Corrosion behaviour of two different brasses in soft and hard waters of different pH

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Brasses are widely used in drinking water for valves and fittings. Good machinability of brasses is chieved by adding lead (Pb) in brass in amounts up to 2.5 mass %. However, in many types of waters commonly used α-β brasses dezinficate. In this process, Pb migrates into water. In Europe, the concentration of lead in drinking water is restricted by Drinking water directive and is limited to 10 µg/L. However, dezincification of small components of drinking water installation can rise its concentration above the allowed value.
In the present study, two types of brasses were tested: the first type with the composition approved by 4 MS innitiative (4 EU member innitiative on approval and harmonization of tests for the hygenic suitability of products in contact with drinking water), and the second with the composition, which is not approved. Both of materials were exposed to three different types of syntetic water that differ in pH, alkalinity and chloride concentration. During the 11 month exposure, electrochemical impedance spectroscopy measurements were conducted regularly – at the beggining every week, later on once per month. At the same time, visual inspection of exposed surfaces is regularly performed. In this study, the correlation between Pb and the amount of Zn and Cu, which were analysed each month, are sought. The results of electrochemical characterization are correlated to microstructural characterization and thre releases of Cu, Zn and Pb.

Key words: drinking water system, brass, corrosion, dezincification, corrosion rate, electrochemical impedance spectroscopy, Raman spectroscopy

1. Introduction

Copper and its alloys with zinc have numerous advantages properties such as physical properties, thermal and electrical conductivity, machinability, wear resistance [1]. Thereby their use in industry of materials cannot be substituted. Beside this, most of copper and brasses are made by recycling [2].

Copper and its alloys with zinc are corrosion resistant due to a formation of patina, which can protect copper and alloy from further corrosion. In the case of aggressive species and conditions, copper and brasses are prone to corrosion as well. Most reported corrosion types for copper alloys with zinc are general corrosion, pitting corrosion and dezincification. Especially in fluids, non- aerated systems and aggressive environments, copper and zinc alloys are prone to more aggressive corrosion. Thereby different ways of protection systems must be foreseen.

In drinking water distribution system brasses are used, most commonly as units like valves, watermeters, etc. Brasses usually vary a lot in quality as a result of the chemical composition and microstructural characteristics. Usually brasses with high percent of zinc are used. Leaded brasses are copper zinc lead alloys. Lead is introduced into brasses in order to improve machinability, while corrosion resistance is not improved [1]. With the addition of tin (Sn) at 1 %, strength and dealloying resistance is increased while Aluminum (Al) is added to stabilize the protective surface film [1].

It is well known that brass alloys are subjected to dealloying, dezincification. In this process brass dissolves, while copper redeposits on the surface by forming a porous layer. Also zinc can be redeposited or can be carried away in the form of soluble salts.

The main concern about Pb in brasses which are in contact with drinking water is its leaching into water. Concentration of Pb in the leaded brass depends on the quality of the brass and can vary up to 8.5% by weight. On the other hand, the highest allowed concentration of lead content in drinking water is 10 μm/L, as defined in EU directive [3]. This limit concentration is valid for adequate method of sampling water sample, for water sample representing a weekly averaged concentration of consumed water. At sampling the highest possible risk, which can affect the human health, has to be taken into account as well. In Slovenia, the lower concentration of lead in drinking water is valid from November 1st 2013, before that time, concentration of 25 mg/L of lead was allowed.

In the USA, the maximum allowed concentration of Pb in material depends upon the total surface of material alloyed with lead in respect to the whole surface of installation in the contact with drinking water. In EU most developed regulations is 4 MS Acceptance schemes where Pb concentration is set regarding the intended use of material [4]. In Slovenia the latter schemes are not applied, however, the challenges with Pb release into drinking water system exist. Due to several cases with exceeded concentrations of Pb found in water at tap in relatively new buildings in Slovenia, recommendation for materials in the contact with drinking water were recently released [5]. It is expected that the risk of polluted drinking water in the future will be minimized.

The drinking water chemistry varies significantly among different regions due to geomorphological constitution of the ground and has a significant influence to leaching of brass. Water impact to increased concentrations of Pb in water due to leaching was well studied in the past [6,7]. Fast tests for determination of susceptibility to leaching of different quality of brasses can give only the first information on this risk for particular alloy. However, this kind of test is not suitable to study the influence of local water to the risk of leaching. Most of studies performed to explain the influence of local water chemistry to leaching were based on monitoring of Pb migration from the alloy to the water during long-term exposures [6, 7].

