# Corrosion of galvanized carbon steel pipes in a new drinking water system – a case study

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Abstract

The main aim of this research was investigation of corrosion damage of a relatively new drinking water system in one of Slovenian hospitals, and assessment of causes for the severe damage. Water drinking system was made from seamless galvanized steel pipes. Most accessories, fittings and valves, were made from brass. It was found that stagnant water from tightness test at commissioning caused the initial corrosion. In addition, Legionella destruction and also prevention treatment led to severe corrosion due to frequent chemical and thermal disinfection of the system.

After the detailed in-situ examination of drinking water pipes, corrosion tests (potentiodynamic polarization and gravimetrical testing of coupons) were performed in order to investigate corrosion susceptibility of materials in system to different disinfection methods. FTIR analysis was performed in order to investigate biofilm formation in cold and hot water systems. Corrosion products on inner wall of pipes was characterized by SEM/EDS and metallographic examination.

Investigation has shown that materials used in this particular drinking water system were highly susceptible to the thermal and chlorine disinfection. Corrosion caused by disinfection was mostly uniform with some larger pits. It was observed that heat affected zone of pipe seams presented the most corrosion susceptible sites.

Zusammenfassung

Das Hauptziel dieser Studie war die Ermittlung von Korrosionsschäden in einer relativ neuen Trinkwasserinstallation in einem der slowenischen Krankenhäuser sowie die Bewertung der Ursachen für die schweren Schäden. Die Trinkwasserinstallation besteht aus nahtlosen verzinkten Stahlrohren. Die meisten Zubehörteile, Rohrverbindungen und Ventile wurden aus Messing hergestellt. Es wurde festgestellt, dass stehendes Wasser von der Dichtheitsprüfung bei der Inbetriebnahme die erste Korrosion verursachte. Darüber hinaus führten die Vernichtung von Legionellen und ebenfalls die Präventionsbehandlungen zu schwerer Korrosion durch die häufige chemische und thermische Desinfektion der Installation.

Nach der detaillierten In-situ-Untersuchung der Trinkwasserleitungen, wurden Korrosionstests (potentiodynamische Polarisation und gravimetrische Prüfung von Probeplatten) durchgeführt, um die Korrosionsanfälligkeit der Werkstoffe in der Installation bei unterschiedlichen Desinfektionsverfahren zu ermitteln. Es wurde eine FTIR-Analyse durchgeführt, um die Bildung von Biofilmen in Kalt- und Warmwasser-Installationen zu untersuchen. Die Korrosion der Rohre wurde anhand der SEM/EDS-Analyse und der metallografischen Untersuchung von Rohrquerschnitten charakterisiert.

Die Untersuchung hat gezeigt, dass die in dieser speziellen Trinkwasserinstallation verwendeten Werkstoffe gegenüber der thermischen Desinfektion und Chlorgasdesinfektion sehr anfällig waren. Die durch Desinfektion verursachte Korrosion war meistens einheitlich mit einigen größeren Narbenbildungen. Die höchste Korrosionsanfälligkeit wurde in den Wärmeeinflusszonen der Rohrnähte beobachtet.

Résumé

L’objectif principal de cette étude était d’examiner les dégâts par corrosion d’un réseau d’alimentation en eau potable relativement récent dans un hôpital de Slovénie, ainsi que d’évaluer les causes des dégâts importants. Le réseau d’alimentation en eau se composait de conduites en acier galvanisé sans soudure. La plupart des accessoires, raccords et soupapes étaient en laiton. L’étude a révélé que de l’eau stagnante due à des essais d’étanchéité lors de la mise en service est à l’origine de la corrosion initiale. De surcroît, un traitement visant à détruire et à prévenir la présence de Legionella a entraîné une corrosion importante en raison des fréquentes désinfections chimiques et thermiques du système.

Après l’examen in situ détaillé des conduites d’eau potable, des essais de corrosion (polarisation potentiodynamique et essais gravimétriques de coupons) ont été menés en vue d’étudier la sensibilité à la corrosion de matériaux du réseau sous l’action de différentes méthodes de désinfection. Une analyse IRTF a été réalisée afin d’étudier la formation de biofilm dans les réseaux d’eau froide et chaude. La corrosion des conduites a été caractérisée par une analyse MEB/EDS et un examen métallographique de coupes transversales des conduites.

