The effect of disinfectants on the properties of water piping material

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The behaviour of metals in contact with drinking water is dependant of different exposure conditions: type of drinking water, the temperature of drinking water, flow, the presence of water softening chemicals etc. In water treatment process also different chemicals are used for disinfection of water system, this can contain high concentration for rare chemical disinfections and lower concentrations for continuous disinfections.
In the present study, the two disinfectants will be studied at high and low concentrations. Different materials that are used in drinking water distribution will be tested. The tested materials will be stainless steel, galvanized steel and copper.
Electrochemical properties of different materials were studied by the use of different electrochemical techniques: linear measurements and potentiodynamic polarization scans.
The effect of type and concentration of disinfectants on corrosion properties of materials in contact with drinking water was studied and the type of corrosion attack was spectroscopically (visual and SEM/EDS analysis) investigated as well.

Key words: drinking water system, corrosion, dezincification, corrosion rate, light microscopy

1. Introduction

The drinking water chemistry varies significantly among different regions due to geomorphological constitution of the grounds. Different types of drinking waters differ due to their alkalinity, pH, hardness, presence of carbonates, sulphates and nitrates [1].

Also the water communities are self-dependent and can use relatively regulation free their own water treatment procedures.

Water treatment procedures can be for different purposes, such as softening by the use of phosphating agents, it can be chlorinated, ozone treated or magnetically treated in order to control microbiological parameters, sometimes only different filters are used to control the size of particles present in water. The goal of disinfection of public water supplies is the elimination of the pathogens that are responsible for waterborne diseases [2].

The quality of the raw water, its content of solids and material that will react with the disinfectant, treatment of the water prior to disinfection, and the manner in which the disinfectant is applied to the water will directly affect the efficacy of all disinfectants [2]. The chemical additions to water might impact materials in contact with differently treated waters [3,4].

In this study the effect of the use of different disinfectant concentrations on two chemistry bases was chosen. One disinfectant is chlorine based and the other is hydrogen peroxide containing silver ions.

The goal of the study is to determine corrosion properties of the materials in contact with typical hard drinking water containing different concentrations of disinfectants. Spectroscopic analysis was used in order to complement electrochemical investigation.

2. Experimental

2.1 Preparation of samples

Metal disc electrodes (working electrodes) were prepared by cutting discs from 2 mm-metal sheets and by grinding the surface to 1200 SiC emery paper.

The materials that we tested were (materials purchased at Goodfellow):

- Stainless steel 304 L
- Copper
- Zinc.

Zinc was chosen in order to resemble galvanized steel pipe for drinking water distribution system.

1.2 Preparation of water testing environment

Water samples were prepared using tap water, collected in 10 L canister on 1st of March 2019.

Water quality, as received from Vo-Ka supplier of water in Ljubljana region is presented in Table 1.

Table 1: Drinking water parameters on 17th January 2019

	Units	Limit/ recommended values	Result of the analysis
pH	/	6.5–9.5	**7.3**
Electrical conductivity (20°C)	μS/cm	<2500	**413**
Odor	/	/	**unremarkable**
Opacity	NTU	<4	**<0.1**
Color	m-1	/	**<0.2**
Total organic carbon - TOC	mg/l	/	**<0.3**
Ammonium	mg/l	<0.5	**<0.01**
Nitrite	mg/l	<0.5	**0.0041**
Nitrate	mg/l	<50	**12.6**
Sulfate	mg/l	<250	**11.2**
Chloride	mg/l	<250	**8.82**
Calcium	mg/l	/	**71**
Orto phosphates	mg/l	/	**<0.006**
Phosphorus - total	mg/l	/	**<0.03**
Total hardness	°N	/	**13.6**
Manganese	μg/l	<50	**0.12**
Iron	μg/l	<200	**<40**
Copper	mg/l	<2	**0.00098**
Lead	μg/l	<10	**<0.1**

Table 2: The tested disinfectant and concentrations

	Izosan	Sanosil Super AG
Protection disinfection	2 mg/L	0.5 g/L
Chemical disinfection	0.1 g/L	25 g/L

Chemical disinfection is usually a high concentration of disinfectant, which is used if water is microbiologically contaminated, while continuous/prevention or protection disinfection is the use of disinfection as a constant concentration added to water delivered to end-users.

