Characterization of corrosion behavior of two different brasses in three types of synthetic water

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α-β brasses can undergo dezinfication in many types of waters. this means that β phase dissolves and 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. In the present study, two types of brasses were selected for the investigation: the first type with the composition allowed (approved) by 4 MS, 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 10 month exposure, electrochemical impedance spectroscopy measurements were conducted regularly. Pb concentration in water where specimens are exposed, is measured.
It was observed that the level of Pb in particular water (highest pH, concentration of chlorides and lowest alkalinity) on not approved brass became higher than in two other waters. Electrochemical impedance results confirm the results of the analysed Pb concentrations.

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 for. 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 main aim of our study was to study Pb ion leaching from brass alloy 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. Different spectroscopic and metallographic techniques were used to analyse the intensity of 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 2 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

	%Zn	%Pb	%Sn	%Fe	%Ni	%Si	%Al	%Cu	%As	%P
A (Z/1075/15)	39.89	1.97	0.234	0.3	0.0789	0.0096		57.4	0.0125	0.0106
B (Z/955/14)	31.62	2.36	0.82	0.664	0.519	0.0513	0.735	62.9	0.0126	
4MS	rest	1.6-2.2	≤ 0.3	≤ 0.3	≤ 0.1	≤ 0.03		57-60	-	

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 800 mL of water. Sampling for ICP-MS analysis on Pb content was executed on 21, 63, 154, 196, 224, 252 and 266 day of exposure. Water in each container was exchanged once a month, 24 hours before execution of electrochemical impedance measurements. Water for Pb detection was taken from the container after 1 month of sample exposure (before exchange 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 [mgHCO_3^-/L]	305	50	50
Cl [mg/L]	30	30	30

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.

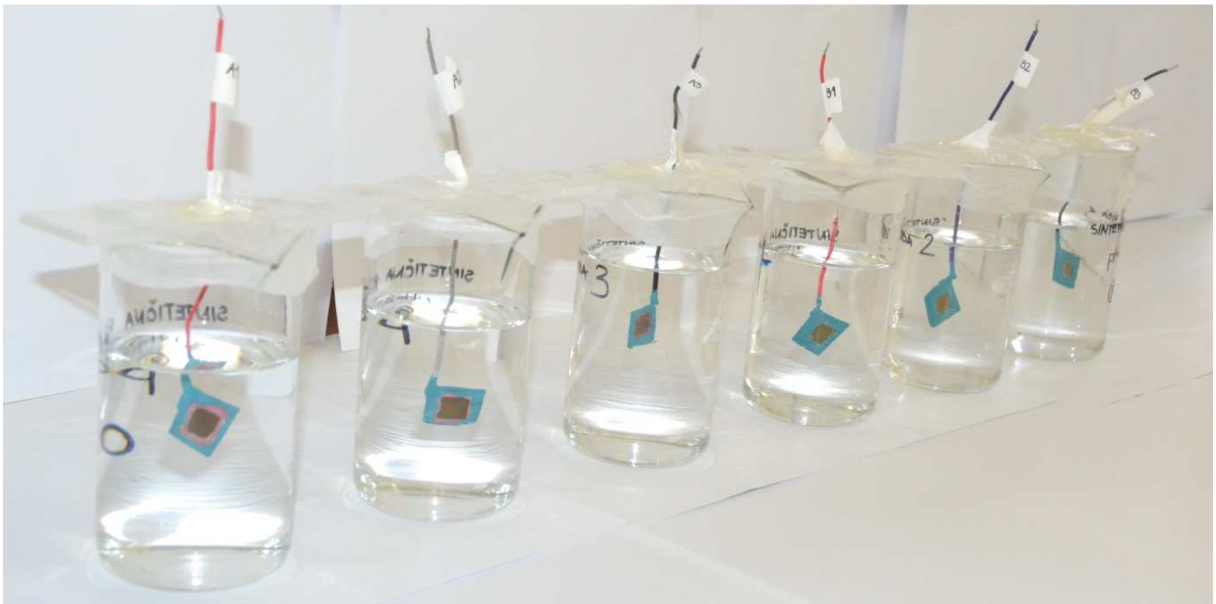
Figure 1: Photo of exposed brasses in different water samples

1.3 ICP-MS analysis and electrochemical impedance spectroscopy analysis

The determination of the total concentration of Pb 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.