The presented study is the upgrade of our previous studies [8]. The main aim of this work is to study the ion leaching from brass alloys in three different water environments, which vary in pH and in alkalinity. For this purpose two commercial brasses, one approved by 4MS Common Composition List for metals [4], and one not, were chosen for experimental work. In this study the concentrations of leached ions such as Pb, Zn and Cu were determined during

11 month of exposure. Different spectroscopic and metallographic techniques were used to analyse the intensity of the possible dezincification.

2. Experimental

2.1 Preparation of brass samples

Two different brass alloys were prepared for long term exposure. The first one is 4MS approved brass (denoted as brass A) and the second one, denoted as brass B, is not approved by 4MS due to its chemical composition. The chemical composition is given in the Table 1.

2×2 cm samples were cut, approximately 1 mm thick and were abraded by SiC grade 320 papers. The samples were cleaned according to Flyg&Symniotis method [8]. Then, electrical contact was attached at the back of the brass sample. Back and edges of the sample were protected by epoxy coating.

Table 1: Chemical composition, defined by optical emision spectroscopy, of the two brass alloys

Main elements [%]	Zn	Pb	Sn	Fe	Ni	Si	Al	Cu
A	41.15	1.95	0.212	0.304	0.0787	0.0090	0.0071	56.2
B	36.40	2.45	0.725	0.768	0.568	0.0548	0.433	58.3
4MS [4]	/	1.9-2.2	≤0.3	≤0.3	0.05-0.15	≤0.03	≤0.2	57.0-59.0

1.2 Preparation of water samples

Water samples were prepared from deionized water by controlling alkalinity, Cl content and pH according to standard EN 15664 [9]. Three different waters were chosen to be studied. Brass samples were exposed into beakers containing 350 mL of water.

Table 2: The different water samples which vary in pH and in alkalinity

	Test water 1 **Very hard, neutral**	**Test water 2** **Soft, weekly acidic**	**Test water 3** **Soft, alkaline**
pH	7.1	6.7	8.4
Alkalinity [mg HCO_3^-/L]	305	50	50
Cl^- [mg/L]	30	30	30

Sampling for ICP-MS analysis on Pb, Cu and Zn content was executed on each months in 11 month exposure period, altogether, 13 anylsis were conducted. Water in each container was exchanged once a month, after the sampling.
The brass samples were denoted according to data in Table 1 and Table 2.
Thus, A is for 4MS approved brass, a number next to a letter A denotes the water sample, thus A1 is 4MS approved brass in very hard neutral water.

1.3 ICP-MS analysis

The determination of the total concentration of Pb, Cu and Zn in analysed samples was carried out by using an inductively coupled plasma mass spectrometer (ICP-MS), model 7700x, from Agilent Technologies (Tokyo, Japan). Experimental working conditions for ICP-

MS were optimized for plasma robustness. Treatment of data was performed with the Agilent ChemStation software. Data processing was based on the peak area.

1.4. Raman analysis

The Raman spectra were obtained with a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer coupled to an Olympus BXFM optical microscope. The measurements were performed using a 514 nm laser excitation line, a 100 × objective lens and a 600 grooves/mm grating, which gave a spectral resolution of 1.99 cm^{-1}/pixel. The power at which the samples were set was 0.14 mW. A multi-channel air-cooled CCD detector was used, with integration times of between 20 and 35 seconds. The spectra are presented without baseline correction.

3. Results and discussion

ICP-MS analysis of Pb, Zn and Cu release in water

All exposure time presented in this study is 44 weeks, approximately 11 months. Brass type A, which quality was approved by 4MS and not approved brass samples (marked as B) were immersed in 3 types of water. Water samples were as follows: hard water with neutral pH=7.1, soft water with acidic pH=6.7 and soft water with alkaline pH=8.4. Water samples were taken each month during 11 month immersion for detection of Cu, Zn andPb concentration in water by ICP-MS method.
ICP-MS analysis was conducted for each water sample.

In Figure 1 the results of ICP-MS analysis for 4MS approved (A) and non-approved (B) brass is shown for samples immersed in synthetic very hard water with pH 7.1.