1.3 Electrochemical measurements

A three-electrode corrosion cell was used for electrochemical testing. The tested metal represented a working electrode, exposing area 0.785 cm^2. A saturated calomel electrode (SCE) served as a reference electrode and graphite rod was used as counter electrode. A PG Gamry instruments (Potenciostat/Galvanostat/ZRA Reference 600, ZDA, 2006) was used.
After one to three hour stabilization at open-circuit potential (OCP), the potentiodynamic measurement was performed starting from –0.25 V vs. OCP, and progressing in the anodic direction up to +1.0 V vs. potential of a reference electrodes at a scan rate of 1 mV/s. At least two measurements were made. All the potentials are reported with respect to the SCE scale.

1.4. SEM/EDS analysis

A low-vacuum scanning electron microscope (JEOL 5500 LV, Japan), equipped with energy dispersive spectroscopy (EDX) Oxford Inca (Oxford Instrument Analytical, UK), was used to observe and analyze the contact surfaces and the formed electrochemical products using an accelerating voltage of 20 kV.

3. Results and discussion

3.1 The effect of concentration of disinfectant

Potentiodynamic measurements were conducted in order to study the effect of water and water containing disinfectants on corrosion properties of stainless steel, copper and zinc.

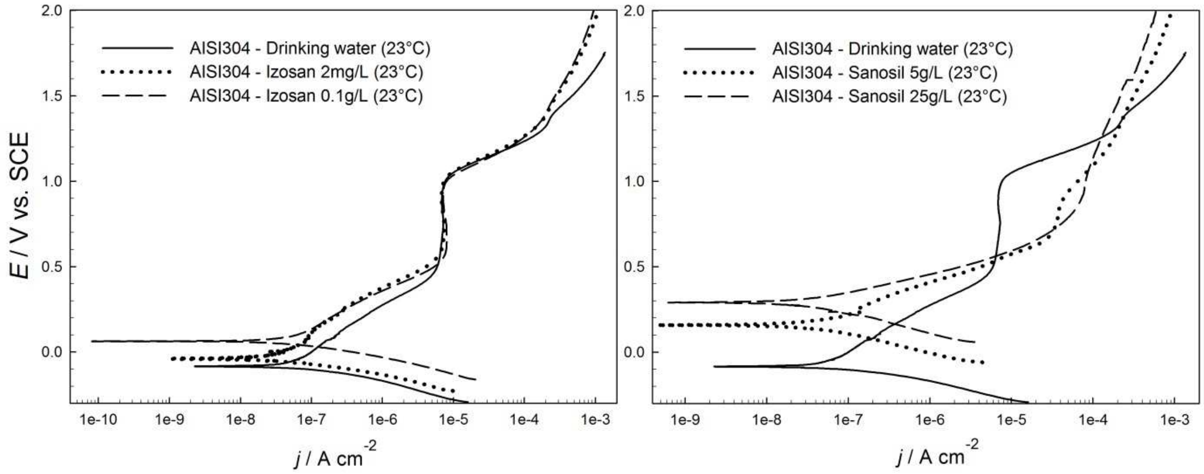

Figure 1: Potentiodynamic measurements for stainless steel 304 L in drinking water at room temperature alone and at different concentrations of disinfectant Izosan G and Sanosil Super AG, scan rate 1 mV/s

Corrosion current density, j_{corr} for stainless steel in a test water is very low at 0.099 μA/cm^2. The potentiodynamic curve exhibits a typical two step passive region in the anodic part of the curve with breakdown potential at E_b at 1.01 V. Smallest and highest concentration of Izosan does not change corrosion behavior much, corrosion current densities decrease slightly with Izosan concentration (Table 3). Izosan probably acts as an oxidant for surface passive film. However, when Sanosil Super AG is added as disinfectant, different corrosion behavior of stainless steel AISI 304 L is observed. Corrosion potential moves to more positive values (Table 3) and corrosion current density decreases to a value close to 30 nA/cm^2. The passive behavior observed in anodic region is changed, however breakdown potential is not as high as in the case of Izosan (Table 3).