1.5. Electrochemical Impedance Spectroscopy

Electrochemical testing was executed in three-electrode corrosion cell with SCE reference electrode and graphite counting electrode. After 24-hour stabilization at open circuit potential (OCP) electrochemical Impedance was measured. A PG Gamry instruments (Potenciostat/Galvanostat/ZRA Reference 600, ZDA, 2006) was used. The frequency scan ranged from 65 kHz to 1 mHz at 10 points per decade with an AC amplitude of ±10 mV. The absolute impedance and phase angle were measured at each frequency. The impedance measurements were carried out at the open circuit potential (OCP) at different times of immersion (1 h, 1day and 7, 21, 63, 154, 196, 224, 252, 266 days) in different samples of water for brass A and brass B.

3. Results and discussion

ICP-MS analysis of Pb released in water

All exposure time presented in this study is 41 weeks, approximately 10 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 samples. Water samples were hard water with neutral pH, soft water with acidic pH and soft water with alkaline pH. Water samples were taken at 21, 63,

154, 196, 224, 252 and 266 days of immersion for detection of Pb concentration in water by ICP-MS method.
ICP-MS analysis was conducted for each water sample.

In Figure 2 the results of ICP-MS analysis for 4MS approved and non-approved brass is shown for samples immersed in synthetic very hard water with pH 7.2.

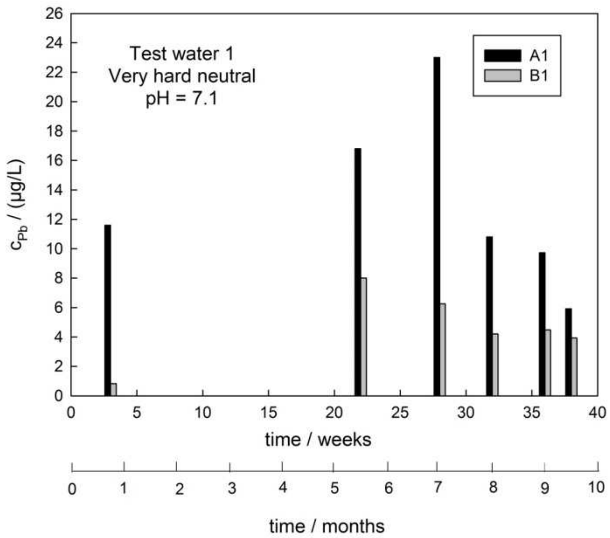

Figure 2: Concentration of lead (Pb) for 4MS approved brass (A) and non-approved brass immersed in neutral alkaline water a), soft acidic water b) and soft alkaline water c)

It can be seen that the release of Pb increases slowly for 4MS approved brass (A) immersed in neutral alkaline water (Figure 2). In the case of 4MS approved brass (A) in alkaline water it can be observed that it increases with time. The concentration at 28 weeks of exposure was highest at 24 µg/L. Then the concentration of Pb decreases by later exposure period. For non-approved brass (B) the concentration of leached Pb is always smaller than that for brass A. In very hard neutral water the highest reached concentration was 8 µg/L. Later Pb analysis showed that the concentrations of leached Pb were decreased.

Soft acidic water at pH 6.7 affected leaching of Pb to a great extent (Figure 3). The difference between the two brasses is very evident. The highest concentration is leached for non-approved brass (B) at 23 weeks of exposure, detected concentration of Pb was 630 µg/L. For 4 MS approved brass (A), the Pb concentration increased at later exposure period, at 28 weeks (7 months) where the concentration was as high as 490 µg/L. By the end of exposure, the release of Pb is smaller and below 40 µg/L, but it is always higher for 4MS approved brass (A).