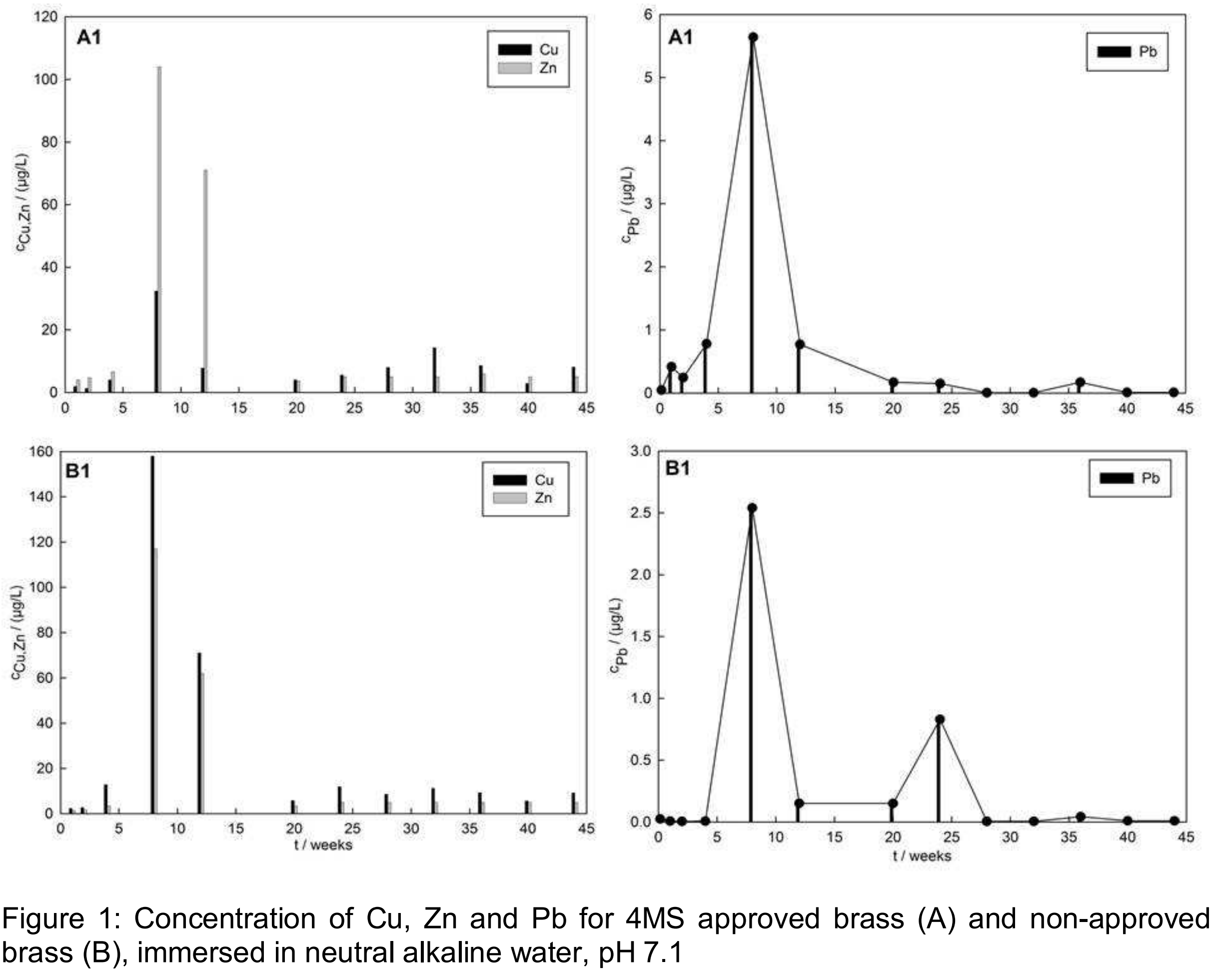

Figure 1: Concentration of Cu, Zn and Pb for 4MS approved brass (A) and non-approved brass (B), immersed in neutral alkaline water, pH 7.1

It can be seen that the release of Pb increases slowly for 4MS approved brass (A1) immersed in neutral alkaline water (Figure 1). Meanwhile, the concentration of leached Zn is highest at8th and 12^{th} week of exposure, at around 104 µg/L and 71 µg/L, respectively. The concentration of Cu is smaller at 8^{th} week of exposure, 32 µg/L. Towards longer exposure period, the concentration of copper is higher than concentration of Zn. Total amount of leached Pb in 1 cm^2 exposed brass samples during 44 week exposure was 2,95 µg.
For non-approved brass (B1) in hard neutral water pH7.1 the concentration of leached Pb is smaller than that for brass A. The highest reached concentration was 2.5 µg/L at 8^{th} week of exposure. Later Pb analysis showed that the concentrations of leached Pb were very small. However, the concentrations of Leached Cu and Zn in this hard water pH7.1 is very high. At 8^{th} week of exposure, the concentration of leached Cu was 158 µm/L and that for Zn 117 µg/L.
It can be concluded that very hard neutral water of pH 7.1 caused preferential dezinfication of alloy A, while Alloy B underwent general dissolution of both α- and β- phases.