Les examens ont révélé que les matériaux utilisés dans ce réseau d’alimentation en eau potable étaient hautement sensibles à la désinfection thermique et au chlore. La corrosion causée par la désinfection était majoritairement uniforme avec quelques piqûres plus importantes. On a pu observer que la zone des raccords des conduites affectée par la chaleur présentait les sites les plus sensibles à la corrosion.

Key words: galvanized carbon pipes, drinking water system, hospital, corrosion

## 1. Introduction

In 2010, Slovenian National Building and Civil Engineering Institute was chosen for the investigation of drinking water system in one of Slovenian hospitals through public tender. Excess content of Legionella in the system have been found soon after the beginning of operation of the system and despite repeated interventions such as temperature and chemical disinfection it was not possible to eliminate Legionella. After a while, high amounts of iron and zinc were found in the system indicating corrosion problems.
Projects for the hospital were elaborated in 1996, whereas construction began only in the year 2000. The project included 4 buildings which water distribution piping system was connected and centralized in one building. Some parts of the building did not begin to use at the completion of construction, but only after some time passed. The whole complex of hospitals began to use between 2003 and 2007.
After Slovenia become independent country and afterwards also a member of European community, the use of EN standards is obligatory. Since then, new projects have to be designed and implemented according to the standards of the series EN 806 [1].

These standards cover only a basic level of this field, and some otherwise very important details cannot be found there. As supplementary information other standards and guidelines should be used, e.g. DIN norms, DVGW and VDI working sheets and guidelines [2-4]. These professional regulations describe much precisely the use of available materials, problems with corrosion and Legionella prevention and possible risks which could be avoided by proper handling.

If these standards are not taken into account, that may lead to a high risk for corrosion of installations. Standards allow the use of zinc coated pipes for drinking water installations only when compatibility of material with disinfection methods is determined beforehand. Unfortunately, standards do not contain instructions or procedure how such evaluation should be done. In the corrosion science, this problem is not well studied [5-9]. One of the reasons is also that this type of steel pipes has been banned in more developed countries with higher standards. Moreover, the use of zinc coated steel pipes is in some countries not allowed anymore.

The main aim of our research work was to investigate that causes for severe corrosion in the system. Beside this, the aim of the study was to investigate compatibility of materials of drinking water system installation with disinfection procedures which were used in the particular investigated water distribution piping system.

## 2. Description of work

In order to reveal causes for very bad corrosion and hygienic condition of drinking water system in a new hospital building, following examinations were performed:

a) Inspection of documents referred to drinking water system in the particular hospital (buildings plans, plan of operation and maintenance, diary of maintenance of drinking water system, evidence of chemical and temperature disinfection, data about temperature measurements in outlets, etc.),
b) Visual examination of corrosion condition of pipes in buildings, comparison of manufactured water system with design plans,
c) Sampling of a representative pipe for hot and for cold water in the site where significant corrosion process was expected, sampling of water,
d) Laboratory tests of pipe sample: metallography, chemical analysis of steel pipe composition, SEM/EDS and FTIR analysis of corrosion products, basic electrochemical measurements; laboratory chemical and physical analysis of water.

<u>Laboratory tests</u>

SEM (JEOL 5500 LV) /EDS (Oxford Inca) and FTIR (Perking Elmer, Spectrum Spotlight 200) analysis were performed on corrosion products of pipes for cold and hot water. After that analysis, corrosion products were removed by exposure to the solution of 50 vol. % HCl with an addition of 0.3 weight % Urotropin. Samples were then cut in transverse and longitudinal direction, cast into epoxy model, grinded with abrasive SiC papers up to grade 4000 and finally polished with 1 µm diamond paste. Unetched and etched samples were examined on metallographic microscope Carl Zeiss at magnifications up to 500×.

In order to examine corrosion properties of galvanized carbon pipes, samples of 0.785 $cm^2$ zinc coated carbon steel were exposed as working electrode in a tri-

electrode electrochemical cell and linear polarization in drinking water with different additions (concentrations) of chlorides was performed. Corrosion rate of zinc coated carbon steel samples (coupons) in two different solutions with disinfectants, SANOSIL® Super 25 (containing hydrogen peroxide and silver) and IZOSAN® G (chore based disinfectants), was also estimated gravimetrically. For this purpose, samples of known exposed area and mass were exposed to different concentrations of disinfectants for different periods and at different temperatures (room temperature and 70 $^{o}$C). After the exposure, corrosion products were cleaned from the surface of samples and weighted. Results of electrochemical and gravimetrical tests were after that compared.

