korozije je rezultat interakcije med bakterijami in raznimi kovinami ter njihovimi zlitinami, zanjo pa je značilna tudi do 100-krat večja hitrost kot pri navadnih tipih korozije. V članku so podrobneje opisani vzroki za nastanek ter potek mikrobiološko vplivane korozije ter njene posledice pri vroče pocinkanih vodovodnih ceveh. V sklepu je podanih tudi nekaj priporočil za zmanjševanje tveganja za pojav mikrobiološko vplivane korozije v vodovodnih ceveh.

Ključne besede: mikrobiološko vplivana korozija, vodovod, tlačni preizkus

1 INTRODUCTION

In a pipeline, which is basically designed to transport liquid, gaseous or solid materials (strewn materials), stagnant or standing water can often occur. Stagnant water and water with a low flow rate, form a potential breeding ground for the development of microorganisms. These not only represent a risk to living organisms, but they also act on non-living materials, such as various metals and other materials. Bacteria, fungi and algae are microorganisms, which among other things can cause an increase in the corrosion of metals and their alloys. For this type of corrosion the name Microbiologically Influenced Corrosion, or MIC for short, is used. Similar considerations also apply to systems that are shown in **Table 1** and are vulnerable in terms of MIC. The table

Table 1: Systems with persistent MIC problems [1]
Tabela 1: Sistemi, kjer se pojavlja mikrobiološka vplivana korozija [1]

Application/System	Problem Components/Areas	Microorganisms
Pipelines/storage tanks (water, wastewater, gas, oil)	Stagnant areas in the interior Exterior of buried pipelines and tanks, especially in wet clay environments Inadequate drying after hydrotesting	Aerobic and anaerobic acid producers SRB Iron/manganese oxidizing bacteria Sulfate oxidizing bacteria
Cooling systems	Cooling towers Heat exchangers Storage tanks	Aerobic and anaerobic bacteria Metal oxidizing bacteria Slime forming bacteria Algae Fungi
Vehicle fuel tanks	Stagnant areas	Fungi
Power generation plants	Heat exchangers Condensers	Aerobic and anaerobic bacteria SRB Metal oxidizing bacteria
Fire sprinkler systems	Stagnant areas	Anaerobic bacteria SRB

also presents the microorganisms that are the most commonly found as a cause of corrosion.

Sulfate-reducing bacteria or SRB are found in a variety of natural environments. They are the best known bacteria that have been found to be involved in MIC problems. The growth of the bacteria occurs in the environment shown in **Figure 1** (left). The bacteria in stagnant or slow-moving water form a biofilm on the surface of the metal, under which the metal corrosion processes run up to 100 times faster than with normal corrosion [2].

For the occurrence of MIC chemical reactions, microorganisms are required and fluids with microorganisms represent a new source of cathode reactants. Although there is no universal agreement about the mechanism by which SRB cause or accelerate metallic corrosion, it is believed that the bacteria bring about a cathodic depolarization of the metal surface by removing hydrogen from the cathodic sites in a sulfate-reducing reaction. The reactions for this proposed mechanism are as follows:

Anodic reaction: $4Fe \rightarrow 4Fe^{2+} + 8e^{-}$ (1)

Electrolytic dissociation of water:

$$8H_2O \rightarrow 8H^{+} + 8OH^{-} \quad (2)$$

Cathodic reaction: $8H^{+} + 8e^{-} \rightarrow 8H$ (3)

Cathodic depolarization by SRB:

$$8H^{+} + SO_4^{2-} \rightarrow 4H_2O + S^{2-} \quad (4)$$

Corrosion product:

$$Fe^{2+} + S^{2-} \rightarrow FeS \quad (5)$$

Corrosion product:

$$3Fe^{2+} + 6OH^{-} \rightarrow 3Fe(OH)_2 \quad (6)$$

Overall reaction:

$$4Fe + 4H_2O + SO_4^{2-} \rightarrow 3Fe(OH)_2 + FeS + 2OH^{-} \quad (7)$$

Therefore, in the case of ferrous alloys SRB cause the formation of iron sulfide (FeS). In the case of a reaction with zinc (Zn), which represents the corrosion protection of steel, the corrosion products are zinc sulfide (ZnS) and its aggregates, which can be found in biofilm, as is shown in **Figure 1** (right).