Soft acidic water at pH 6.7 affected leaching of Pb to a smaller extent (Figure 2). However, the concentration of leached Zn in soft acidic water is extensive, it is increasing throughout exposure period. It amounts to as high as 918 µg/L. The concentration of leached Pb is highest at 8^{th} week of exposure, at 3.14 µg/L.
The difference between the two brasses is very evident. The highest concentration is leached for non-approved brass (B) at 8th week of exposure, detected concentration of Pb was 0.87 µg/L. Here, the concentration of leached Zn increases with exposure time, at about 205 µg/L at 32^{nd} week of exposure. The dissolution of Cu is not extensive, as well.

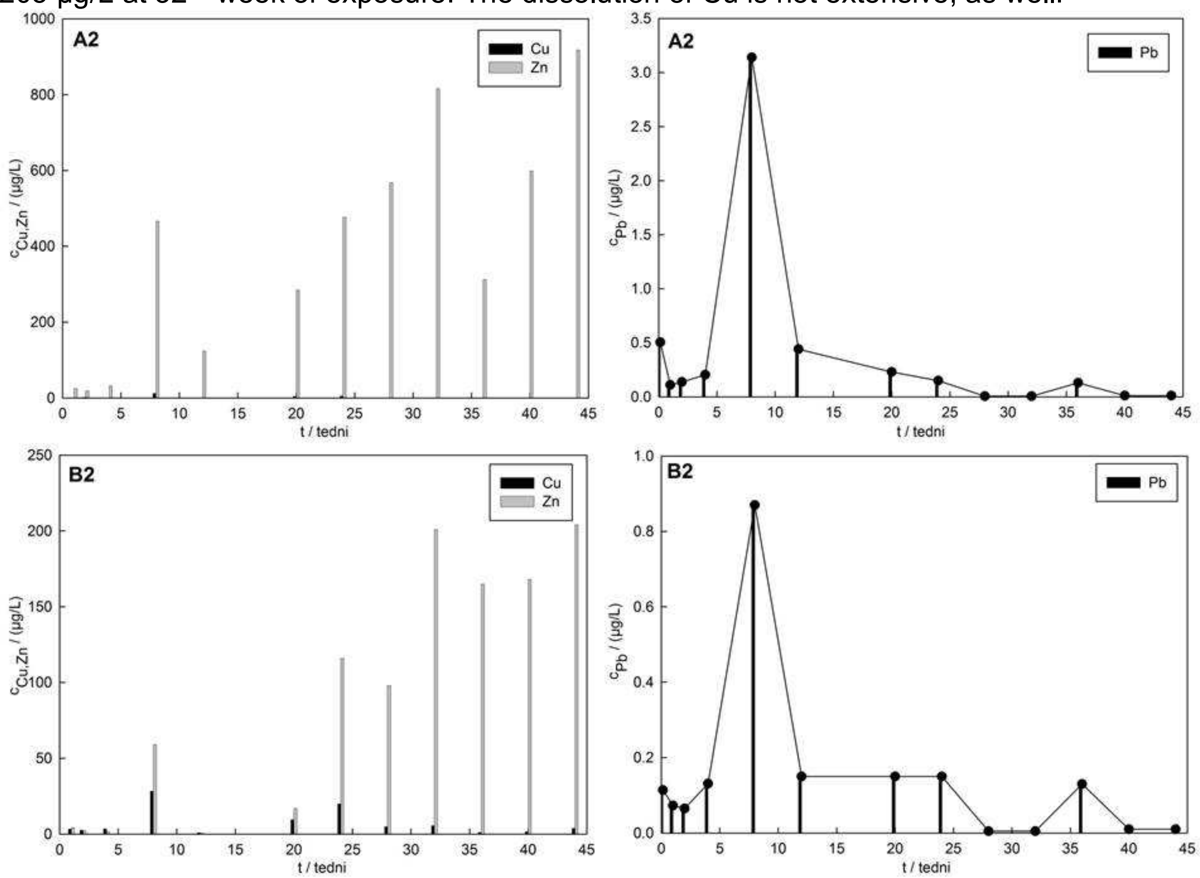

Figure 2: Concentration of zinc (Zn), copper (Cu) and lead (Pb) for 4MS approved brass (A2) and non-approved brass (B2) immersed soft acidic water pH 6.7