## 3. Results and discussion

### 3.1. Results of documents review and in situ examination of drinking water system

Based on the review of documentation it was find out that between years 2006 and 2008 at least 8 temperature shocks were carried out in hot drinking water system at the hospital. From 2008 to 2010 temperature shocks were performed on the hot drinking water system regularly according to the plan. Temperature shocks were not carried out on cold drinking water system. Chlorine shocks were performed every time when the drinking water system of each part of hospital complex was finished. Up to 2007, when automatic biocide dosing device of chlordioxide was installed, at least 10 chemical disinfections were performed. Because of the dosage of different chlorine containing substances directly to the reservoir for cold water, recommended local concentrations of chlorine were probably exceeded.

In 2008 analysis of minerals have shown exceeded concentration of iron and zinc in drinking water. Since 2007, presence of more than 100 CFU/litre legionella in drinking water was confirmed several times.

Examination of drinking water system identified several deficiencies, like are:

- dead legs (25 dead legs were found and removed) – because of changing of intended use of individual rooms during and after construction, dead legs occurred,
- missing ball valves which hindered proper implementation of temperature/chemical disinfection; also, closing of dead legs in the case of longer non-use was not possible,
- missing or too thin isolation of drinking water hot and cold pipes – due to this reason overheating of cold water pipes was present,
- circulation system ends positioned far away from outlets (but 3 litre rule was considered)

### 3.2. Laboratory visual examination of inner wall of pipes

One pipe for hot, and one for hot water taken from the drinking water system in the hospital, were in laboratory cut along longitudinal axes in order to get an insight to the condition of inner wall. On the figure 1a and 1b inner side of pipes for hot and cold water, respectively, after 7 years of use, can be seen.

Figure 1a: Interior of hot water pipe

Figure 1b: Interior of cold water pipe

On Figures 2a and 2b, inner surfaces after cleaning of corrosion products for both pipes are presented.

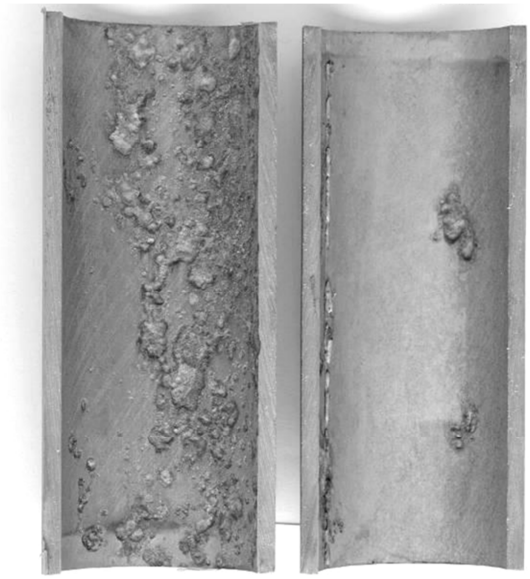


Figure 2a: Interior of hot water pipe after corrosion products removal

Figure 2a: Interior of cold water pipe after corrosion products removal

As it can be seen from figures, pipe for cold water is severely corroder in comparison to pipe for hot water. On the pipe of cold water thick reddish-brown corrosion products are deposited, whereas on the pipe of hot water corrosion products are not

so extensive. In the hot water pipe surface, zinc coating is still present, its damage is only local, as observed under reddish-brown corrosion products. On both pipes, a severe localized corrosion pits with depths from some tenth of millimetres up to more than 1 millimetre occurred at the sites with the thicker corrosion products. Seem along the pipe of cold water is heavily attacked (Figure 2a).

### 3.3. SEM/EDS analysis of corrosion products

EDS analysis was performed on corrosion products of hot and cold water pipes. Results of analysis of corrosion products can be seen on Table 1, where analysed spectrum S1 is average value of 6 different spectra taken at corrosion products on cold water pipe, and spectrum S7 an average value of spectra from S7 to S10 on hot water pipe.