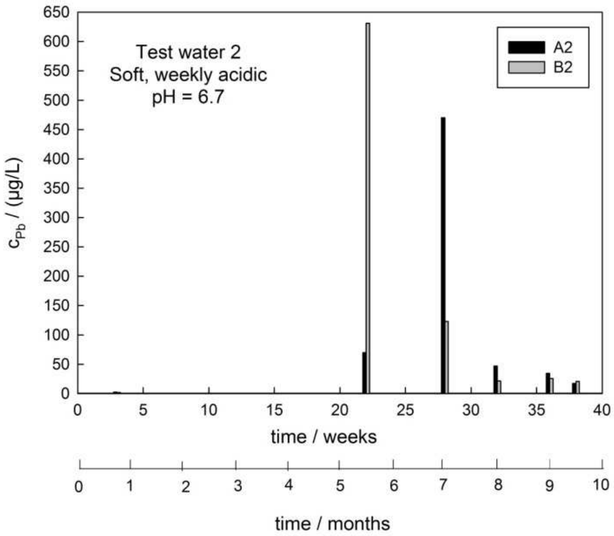

Figure 3: Concentration of lead (Pb) for 4MS approved brass (A) and non-approved brass (B) immersed soft acidic water

The release of Pb for not approved brass (B) immersed in soft alkaline water with pH 8.4 is very high in comparison to 4MS approved brass (A) (Figure 4). The highest concentration was detected for non approved brass (B) at 28 weeks of exposure, 6730 µg/L (Figure 4). After this period the concentration of leached Pb decreased but is higher for non- approved brass (B).

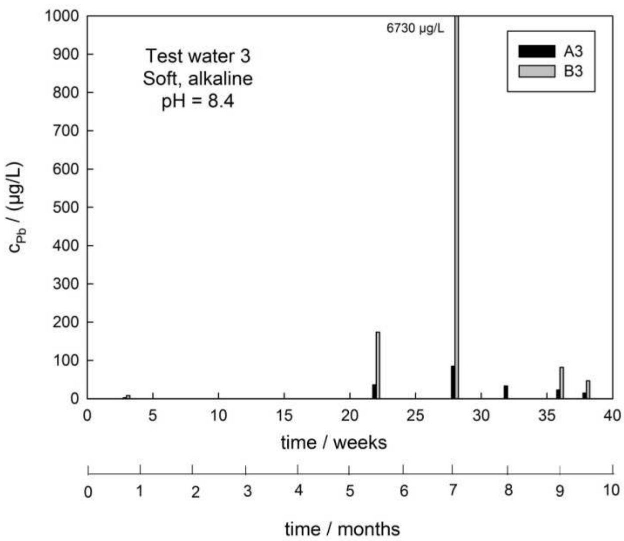

Figure 4: Concentration of lead (Pb) for 4MS approved brass (A) and non approved brass (B) immersed in soft alkaline water

It can be concluded that in neutral alkaline media, the release of Pb is the smallest, it was smaller for non-approved brass (B). Soft acidic water is more corrosive, release of Pb is comparable for 4MS approved brass (A) and non- approved brass (B). In alkaline soft water, 4MS approved brass (A) behaved similar to neutral alkaline water, while none the leached concentration of non-approved brass (B) was as high as 6800µg/L.

Electrochemical impedance results

Electrochemical impedance spectra were collected at different immersion times for the two brasses in three different waters. The results of total impedances, read from impedance spectra at lowest measured frequencies, are presented in Figure 5.

Each water represents unique corrosive behavior for the different brasses.
In neutral alkaline water (Figure 5a), the total impedance decreased in the early exposure period for both brasses, which means that the brasses were undergoing corrosion process. The impedance increased for both alloys at approximate 140 days of exposure. Probably protective film on exposed brasses was developed. Not approved brass (B) behaved better since higher total impedance was measured, which means higher resistance to corrosion. The concentrations of leached Pb ions prove the observation of impedances: the higest measured impedance 180 kΩ cm^2 for brass A resulted in low leached Pb concentration (9 µg/L), while for brass B, total impedance was 90 kΩ cm^2 and the leached Pb concentration was 40 µg/L in total 91 day of exposure. Meanwhile at the end of exposure impedance decreased again for both brasses and are comparable, a bit lower for not approved brass (Figure 5a).