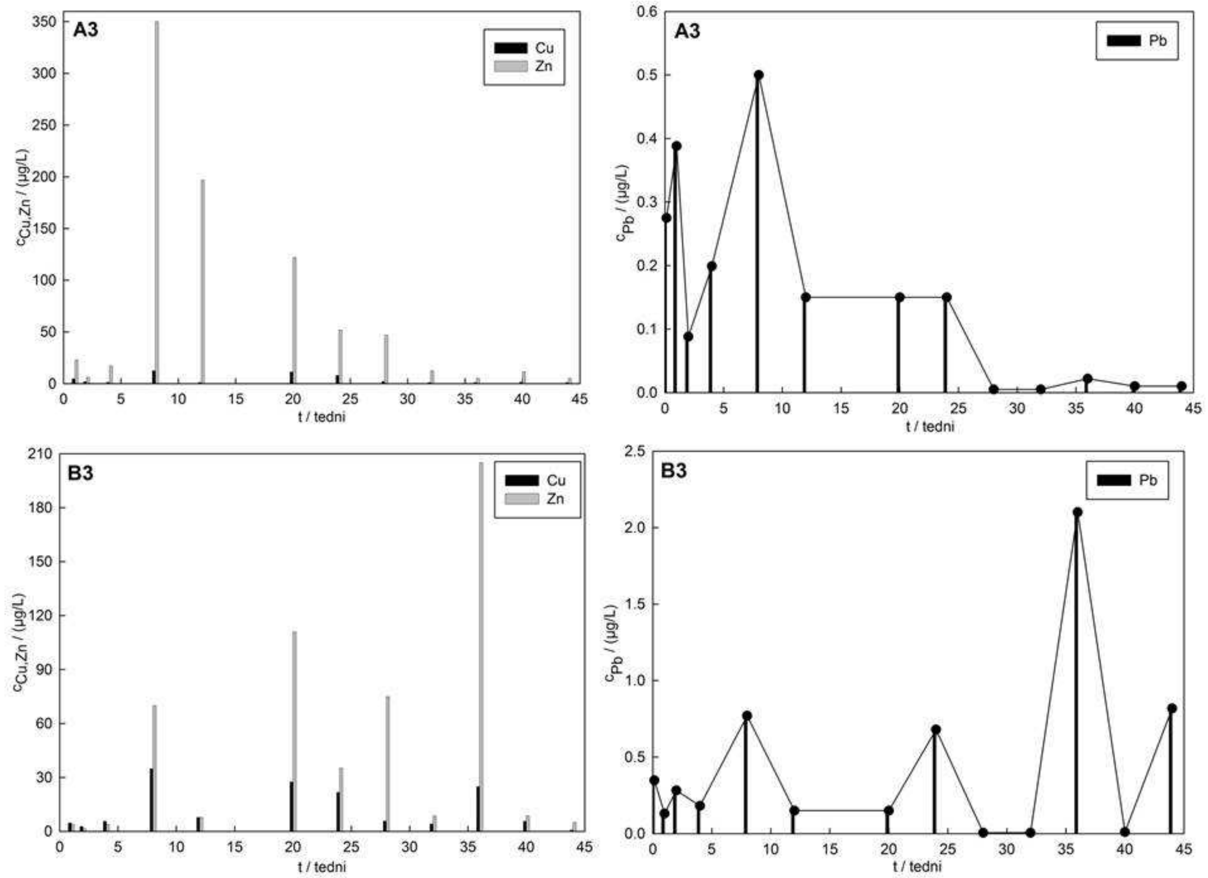

Figure 3: Concentration of zinc (Zn), copper (Cu) and lead (Pb) for 4MS approved brass (A3) and non-approved brass (B3) immersed in soft alkaline water pH 8.4

The release of Pb for not approved brass (B) immersed in soft alkaline water with pH 8.4 is higher in comparison to 4MS approved brass (A) (Figure 3). Zn concentration for non-approved brass (B) at 36 weeks of exposure, was 205 µg/L, for approved brass A3 it was as high as 350 µg/L at 8th week of exposure (Figure 3). After this period the concentration of leached Zn decreased.

In Table 2 the total mass of Pb, Zn and Cu during 11 month exposure is presented for the two different barsses in different waters. It can be seen that the the total amount of Lead is leasched from A and B is the highest in very hard, neutral water.
In soft acidic and soft alkaline water both brasses are prone to decinfication, preferential dissolution of Zn rich phase in $\alpha + \beta$ brasses.

