Lead in drinking water - health and durability risk of different copper alloys used in water distribution systems

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Abstract

Several components from a drinking water supply systems are made from different type of copper alloys and are still in use. Like other metallic materials, copper and its alloys are prone to corrosion in drinking water, or, in certain cases, are initiator of corrosion due to formation of galvanic couple with less noble metal. Commonly observed corrosion processes of copper alloys in practice are stress corrosion cracking and dezincification phenomenna. First type of corrosion processes leads to sudden failures of single components and cause leakage of the system. On the other hand, due to dezincification, constituent elements of alloy are released into drinking water where they can cause galvanic corrosion of components from different metals, and/or health problem because of migration of different species, such are Pb, Cu, Ni, Fe, etc. into the water. Dynamic tests provide information on health risk due to migration of dangerous species from metal components into water; however, they do not give material durability information.

The main aim of our study was to investigate possibility of fast and reliable technique for determination of corrosion processes on different copper-based alloys by using electrochemical tests. During evaluation phase results of electrochemical tests were compared with case study observation and with various microscopical investigations.

1. Introduction

Brasses are indispensable materials for products of drinking water installation systems. Valves, connecting fittings, water meters, and other elements, are made by different processing (mechanical, casting, forging) and in order to improve above all mechanical finishing, lead (Pb) is added. Concentration of Pb depends on the quality and vary up to 8.5% by weight.

With the tightening of the maximum permissible amounts of Pb in water by World Health Organization (WHO) and subsequently Drinking Water Directive (DWD) due to health risks, the concentration of Pb in brasses was reduced. In European Union (EU) suitability of materials for contact with drinking water have to be defined by each state, however, in United States of America (USA), that is defined in Public Law (PUBLIC LAW 111–380—JAN. 4, 2011). 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. On the other hand, in the EU most developed regulations on that field (4 MS Acceptance schemes) allowable concentration of Pb regarding to the product intended use is set. In Slovenia the latter schemes does not apply and unfortunately this area is not under any control. Due to several cases with exceeded concentrations of Pb found in water at tap in relatively new buildings in Slovenia (up to 10 years), and also due to pressure of WHO to implement Water Safety Plans into national regulation, recommendation for materials in the contact with drinking water are under construction in Slovenia. It is expected that their issue will reduce the risk of polluted drinking water in the future.

The drinking water chemistry varies significantly among different areas 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 [1, 2]. 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 test cannot be used to explain 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 [1-3]. During some of them corrosion parameters such are voltage and/or galvanic currents were measured and interpreted. Mentioned tests were performed in a freely corroding system where the corrosion processes are not accelerated, therefore they can be very much time consuming. On the other hand, no results of electrochemical testing of brasses in drinking water are found. EIS study [4] on pure copper material in drinking water have shown the suitability of this method to investigate the influence of chemistry of drinking water to the corrosion processes.

The main aim of our research work was to apply basic and widely used electrochemical methods such are potentiodynamic polarization and electrochemical impedance spectroscopy to investigate possibility of faster corrosion characterization of brasses. For this purpose two commercial brasses, one approved by 4MS Common Composition List for metals [5], and one not, were chosen for experimental work. Different spectroscopic and metallographic techniques were used to analyse the intensity of dezinfication.

2. Experimental

2.1. Materials

Two types of brasses, were chosen for present investigation: one which chemical composition conforms to the quality CuZn40Pb2, which was approved in 4MS Common Composition List for metals [5], marked as A, and another brass which was not approved by 4 MS, marked as B. Chemical compositions of both materials and for the quality CuZn40Pb2 are presented in Table 1. Chemical composition was determined by optical emission spectroscopy (SpectroMaxx, Uk, 2011).

Table 1: Chemical composition of investigated brasses, all elements in weight %

	Zn	Pb	Sn	P	Fe	Ni	Si	As	Cu
A	39.89	1.97	0.234	0.0106	0.312	0.0789	0.0096	0.0125	57.4
B	36.12	2.33	0.770	0.0113	0.616	0.395	0.0443	0.0135	59.0
CuZn40Pb2	rest	1.6-2.5	≤ 0.3	-	≤ 0.3	≤ 0.3	-	-	57-59
4MS	rest	1.6-2.2.	≤ 0.3	-	≤ 0.3	≤ 0.1	≤ 0.03	-	57-60

2.2. Electrochemical tests

Test specimens were cut from the water meter body and represented working electrodes, each with an exposed area of approximately 1 cm^2. A saturated calomel electrode (SCE) was used as a reference electrode, and a graphite electrode as a counter electrode. All tests were conducted in local drinking water from Ljubljana water supply system with the properties reported in Table 2.