a) **b)** **c)**

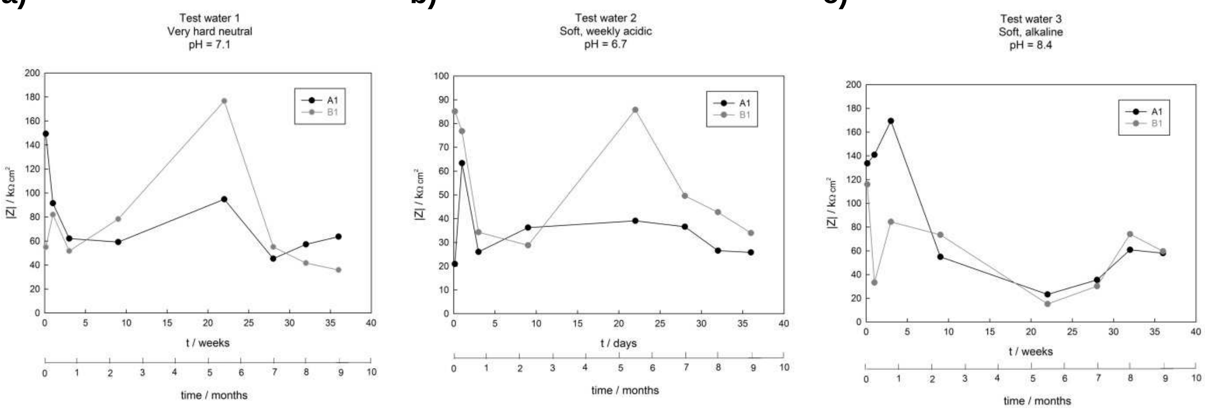

Figure 5: Total impedance of brass A and B in three different water samples, alkaline neutral a), acidic soft b) and soft alkaline c)

In soft acidic waters the total impedances for both brasses decreased in early exposure period to approx. value of 40 kΩ cm^2 for both brasses. It increases at 150 days of exposure, similar to values measured in alkaline neutral waters. High impedance and better corrosion resistance was measured for not approved brass (value of leached ions 650 µg/L for non-approved brass B) and 450 µg/L for approved brass. At the end of 10-month exposure both brasses behaved similarly.
In soft alkaline water the impedance decreases and stays low during 10 month exposure period (Figure 5c). The leached concentrations of leached ions are as high as 100 µg/L for approved brass but very high for not approved brass (6680 µg/L).
The high concentration of leached Pb in soft alkaline water might be a result of microstructural characteristics of the different brasses. Further analysis and metallographic investigation will offer new findings in understanding mechanisms of the leaching of Pb in different brasses in different waters.

Spectroscopic results

In Figure 5, photo images for A1, A2, A3 and B3 samples after 1 week and after 38 weeks are presented. Raman analysis was executed after 38 weeks of exposure. The dots in Figure 5b 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 1154, 1504 and at 2656 cm^{-1} might show the presence of carbonate species, similar as mineral azurite. Unfortunately, the samples for B1 and B2 were not Raman active, so no Raman spectra could be measured. For brass B3 in soft alkaline water it can be observed that cuprite was formed along with CuZn carbonate, possibly a mineral similar to azurite, $Cu_3(CO_3)_2(OH)_2$. The bands for carbonate are depicted with * in the Raman graphs (Figure 6c).