Table 2: Total mass of leached ions during 44 month of exposure for two different brasses

	Very hard, neutral water	Soft, weekly acidic	Soft, alkaline	Very hard, neutral water	Soft, weekly acidic	Soft, alkaline
	A1	A2	A3	B1	B2	B3
Σ m_{Pb} / µg	2.95	1.78	0.68	6.52	0.65	1.97
Σ m_{Cu} / µg	34.63	10.12	16.82	308.47	29.59	51.23
Σ m_{Zn} / µg	78.68	1623.90	296.81	218.73	362.91	184.94

Metallographic analysis and spectroscopic results

In Figure 4, metallographic images for A1, A2, A3 and B1,B2 and B3 samples after 44 week are presented.

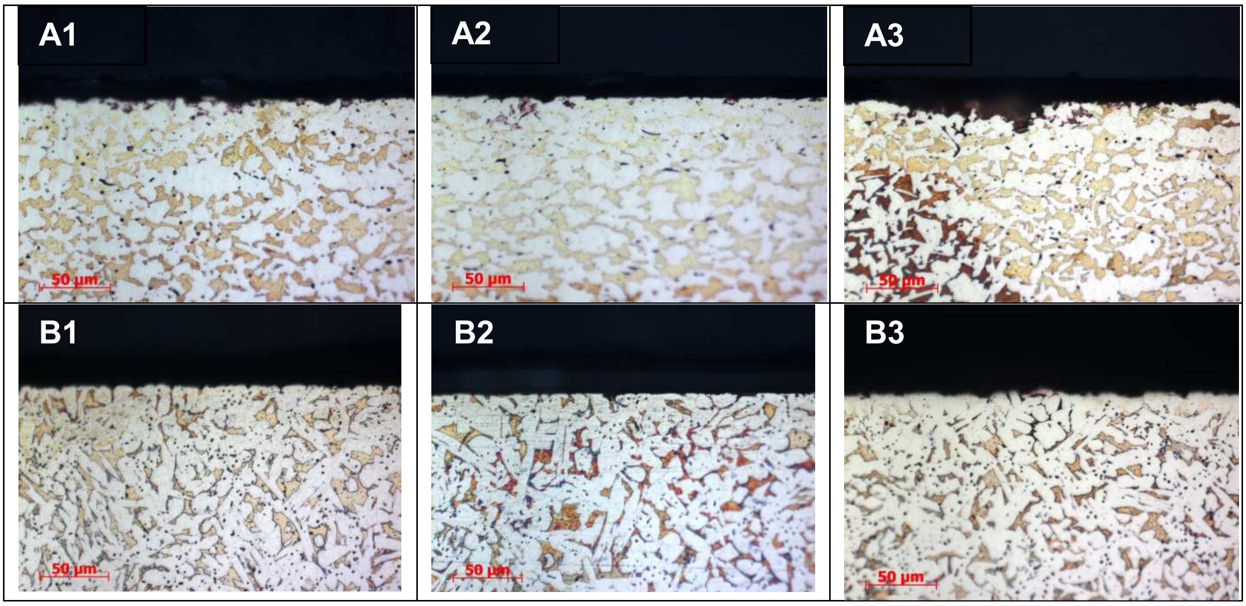

Figure 4: 4 MS approved brasses (A1, A2, A3) and not approved brass (B1, B2 and B3) after 44 weeks of exposure to different synthetic waters

Metallographic analysis showed that both brasses underwent dezincification processes (Figure 4). Namely, β' phase dissolved preferentially from the surface of both exposed brasses.
The extent of dissolved β' phase is higher for A brass in neutral and in basic soft water (A1 and A2, 10-15 μm), while in soft acidic water (A2) is more pronounced at 20-25 μm. Redeposition of copper is evident for A brasses.
The extent of dissolved β' phase for B brass in neutral, soft acidic and in basic soft water is similar at 5-10 μm.

Raman analysis was executed after 44 weeks of exposure.
The dots in Figure 5 represent the place at which Raman analysis was executed.
It can be observed that in neutral hard water (A1) and soft acidic water (A2), cuprite is formed. Cuprite can be found with pronounced bands at 145, 217, 422, 529 and 642 cm^{-1}.
Three different areas were found on A3, 4MS approved brass in soft neutral water sample. Cuprite is formed at the most of the exposed are, whereas also bands at 1123, 1155, 1506 might show the presence of carbonate species, similar as mineral azurite.
Raman analysis was performed also on non-approved brass B, presented in Figure 6. It can be observed that cuprite was formed along with CuZn carbonate, possibly a mineral similar to azurite, $Cu_3(CO_3)_2(OH)_2$ in all exposed brass samples.