Table 3: Electrochemical parameters extracted from potentiodynamic measurements for 304 L in the presence of different concentrations of disinfectants Izosan G and Sanosil Super AG

	E_{corr}/ V	j_{corr} (μA/cm^2)	E_b (V)
Drinking water	–0.102	0.099	1.03
Izosan 0.2 mg/L	–0.040	0.060	1.01
Izosan 0.1 g/L	0.062	0.035	0.99
Sanosil 0.5 g/L	0.158	0.031	0.87
Sanosil 25 g/L	0.290	0.026	1.03

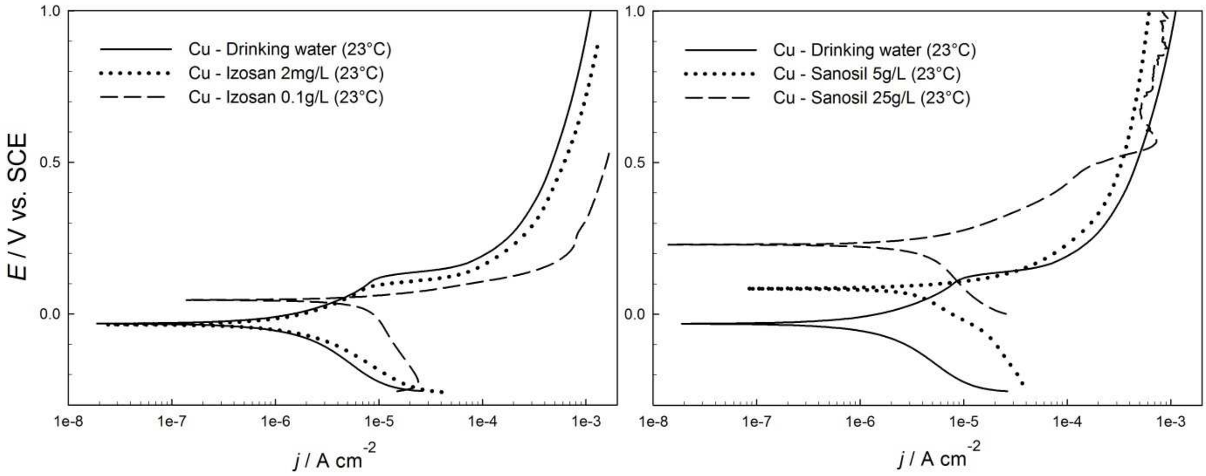

Figure 2: Potentiodynamic measurements for copper in drinking water alone and at different concentrations of disinfectant Izosan G and Sanosil Super AG, scan rate 1 mV/s, at room temperature.

In drinking water as test solution corrosion current density j_{corr} for copper is 3.40 μA/cm^2. The potentiodynamic curve exhibits a narrow passive region in the anodic part of the curve with E_b at 0.116 V. Smallest concentration of Izosan does not change corrosion behavior much. However, the highest tested concentration of Izosan increased corrosion current density to 8.60 μA/cm^2, corrosion potential increased and no passive region is observed in the anodic part of potentiodynamic curve (Table 4). When Sanosil super AG is added to water, the corrosion current density increases in both cases, however, to a much larger extent in the case of the highest concentration, where corrosion current density is 30 times higher than in drinking water (Table 2).

Table 4: Electrochemical parameters extracted from potentiodynamic measurements for copper in the presence of different concentrations of disinfectants Izosan G and Sanosil Super AG

	E_{corr}/ V	j_{corr} (μA/cm^2)	E_b (V)
Drinking water	–0.032	3.40	0.116
Izosan 0.2 mg/L	–0.035	3.45	0.086
Izosan 0.1 g/L	0.045	8.60	0.266
Sanosil 0.5 g/L	0.084	5.34	/
Sanosil 25 g/L	0.229	92	0.484