Table 1: EDS spectra of corrosion products found in inner surfaces of hot and cold water

| **Spectrum** | **C** | **O** | **Si** | **P** | **S** | **Cl** | **Ca** | **Fe** | **Cu** | **Zn** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cold water pipe | | | | | | | | | | | |
| **S 1** | 4.10 | 46.47 | 0.77 | 1.17 | 0.46 | 0.10 | - | 44.99 | - | 1.93 | 100.00 |
| Hot water pipe | | | | | | | | | | | |
| **S 7** | 0.74 | 7.09 | - | 1.03 | - | 0.13 | 0.87 | 60.46 | 3.84 | 25.83 | 100.00 |

On the surface of hot water pipe, the presence of Ca and P revealed carbonation and phosphate layer, which is also visible by naked eye as a light-grey layer (Figure 1a). In addition, the amount of Zn found on the surface of this pipe was much greater (approximately 10 times greater) than that found in corrosion products of cold water pipe. It is believed that carbonate/phosphate layer formed intensively because of higher temperatures in hot pipes protected by Zn coating against corrosion. Based on this observation obtained by EDS analysis it can be concluded that all Zn coating on inner wall of cold water pipes was removed during operation of the system. Corrosion products which were found locally on the surface inside hot pipes were mostly iron oxides, but also Zn and Cu were found. Larger amount of Cu in corrosion products of hot water pipe can be explained by galvanic corrosion of brass accessories like are fittings and valves, but also chlorine caused corrosion of copper alloys in this system cannot be excluded. In that case, Cu corrosion products released in the drinking water system by flowing of water and have been deposited to the Zn coated surface. Cu ions caused micro-galvanic couple on Zn coating and caused its local corrosion. In corrosion products of cold water pipe, Ca was not found. In that case corrosion products consisted mostly from different iron oxides. In addition, significant amount of S, which could be explained with biofilm formation inside pipes, was found.
FTIR analysis also proved presence of organic compounds on corrosion products of both pipes, which is visible as a C-H pike on FTIR spectre (Figure 3).

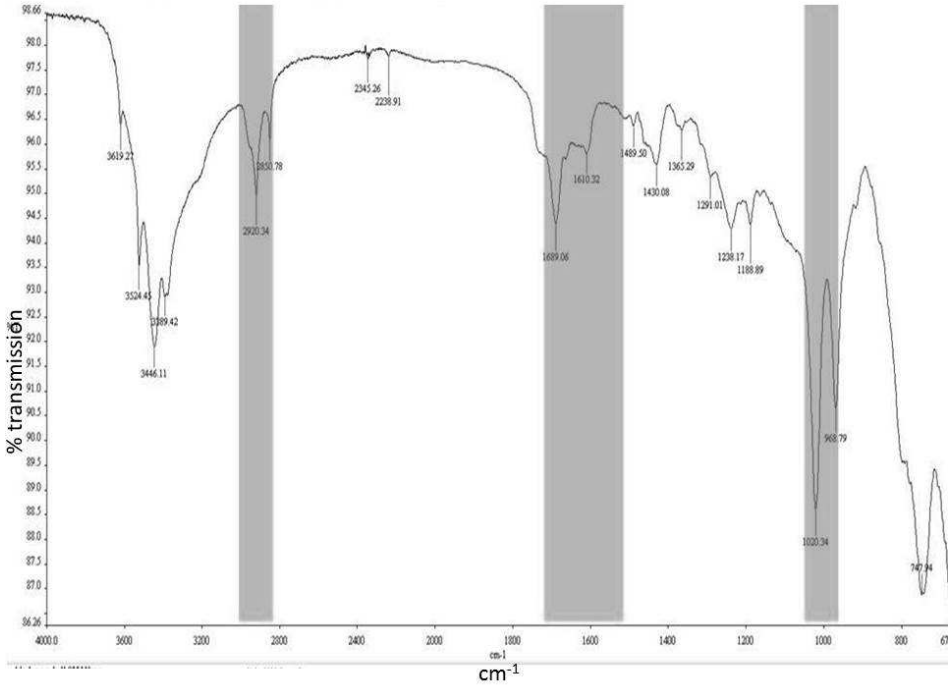



Figure 3: FTIR spectra of biofilm found in corrosion products in cold water system

The bands in the region from 300 and 2850 $cm^{-1}$ evidence the presence of C-H bonding, the two bands in the region 1750 and 1500 $cm^{-1}$ show the presence of carbonyl group (C=O bonds). Also the presence of biofilm are confirmed by bands at 1100 and 969 $cm^{-1}$[10, 11]