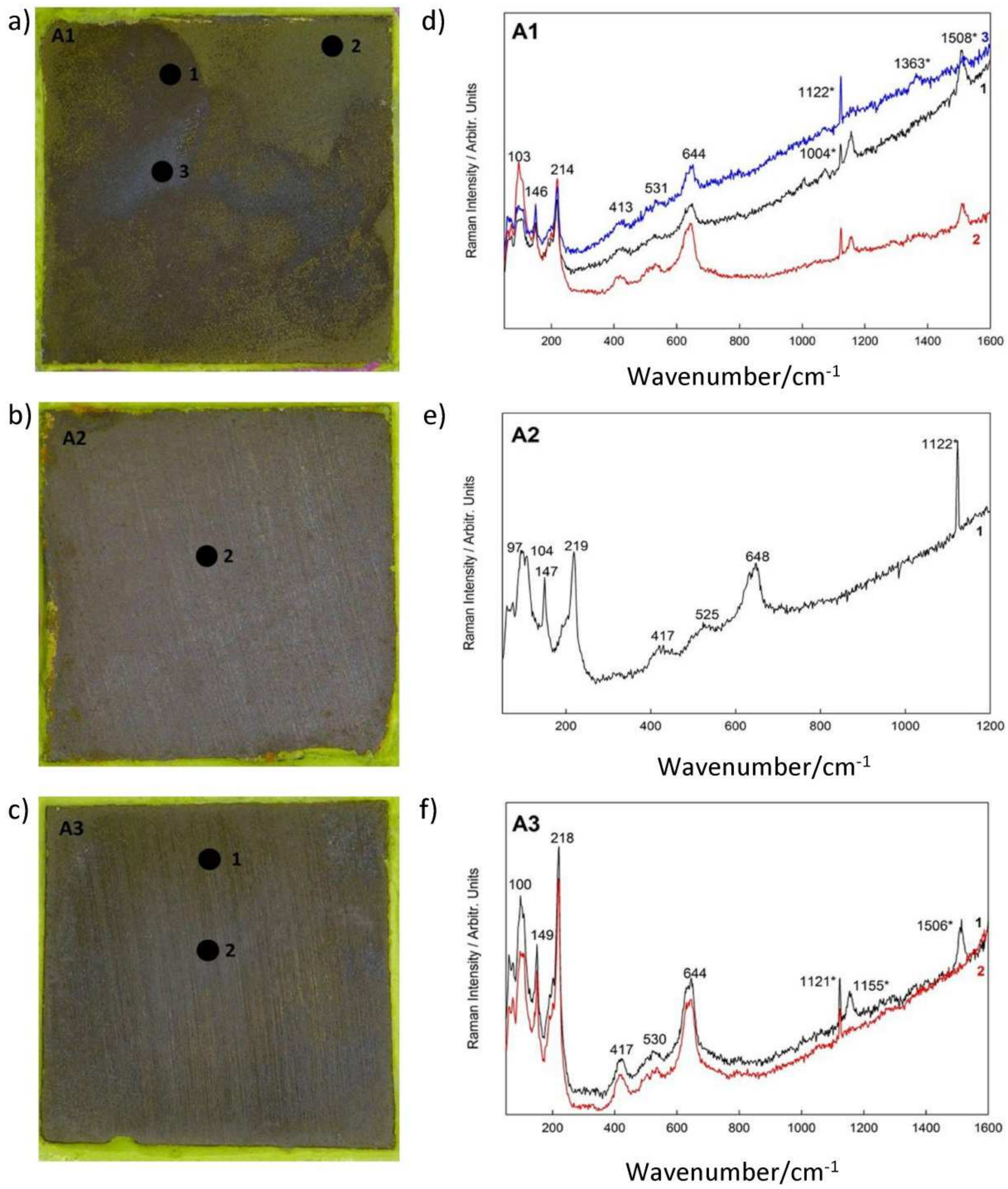

Figure 5: Images of 4 MS approved brass (A1, A2, A3) after 44 weeks of exposure and Raman analysis