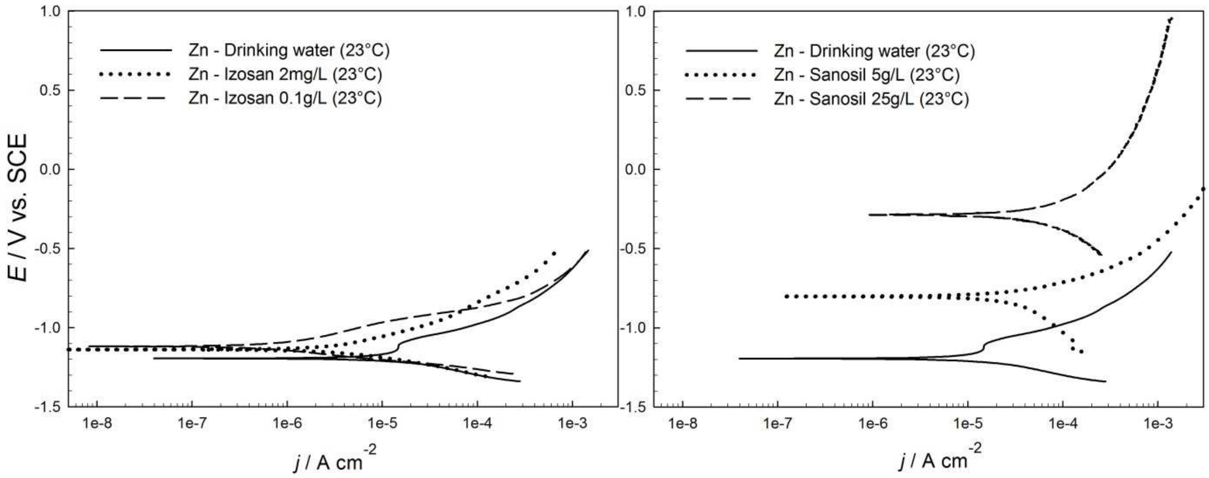

Figure 3: Potentiodynamic measurements for zinc in drinking water alone and at different concentrations of disinfectant Izosan G and Sanosil Super AG, scan rate 1 mV/s, at room temperature

Corrosion current density j_{corr} for zinc in drinking water alone is quite high at 9.54 μA/cm^2 and corrosion potential E_{corr} is at –1.191 V (Table 5). When Izosan (chlorine based disinfectant) is added to water, the lowering of corrosion current is observed, the effect is more pronounced for higher Izosan concentrations (10 times lower corrosion current density). Most probably it can be assumed that Izosan provoked oxidation of Zn surface to ZnO, which can be then observed as lowering of corrosion current density. This fact can be confirmed by SEM/EDS investigation.
Very different behavior is observed studying disinfectant Sanosil Super AG, which at small and high concentrations induces higher corrosion current density for 2 or 4-times (Table 5).

Table 5: Electrochemical parameters extracted from potentiodynamic measurements for zinc in the presence of different concentrations of disinfectants Izosan G and Sanosil Super AG

	E_{corr}/ V	j_{corr} (μA/cm^2)	E_b (V)
Drinking water	–1.191	9.54	–1.10
Izosan 0.2 mg/L	–1.14	2.90	/
Izosan 0.1 g/L	–1.12	1.0	/
Sanosil 0.5 g/L	–0.803	42.2	/
Sanosil 25 g/L	–0.287	20.5	/

3.2. Spectroscopic results

Different materials (stainless steel AISI 304 L, copper and zinc), that usually come in contact with different types of drinking water, were exposed to different concentrations of disinfectants on chlorine and oxygen based formulas for 2 weeks at room temperature. After the exposure, the surfaces of metal materials were optically checked and morphology of the surfaces was analyzed by electron microscopy and analyzed by EDS.

In Figure 4, images for stainless steel AISI 304 L, copper and zinc samples after 14 days of exposure to water and different concentrations of disinfectants (Izosan) are presented. It can be observed by naked eye that stainless steel and copper did not change after exposure to water for 14 days, while on zinc, a slight change on surfaces is observed.
In low concentration of disinfectant, some changes are observed on stainless steel and on zinc surfaces, while a high concentration of disinfectant affected all types of metal upon

exposure to water with disinfection. The surfaces were then analysed by electron microscopy.