### 3.4. Water analysis

Chemical and physical parameters were extracted on water samples. The water samples were taken from 4 different taps of drinking water system after 48 h of stagnation of water. The sampling was planned after temperature shock treatment beforehand. The maximal temperature on hot water outlet was during sampling in average 61 $^{o}$C, and on cold water outlet 13 $^{o}$C. Constant temperature of hot water on outlet was achieved after 2 minutes from the opening of the tap.
Results of chemical and physical analysis of water from investigated drinking water system can be seen in Table 2.

Table 2: Results of chemical and physical analysis of water

| . | Unit | Recomended values | Outlets | | | |
|---|---|---|---|---|---|---|
| | | | H1 101 | E4 47 | E98 01 | E99 61 |
| **pH** | | 6,5-9.5 | 7,8 | 7.5 | 7.1 | 7.5 |
| **Electrical conductivity (20℃)** | µS/cm | ≤2500 | 440 | 450 | 420 | 440 |

| . | Unit | Recomended values | Outlets | | | |
|---|---|---|---|---|---|---|
| | | | H1 101 | E4 47 | E98 01 | E99 61 |
| **Odor** | | | Brez | Brez | Brez | Brez |
| **Turbidity** | NTU | | 0.6 | 0.4 | 18 | 1.1 |
| **Colour** | m-1 | | <0.10 | <0.10 | <0.10 | <0.10 |
| **Oxidativity** | mg/l | <5 | <0.5 | <0.5 | 0.6 | 0.5 |
| **Total organic carbon - TOC** | mg/l | | 0.7 | 0.8 | 5.4 | 1.1 |
| **Amonium** | mg/l | <0.5 | <0.013 | <0.013 | 0.064 | 0.077 |
| **Nitrites** | mg/l | <0.5 | <0.007 | <0.007 | 0.01 | 1.1 |
| **Nitrates** | mg/l | <50 | 13 | 14 | 4 | 13 |
| **Sulphate** | mg/l | <250 | 11 | 12 | 12 | 12 |
| **Chlorides** | mg/l | <250 | 11 | 10 | 11 | 10 |
| **Chlorites** | mg/l | | <0.2 | <0.2 | <0.2 | <0.2 |
| **Chlorates** | mg/l | | <0.2 | <0.2 | <0.2 | <0.2 |
| **Calcium** | mg/l | | 23 | 21 | 49 | 23 |
| **Orto phosphates** | mg/l | | 0.74 | 0.74 | 0.14 | 0.22 |
| **Phosphorus-total** | mg/l | | 1.62 | 1.65 | 0.826 | 1.59 |
| **Hidrogenkarbonati** | mg/l | | 240 | 260 | 260 | 260 |
| **Drying residue (105℃)** | mg/l | | 270 | 270 | 260 | 270 |
| **Drying residue (180℃)** | mg/l | | 250 | 260 | 260 | 270 |
| **Manganese** | µg/l | <50 | <1.0 | <1.0 | 30 | 1.8 |
| **Iron** | µg/l | <200 | <100 | <100 | **4500** | 120 |
| **Copper** | mg/l | <2 | 0.027 | 0.023 | 0.14 | 0.052 |
| **Zinc** | µg/l | <3000* | 200 | 200 | **14000** | **8300** |
| **Chlorides - free** | mg/l | | <0.02 | <0.02 | <0.02 | <0.02 |

With this analysis high contents of Fe and Zn were found in drinking water, which is characteristic for heavily corroding systems. Based on that observation it is assumed that content of Fe in the system will remain more or less the same in the future, however, concentration of zinc will slowly decrease due to total dissolution of Zn layer and removal from the system by water.

Microbiological analysis of water surprisingly showed very high amount of Legionella colonies in one of the taps (>15000 CFU/l). Because of the fact that temperature shock was executed a short time before sampling the water for analysis, it can be

concluded that this disinfection was not successful. That is reasonable, because temperature shocks were due to technical problems performed only in the system for hot water.