In addition to SRB, other types of bacteria that cause the MIC of metals are known, such as Desulfovibrio, Gallionella or Pseudomonas. They attack various types of metals, like iron, stainless steel, aluminum, zinc and copper [4]. Pipelines with a pH of the water between 4 and 8 and a temperature from 20 °C to 45 °C are, in terms of microbiology, ideal for the growth of microorganisms [5]. In addition to the temperature, the pH and the oxygen content, the development of bacteria is also affected by other physico-mechanical factors, such as the surface energy, the surface roughness of the metal, and the fluid flow rate. A useful diagram for assessing the risk of MIC in a pipeline was given by Krooneman et al. [6] (see **Figure 2**). What is emphasized in this figure is that microorganisms, like human beings, are able to live only in certain conditions, of which the fluid-flow velocity is extremely important. As a threshold the flow velocity in **Figure 2** is given as 1.5 m/s. Below this velocity the formation of a bacterial biofilm is possible, but above this value there are fewer options because the fluid flow velocity is too high. Johnsen and Bardal mention that microorganisms may also form a biofilm in a fluid-flow velocity of about 4.5 m/s [7]. Without regard to this suggestion, it is a fact that by reducing the flow velocity, the mechanical force that can prevent the formation of biofilm on the wall of the pipeline is also reduced. The development of MIC is therefore more likely.

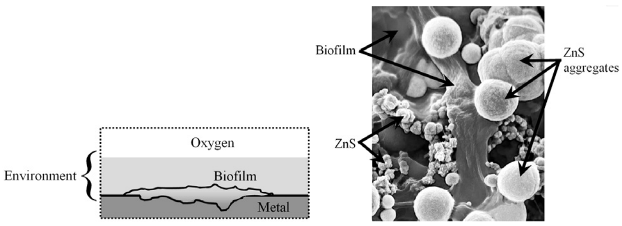


Figure 1: Components of the environment for the development of MIC (right) and microscopic photograph of biofilm in the case of zinc corrosion (left) [3]

Slika 1: Sestavni deli okolja za razvoj mikrobiološke vplivana korozije (desno) in mikroskopski posnetek biofilma v primeru korozije cinka (levo) [3]

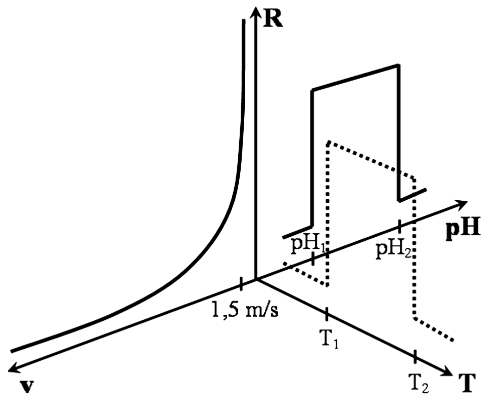


Figure 2: Schematic relationship between the flow velocity and the pH of water and the temperature T with respect to the corrosion rate R

Slika 2: Shematski prikaz odvisnosti hitrosti korozije R od hitrosti pretoka fluida v, temperature T in kislosti fluida pH

2 EXPERIMENTAL WORK

For this study of the impact of stagnant water on MIC a real object was used. A water pipeline in a hospital building, which was completed in 2002, was analyzed.

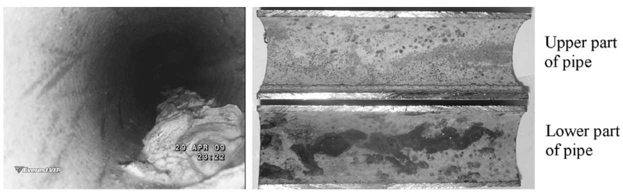


Figure 3: Corrosion products on the lower part of the pipe in its interior (left) and the longitudinally cut pipe (right)

Slika 3: Korozijski produkti na spodnje delu cevi v njeni notranjosti levo ter vzdolžno razrezana cev

Hydrotesting was performed before the acceptance of the pipeline. For the implementation of the hydrotest ordinary drinking water was used. This water was not additionally chemically treated. The normal use of the water pipeline in the object started in 2006. In the meantime, the system was wholly or partly emptied. Since then, until the end of 2008, eight heat shocks with a water temperature higher than 70 °C and several chlorine shocks were carried out in the water-supply system.

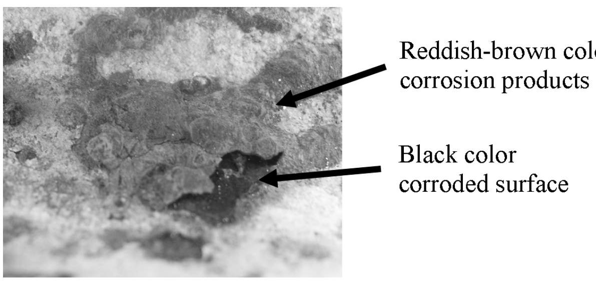
The water supply system in the object was built from galvanized steel pipes of different diameters with the chemical composition in mass fractions of the base steel: C-0.10; Si-0.13; Mn-0.48; P-0.04; S-0.02 and Fe-Balance. The measured thickness of the galvanized layer of zinc (hot-dip galvanizing) ranged from 35 μm to 90 μm. Inspection of the corrosion inside the water pipe was carried out using a Everest PLS 500 DA videoscope. Selected parts of the pipes were cut from the system and further analyzed by macro sections. The corrosion products were also chemically analyzed using energy-dispersive X-ray spectroscopy (scanning electron microscope JEOL 5500 LV with an EDX analyzer).