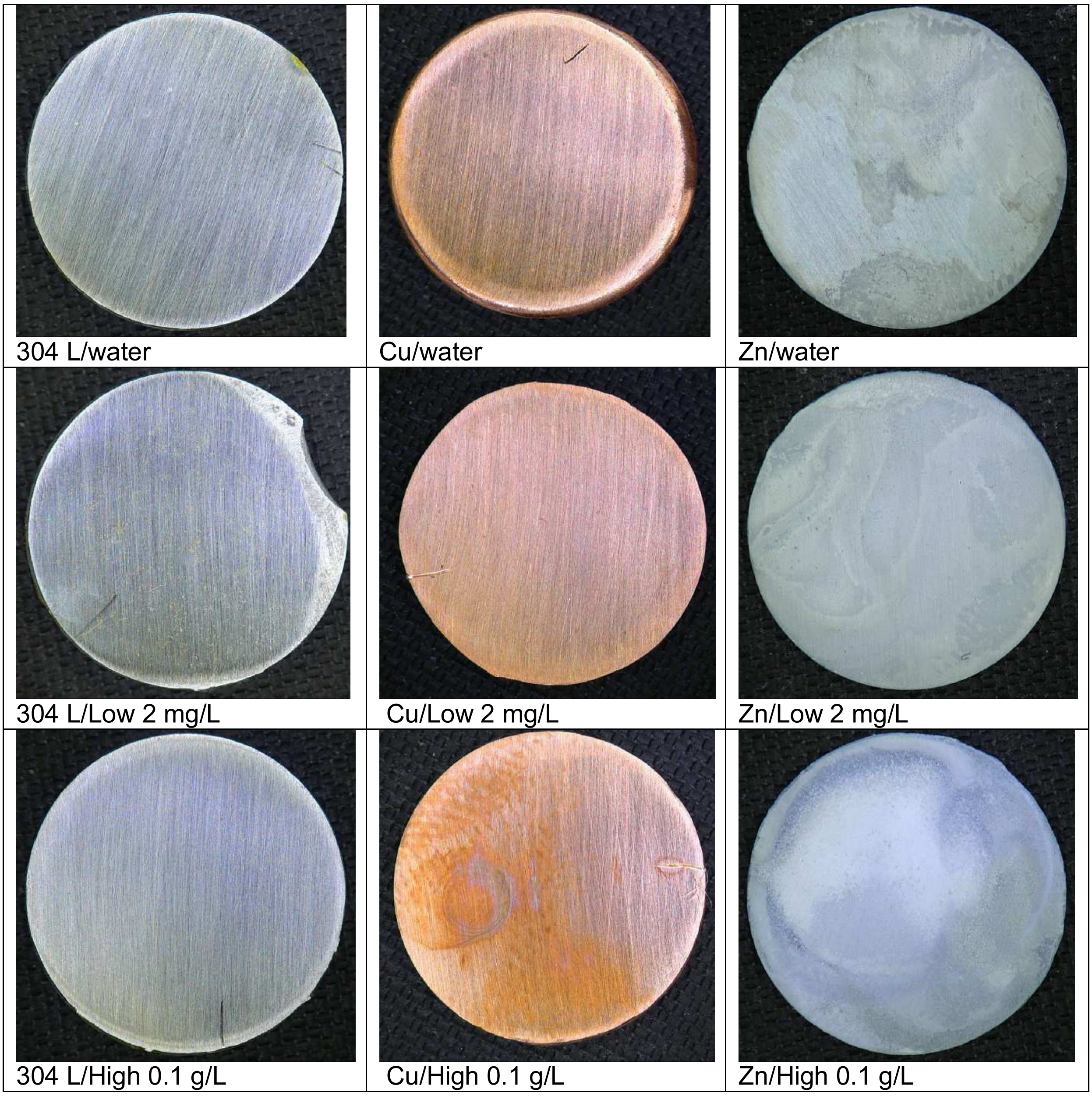

Figure 4: Stainless steel AISI 304 L, copper and zinc, exposed for 14 days to water with different concentrations of Izosan (low and high concentration)

SEM investigation was conducted after 14 days of exposure. SEM images are shown in Figure 5.