### 3.5. Metallographic examination

Metallographic samples were prepared from pipes of hot and cold water in different directions after removal of corrosion products. Microstructure of steel of both pipes is ferrite-pearlite, with fine grains from 7 to 12 µm. In the core of pipe wall stringer like microstructure was observed. In the heat affected zone of cold water microstructure was dendridic and passes into ferrite-pearlite (Figure 4a). Heat affected zone is very wide, more than normally should be. Such microstructure is very sensitive to corrosion. In the case of investigated pipes weld on pipe was the weakest site of steel. In one randomly taken sample the remaining wall thickness was only 0.2 mm, which was alarming fact (Figure 4b).

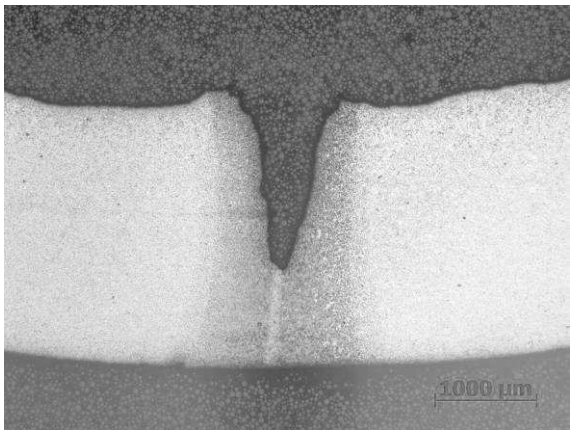



Figure 4a: Weld on cold water pipe, etched

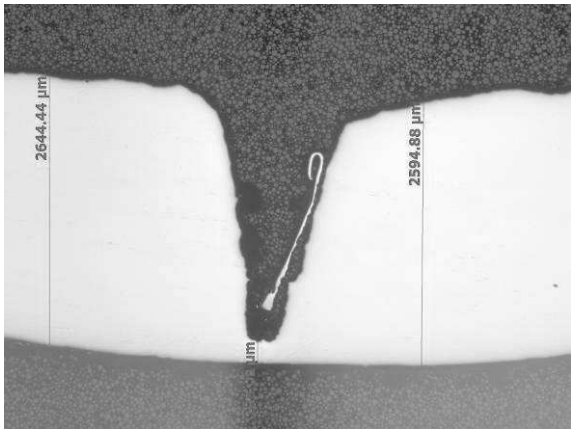



Figure 4b: Remaining wall thickness of cold water pipe reduced by corrosion

Metallographically measured maximal rest thickness of Zn coating inside the pipe of hot water was up to 55 µm (Figure 5a). Cracking and scaling of coating was also observed (Figure 5b) and it is believed that temperature shocks caused delamination of zinc coating from steel surface. Zinc coating was locally completely removed and larger corrosion pits where observed. Inside of cold water pipe, zinc coating was completely corroded. Inner surface of this pipe was covered with large corrosion caves. Corrosion products above such damage can be ideal medium for microorganisms such is legionella.

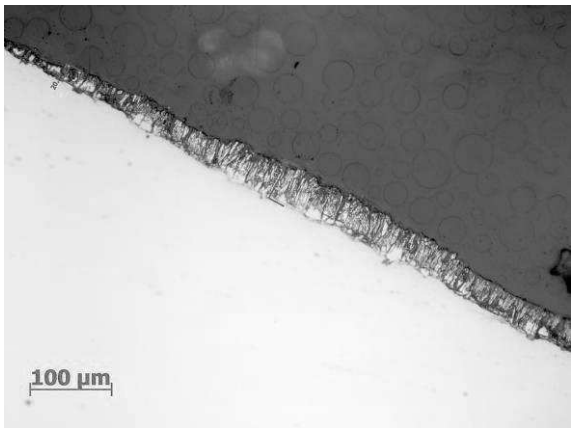
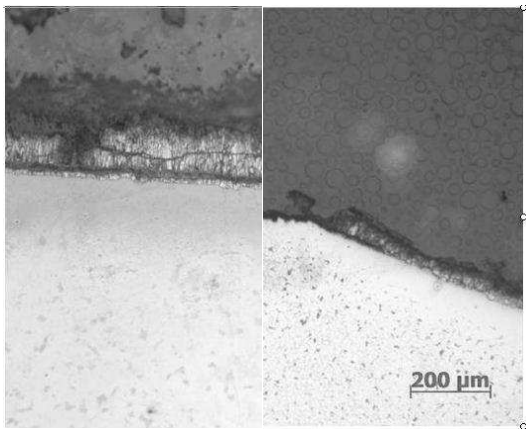