3 RESULTS AND DISCUSSION

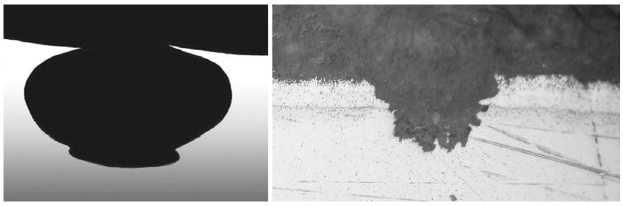
3.1 Appearances of corroded sites

When inspecting the pipe interior the first finding was that it was coated with a carbohydrate biofilm. Corrosion, which is much more intense in the lower part of the pipe (see **Figure 3**), shows that the corrosion process started mainly due to stagnant water and an incompletely drained water-supply system. This shows the explicit effect of stagnant water, probably after the hydrotest, or at another time, when the system was, for a longer period, only partially drained. The smaller quantity of stagnant water was a very appropriate medium for the growth of microorganisms and the further development of MIC. The microorganisms dissolve zinc and iron and even lower-quality stainless steel (e.g., 18Cr-8Ni austenitic stainless steel AISI 304) does not passivate in such a medium [8].

The color of the corrosion products is an essential indicator in the investigation of MIC. The reddish-brown deposits with a black corroded surface in **Figure 4** may



Slika 4: Korozijski produkti na površini cevi
Figure 4: Corrosion products on the surface of the pipe



Slika 5: Prečni presek korozijske poškodbe levo tipična pri nerjavnih jeklih [10], desno v našem primeru pri pocinkanju na notranji strani cevi
Figure 5: Cross-section illustration of an ink-bottle-type pit noted in the case of stainless steel (left) [10] and the cross-section of the pit in the investigated case of galvanized carbon steel (right)

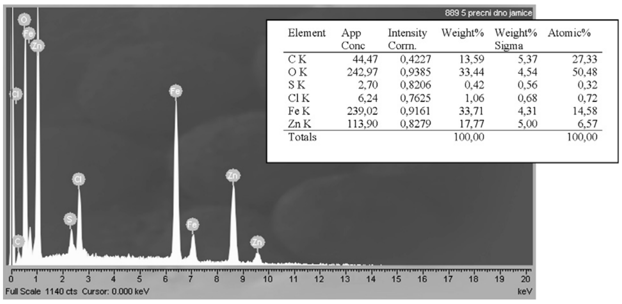
be good indicators of the SRB and iron-oxidising bacteria. The black corroded surface under the carbohydrate biofilm was an indication of the iron sulfide formation. A chemical analysis of the corrosion products was not performed. A distinctive smell of rotten eggs, which indicates hydrogen sulfide gas produced by the SRB, arises during the removal of the biofilm.

A classification of the morphological types of surface corroded sites was made, but on this basis it was not possible to make a single conclusion. Similar data have been obtained by other authors, e.g., in [9], where it was found that the corrosion surface morphology was related to the chemistry at the metal surface and not to the presence or absence of microorganisms.

At the next stage the study was extended with a metallographic examination of the cross sections of corroded sites. The researchers in [10] described ink-bottle-shaped pits in the stainless steel as diagnostic of MIC (**Figure 5** left). This, in our case (**Figure 5** right), was not confirmed, but it is true that in our case the material was galvanized carbon steel. After the breakthrough of the zinc protective layer, the corrosion of the underlying steel started. It is possible that the further growth in the depth of the corrosion in the carbon steel could develop a similar form as in **Figure 5** (left).