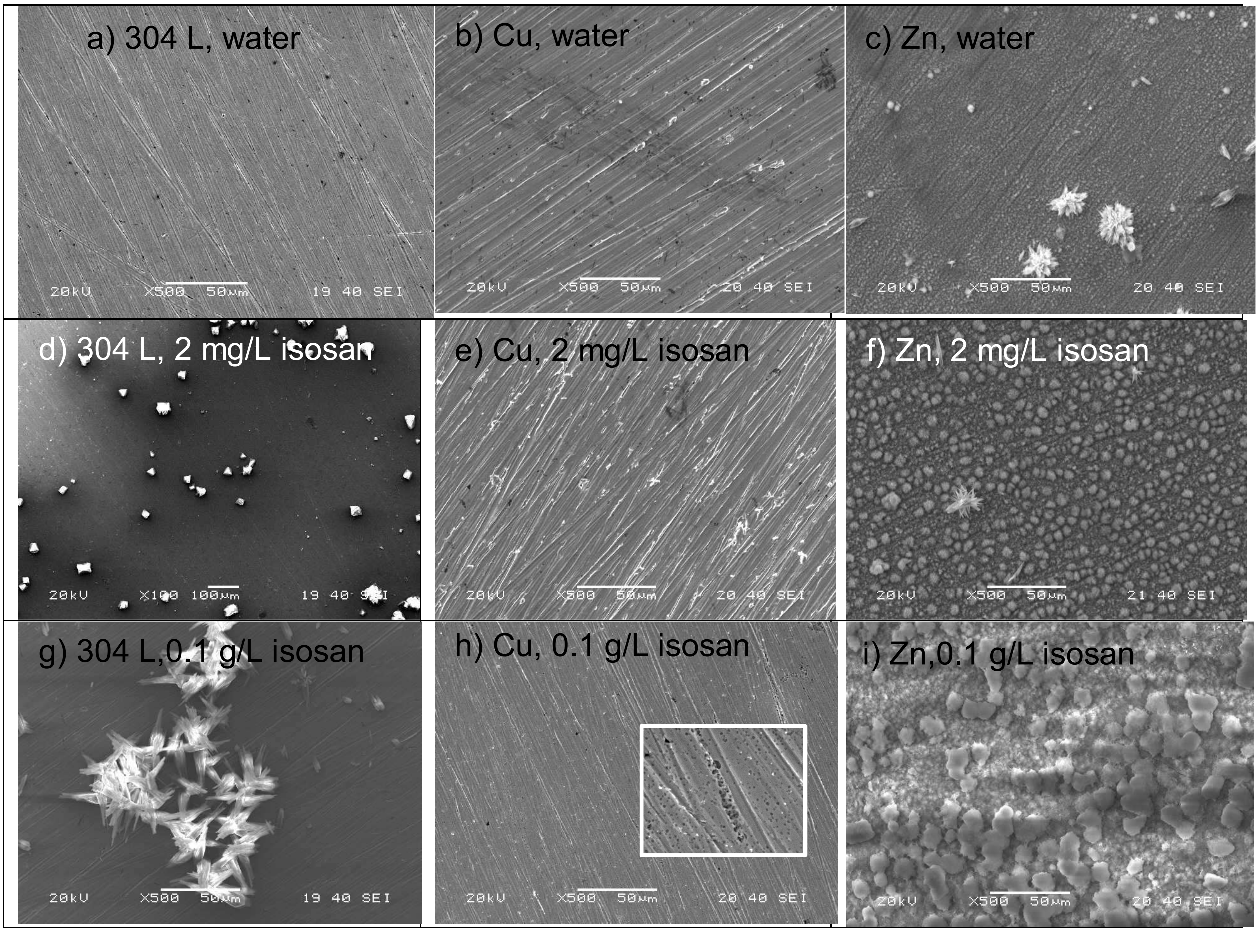

Figure 5: SEM images stainless steel AISI 304 L, Cu and Zn surfaces, exposed to water containing different concentrations of Izosan G after 2 weeks, the inset in Figure 5h displays SEM image at 3000-times magnification

SEM investigation has shown that samples exposed to water only, did not suffer from any signs of early corrosion on copper and stainless steel AISI 304L (Figures 5a and 5b), However, zinc already corroded only upon exposure to water (Figure 5c). EDS analysis confirmed the presence of Zn and O, supposing that ZnO has formed.
In water with low concentration of Izosan at 2 mg/L, surface deposits started to appear on stainless steel 304 L surface, while on copper, no sign of corrosion is detected. EDS analysis showed a presence of carbon, oxygen and calcium, which confirmed the formation of Calcium carbonate. On zinc surface, round crystals formed which covered the whole surface. EDS analysis showed the presence of Zn and O. Spike-like formation of crystals on Zinc surface showed a presence of calcium carbonate.
In high concentration of Izosan in water, big agglomerates of calcium carbonate was found on 304 L surface, while on copper, very fine pitting was observed (image as inset in Figure 5h). On zinc surface in a high concentration of disinfectant in water, a thick formation of ZnO was observed as confirmed by EDS.

4. Conclusions

Main conclusions of the presented study are:

- Electrochemical investigation showed that different concentrations and type of disinfectants used as disinfection in drinking water have different effects on corrosion properties of stainless steel 304 L, zinc and copper.

- It was shown that Izosan (chlorine based disinfectant) does not affect corrosion properties of stainless steel much, but Sanosil super AG affects electrochemical behavior of stainless steel.
- Our study showed that a high concentration of chlorine based disinfectant affects electrochemical behavior of copper, so does low and high concentrations of Sanosil super AG.
- The reduction of corrosion current density on zinc is attributed to formation of ZnO in water containing chlorine based disinfectant, while Sanosil super AG increased the corrosion current density pointing at intensive corrosion reactions.
- SEM/EDS analysis confirmed the presence of ZnO on zinc surfaces, also some calcium carbonate deposits were found.

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