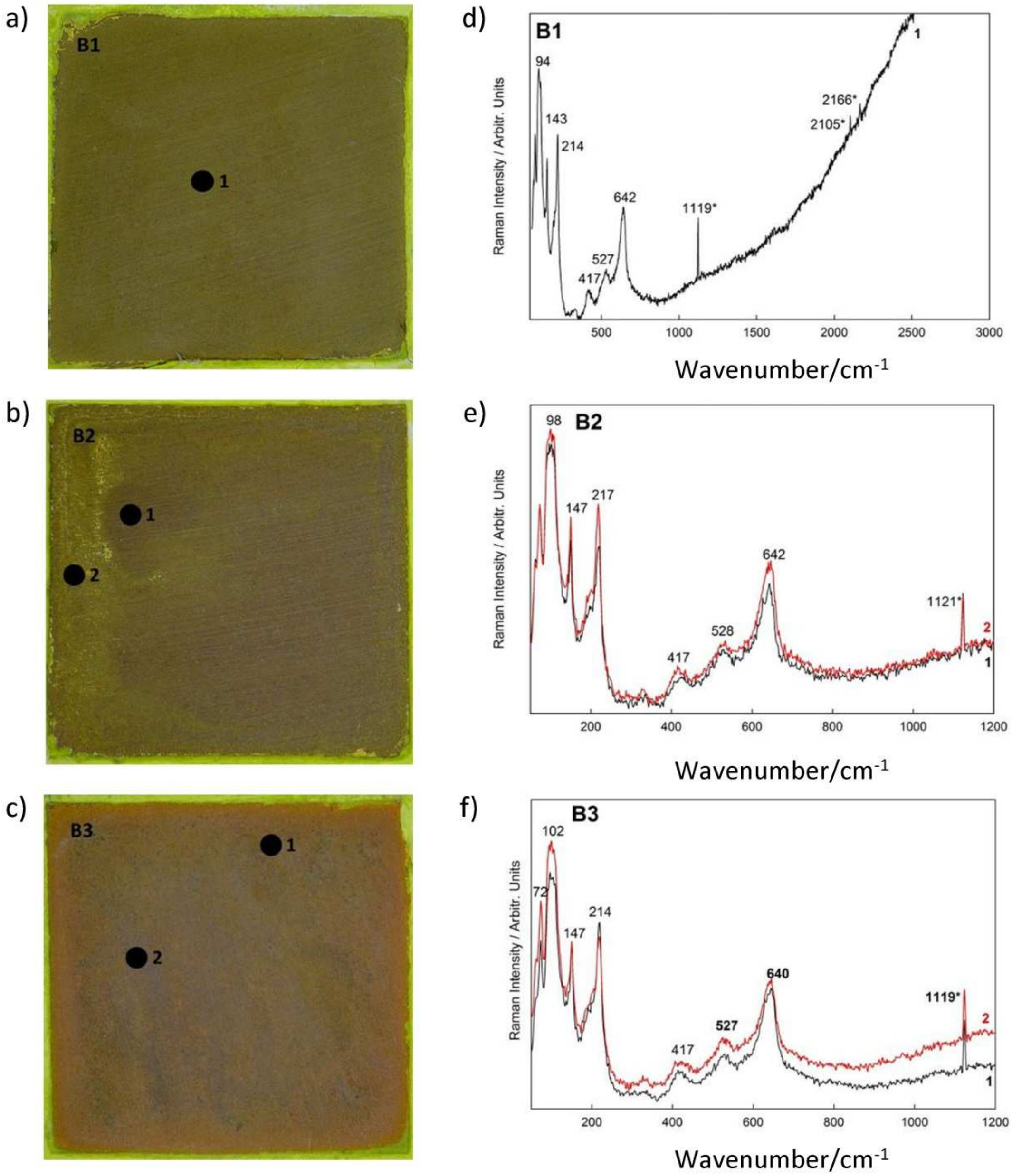

Figure 6: Images of non- approved brass (B1, B2, B3) after 44 weeks of exposure and Raman analysis

4. Conclusions

Main conclusions are:

- Dezincification is similar in both alloys, while the total zinc dissolution was higher for approved brass in soft acidic and soft alkaline water.
- The reason for such behavior is higher amount of β' phase in 4MS approved brass.
- After 7 months of exposure the concentration of leached Pb was decrease in all water samples for both investigated brasses.
- In very hard, neutral water non-approved brass underwent general corrosion, since the amount off all leached ions is high.
- After 11 month of exposure the main corrosion product on all brass surfaces is cuprite.

The presented study showed that the different waters have different effects onto different brasses; a particular water can be more aggressive towards one type of alloy than the other.

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