Figure 5a: Zinc coating inside hot water pipe




(a) (b)

Figure 5b: Cracking (a) and scaling (b) off the zinc coating of hot water pipe

### 3.6. Electrochemical and gravimetrical tests

During the investigation, the effect of temperature and chemical disinfection was examined by electrochemical tests. Loss of zinc coating was determined in different concentrations of chlorine and at two different temperatures. The electrochemical measurements were performed in order to get accurate corrosion rate (CR) information, among which corrosion potential, polarization resistance and corrosion behaviour observed by potentiodynamic curves.

Two different concentrations of chlorine admixtures were added into drinking water: 20 and 50 mg/l. Electrochemical measurements were carried out at room temperature (20 $^{o}$C) and at elevated temperature (70 $^{o}$C). This data were compared with gravimetrical data which were carried out in two different disinfectants, which were used for chemical disinfection of investigated drinking water system.

From the electrochemical polarization measurements polarization resistance was determined. Polarisation resistance is a measure how certain metal resist the corrosion. The lower it is, the more susceptible is the investigated metal. Larger the polarization resistance, lower the corrosion rate. Corrosion rates, calculated from the data of polarization resistance, are shown in the Table 3.

Table 3: Corrosion rates (CR) of zinc in drinking water with two different additions of chlorides at two different temperatures

| | **Zn** | **Zn+10 mg/l $Cl^-$** | **Zn+50 mg/l $Cl^-$** |
|---|---|---|---|
| **CR [µm/year] at 20℃** | 71 | 276 | 953 |
| **CR [µm/year] at 70℃** | 41 | 46 | 81 |

Corrosion rate of zinc in cold water without addition of chlorides obtained by linear polarization is 71 µm/year, which is more than average thickness of zinc coating of drinking water steel pipes. Additions of chlorides increases corrosion rate of zinc coating. In hot water without chlorides, corrosion rate is of about half in comparison to the cold water. Lower corrosion rate in that system could be probably due to formation of ZnO, which contributes to more resistant system. Addition of chlorides increases corrosion rate, nevertheless, influence of increasing content of chlorides is not that significant as in cold water.

Gravimetrical determination of corrosion rate was carried out on zinc coated steel sheets at two different concentrations of two different disinfectants that were used for disinfection of investigated drinking water system. For the first disinfectant, IZOSAN ® G, the recommended concentration of 0.4 g/liter, which is commonly used for continuous disinfection of drinking water, was used. Additionally, in order to study effect of overdosing of this disinfectant, increased concentration of 4 g/liter was used. Corrosion rates of Zn coated steel sheets were determined after 1, 4, 16, 20 and 24 hours of exposure in disinfectant and can be seen on Figure 5.

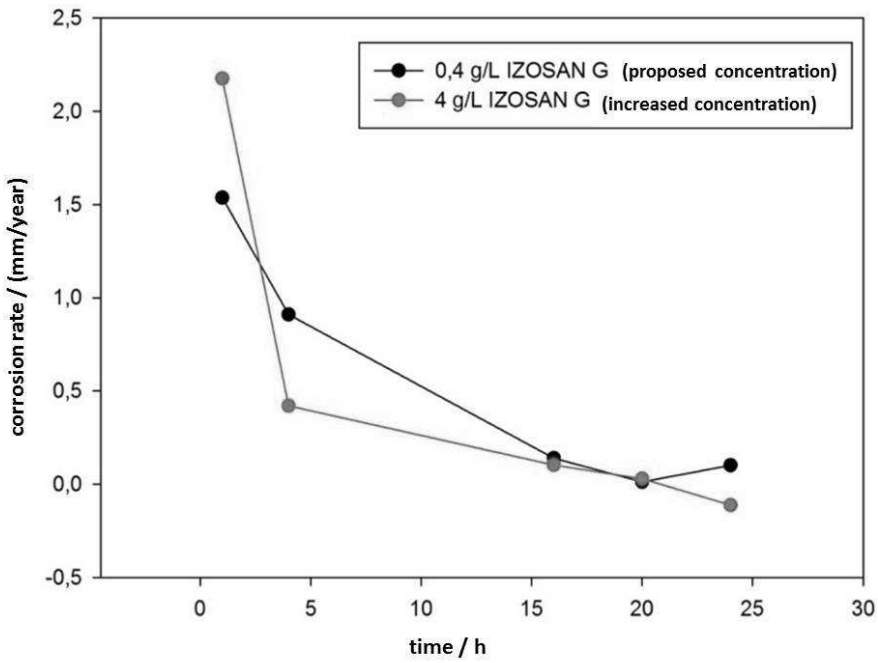



Figure 5: Corrosion rate of Zn in tap water solution of 0.4 g/l (recommended concentration) and 4 g/l (increased concentration) of disinfectant IZOSAN ® G