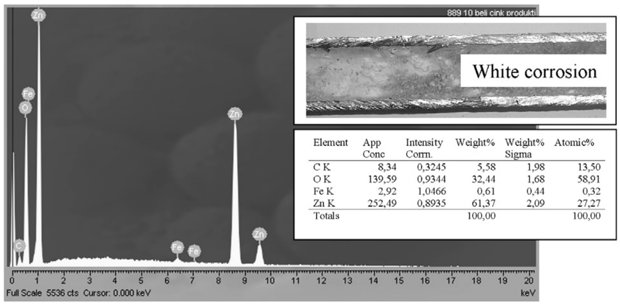
3.2 EDX analysis

The corrosion products formed in the pit were analyzed with the EDX method and the graph in **Figure 6** shows peaks for iron (Fe), zinc (Zn), oxygen (O) and sulfur (S). As already shown by Equation 7, in the MIC iron sulfide (FeS) was formed as a corrosion product. For this reason, the EDX analysis of the corrosion products detected some amount of sulfur (w = 0.42 %), which is characteristic of this type of corrosion. The presence of sulfur in conjunction with the zinc was also suggested by the presence of zinc sulfide (ZnS) in the corrosion products. In addition, we have also found a significant amount of chlorine in the corrosion products, probably in the form of Cl^- ions. Thus, the large amount of chlorides is probably due to the implementation of chlorine shocks in the water supply system. The effect of chlorine on the creation of new corrosion pits and the deepening of the



Element	App Conc	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	44,47	0,4227	13,59	5,37	27,33
O K	242,97	0,9385	33,44	4,54	50,48
S K	2,70	0,8206	0,42	0,56	0,32
Cl K	6,24	0,7625	1,06	0,68	0,72
Fe K	239,02	0,9161	33,71	4,31	14,58
Zn K	113,90	0,8279	17,77	5,00	6,57
Totals			100,00		100,00

Slika 6: EDX analiza produktov mikrobiološke vplivane korozije na površini pocinkanega jekla
Figure 6: EDX analysis of the corrosion products formed on the galvanized steel surfaces with microbiologically influenced corrosion



Element	App Conc	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	8,34	0,3245	5,58	1,98	13,50
O K	139,59	0,9344	32,44	1,68	58,91
Fe K	2,92	1,0466	0,61	0,44	0,32
Zn K	252,49	0,8935	61,37	2,09	27,27
Totals			100,00		100,00

Slika 7: EDX analiza produktov in posnetek dela cevi (zgoraj desno) z belo korozijo pocinkanega jekla
Figure 7: EDX analysis of the corrosion products and photograph of pipe section (top right) with the white corrosion of galvanized steel

already formed pits due to MIC, was not the subject of this investigation.

For a comparison, we also analyzed a water pipe on which we could only find traces of white corrosion (**Figure 7**, top right). From the analysis of the corrosion products on the galvanized surface we found that the corrosion products consisted only of the products of zinc with the oxygen bound as zinc hydroxide ($Zn(OH)_2$) (**Figure 7**). We have also found traces of iron. As the proportion of iron in these corrosion products was very small, we concluded that it originated from the lower layers of zinc coating in which there can be from 7 to about 20 weight percent of iron (Fe) in the form of various intermetallic phases.

3.3 Water-quality analysis

In this investigation we also analyzed the water quality of the water-supply system, which in operation was subject to MIC. Ten samples of water were taken and analyzed using flame atomic absorption spectrometry (FAAS) and inductively coupled plasma mass spectroscopy (ICP-MS) to determine the concentration of the dissolved iron and zinc. Two samples were taken at the terminal to the city water-supply system and show that iron and zinc were not from the city water-supply system. Among eight samples of water originating from the observed water-supply system, an increased content of iron up to 38 mg/L was found. Similarly, the content of zinc was above 26 mg/L. The results are comparable to a similar analysis of water under laboratory conditions in [11], where the values of the zinc content in the water amounted to about 28 mg/L in samples with MIC. The measured proportion of the zinc and iron contents in the water are higher than the permissible and/or recommended limits for drinking water, which are 0.2 mg/l for iron and 3 mg/l for zinc [12].

4 CONCLUSIONS

The present paper describes the occurrence of MIC in galvanized steel on a real object, as a result of the activity of microorganisms in stagnant water. The results of the analyses of the corrosion products, especially the EDX analyses, show that in the corrosion products there are both elements and compounds (e.g., sulfur in the form of FeS and ZnS) reflecting the activity of the microorganisms. The corrosion products found originate from corrosion due to SRB and iron-oxidizing bacteria, the presence of which was not proved with a biological analysis.

It is concluded that it is necessary to avoid the occurrence of stagnant water in water-supply systems, because it represents a potential source of microorganisms leading to the development of MIC. The emergence of stagnant water is often the result of irregularities in the construction, the improper execution of the hydrotest or because of the system itself (e.g., fire-protection sprinkler systems). To avoid the occurrence of MIC, some recommendations need to be considered:

- When designing and constructing a water-supply system a blind branch should be avoided. The design of horizontal pipelines needs to be "self-draining".
- The pipeline must be constructed so that the velocity of the fluid flow is at least 1.5 m/s.
- Only chemically treated water should be used to fill the fire-protection sprinkler system.
- Demineralized drinking water should be used to carry out the hydrotest. As soon as possible after the completion of the hydrotest, it is necessary to drain and dry the pipeline.

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