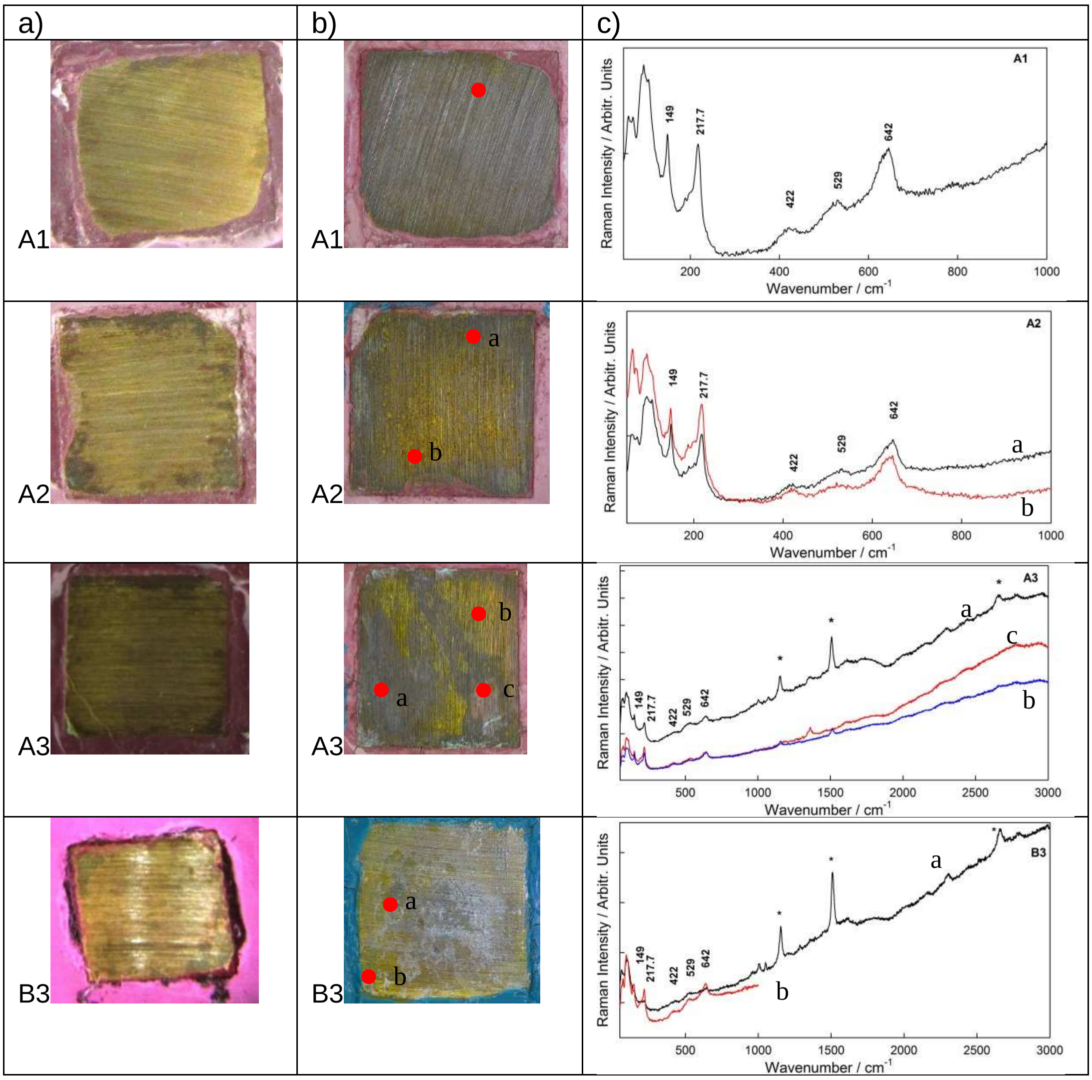

Figure 6: 4 MS approved brass (A1, A2, A3) and not approved brass (B3) after 7 days a) of exposure and after 220 days of exposure b), Raman analysis c)

4. Conclusions

Main conclusions are:

- Immediately after exposure (14 days) of brasses into test waters, the concentrations of analysed Pb are relatively low in comparison to analysed concentrations of Pb in the later months of exposure showing at the delaed time for dezincification to take place. The highest detected concentration of analysed Pb was in soft acidic water for 4MS approved alloy (A), and in soft alkaline water for non-approved brass (B)
- In test soft acidic water, the concentration of Pb is increased after 6 months of exposure for 4MS approved brass (A) when compared to non- approved brass (B)

- After 7 months of exposure the concentration of leached Pb was decrease in all water samples for both investigated brasses

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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