Corrosion rate decreases with the time of exposure because of formation of corrosion products. During the corrosion products deposition, Zn reacts with oxygen and chlorine, which increases mass of corrosion products. Corrosion products cannot be removed from the surface without removing Zn from the surface. Therefore, corrosion rates determined for longer exposure times are not relevant.
Corrosion rates in second disinfectant, SANOSIL ® Super 25, based on hydrogen peroxide, are small in comparison to the IZOSAN ® G and are approximately 2

µm/year and should not cause observed corrosion damage on inner surfaces of pipes. Unfortunately, it was found during laboratory tests that SANOSIL ® Super 25 reacts with Zn and forms ZnO and $Zn(OH)_2$. As a result, Zn is removed from the system. It can be assumed that Zn coating was locally removed from investigated drinking water pipes by these reactions.
Nevertheless, results of laboratory tests have shown that also in the case where no chlorides are present in water, Zn coating of cold water pipes will be removed in one year. Corrosion rate in hot water is lower than that in cold water. Lower corrosion rate/damage found in the system is a result of carbonation layer formation on the surface of pipes which protects Zn from corrosion. Zn coating in hot water pipes is generally well preserved.

## 4. Conclusions

Corrosion condition of drinking water system after only a few years of use lead to premature failure. Main reasons can be argued from the different views:

- Design:
  - very long pipelines where stagnation of water could not be avoided, large loss of water temperature,
  - central preparation of hot water (one heating station), too low temperature achieved at the end user and
  - dead legs.
- Construction:
  - missing isolation: development of Legionella
- Material:
  - galvanized steel pipes with poor quality seams and
  - accessories made from brass (galvanic couples, presence of large amount of Cu ions in corrosion products)
- Legislation:
  - obligatory initial chemical disinfection with chlorine compounds,
  - leak testing was executed by water which was (as after chemical disinfection) not removed from the system totally and
  - temperature and chemical disinfection of the system because of infection by Legionella.

From laboratory test it can be concluded that:

- zinc coated steel pipes are not resistant to corrosion in cold water because of fast removal of protective coating from the surface even in the case when chlorides are not present in water,
- higher chloride content in water, as well as higher temperature, faster dissolution of zinc was evidenced,

- higher loss of Zn coating was found in cold water where formation of carbonation layer was disabled.

5. References


1. SIST EN 806Specifications for installations inside buildings conveying water for human consumption
2. DIN 1988 - Drinking water supply systems
3. DVGW W 551: 2004 - "Trinkwassererwärmungs- und Trink-wasserleitungsanlagen – Technische Maßnahmen zur Verminderung des Legionellenwachstums - Planung, Errichtung, Betrieb und Sanierung von Trinkwasser-Installationen"
4. VDI 6023-1: 2006 Hygiene in Trinkwasser – installationen Anforderungen an Planung Ausführung, Betrieb und Instandhaltung
5. L. Gosar, D. Drev, materiali in tehnologije 45 (2011) 639-644
6. Bacskai, J. Lehoczky, Korrrozios Figyelo, 51 (2011) 76-80
7. M. Suban, R. Cvelbar, B. Bundara, materiali in tehnologije, 52 (2010) 379-383
8. M. Carbucicchio, R. Ciprian, F. Ospitali, G. Palombarini, Corrosion Science, 50 (2008) 2605-2613
9. E. Otero, JJ. Royuela, Corrosion Science, 34 (1993) 1581-1593
10. J. Schmitt, H-C Flemming, FTIR spectroscopy in microbial and material analysis, Inter. Biodeterioartion¸Biodegradation 41 (1988) 1-11
11. Helmut Gunzer, Hans-Ulrich Gremlich, IR Spectroscopy, Wiley-VCH, 2002