Table 2: Results of chemical analysis of water

	Unit	Recommended values	Results of used water
pH		6.5-9.5	7.8
Electrical conductivity (20℃)	μS/cm	≤2500	440
Odour	-	-	No odour
Oxidativity	mg/l	<5	<0.5
Total organic carbon – TOC	mg/l	-	0.7
Ammonium	mg/l	<0.5	<0.013
Nitrites	mg/l	<0.5	<0.007
Nitrates	mg/l	<50	13
Sulphates	mg/l	<250	11
Chlorides	mg/l	<250	11
Chlorites	mg/l	-	<0.2
Chlorates	mg/l	-	<0.2
Calcium	mg/l	-	23
Ortho phosphates	mg/l	-	0.74
Phosphorus-total	mg/l	-	1.62
Hydrogencarbonates	mg/l	-	240
Manganese	μg/l	<50	<1.0
Iron	μg/l	<200	<100
Chlorides – free	mg/l	-	<0.02

Electrochemical characterization of the corrosion behaviour of the differently prepared surfaces of the investigated stainless steel was performed by the following electrochemical test methods: measurements of corrosion potential (E_{corr}), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). All the electrochemical measurements were carried out by using a Gamry Reference 600 high performance, stand alone, computer-controlled potentiostat/galvanostat/ZRA, and analyzed by Gamry Echem Analyst software. The Tafel curves, linear polarization, and potentiodynamic polarization, were started when the corrosion potential reached a stable state – a constant value (with a permitted minimum drift) after 3 hours. The potentiodynamic scans were conducted at a potential that was exactly 250 mV below Ecorr up to 1200 mV, at a scan rate of 1 mV/s. All the potentials in this paper are defined relative to the saturated calomel electrode (SCE), i.e. 241.5 mV. The EIS in the frequency range from 65k Hz to 1 mHz was measured after 1h, 24h, 48h, 3 days, 4 days, 7 days, 10 days, 14 days, 17 days, 3 weeks, and up to 26 weeks of exposure inside the corrosion cell (details of measurement periods can be seen in the Table/Figure xx at Results). The perturbation of signal was 10 mV and 7 points per decade.

2.3. Microscopical examinations

2.2.1 Microstructural analysis

Metallographic samples prepared from both materials were subjected to detailed metallographic examination, using a CARL ZEISS AXIO Imager M2z optical microscope. Before the examination, test specimens passed a test for determination of resistance to dezincification, performed according to the standard EN ISO 6509 [6]. Test specimens were exposed to 1% aqueous solution of copper (II) chloride at 75 ^{o}C for 24 hours. After the exposure was finished, specimens were prepared by cutting across significant damage observed on the surface. The surfaces of the metallographic specimens were brushed, polished and etched in Klemm II etching solution in order to reveal microstructure of the brass and to determine the depth of dezincification.

2.2.2 SEM/EDX analysis

Characterization of the condition of the surface at various times after the beginning of exposure was performed by SEM (scanning electron microscopy) combined with EDS (energy dispersive x-ray microanalysis). A low vacuum JEOL 5500 LV, JEOL, JAPAN (Japan) Scanning electron microscope, equipped with an Oxford Inca energy dispersive spectrometer (Oxford Instrument Analytical, UK), was used to analyse the corrosion products in the inner part of pipes using an accelerating voltage of 20 kV.

2.2.3 Raman spectroscopy

Specimens surface were examined also by using the Raman spectroscopy a few times during the whole duration of experiment. Raman spectra were recorded with a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer coupled to an Olympus BXFM optical microscope. The measurements were performed using a 633 nm laser excitation line, a 100× objective lens and a 600 grooves/mm grating, which gave a spectral resolution of 2 cm^{-1}/pixel. A multi-channel air-cooled CCD detector was used, with integration times of between 20 and 30 seconds with the scanning range was 50-1000 cm^{-1}. The presented spectra are not baseline corrected.

3. Results and discussion

Materials for the research work were selected based on the results of extensive case study of increased lead level in 10 years old house building where every apartment has its own drinking water installation from the water meter. Results of research have shown that the main reason for the increased lead level was severe leaching of brass in a few years (the highest amount of water flow through water meter in 3 years was 350 m^3). Chemical composition of material of water meter body revealed certain content of Pb, Sn, Fe and Ni, and it has (due to high enough concentration of Zn) duplex ($\alpha + \beta$) structure. This material is marked with A in the present research. As the opposite (reference) material, brass with composition, which was approved [5] for drinking water application, was selected (marked as brass B).

3.1. Microstructural examination

Metallographic photography's shown on Figures 1 to 4 presents the cross-section of brasses A and B after the test for the determination of dezinfication. This analysis revealed that the front of dezinfication was very even along all surface of brass A. In the case of brass B, dezinfication attacked surface locally. On the figures a and b, unattacked brass is light yellow, and the attacked area is copper coloured (on black/white mode on the Figure a attacked area do not contain darker phase; on Figure b dezinficated layer contain a lot of small black spots where Zn is already leached out). The depth of dezinfication of the brass A was between 100 and 200 µm; the depth of localized dezincficated spots on the surface of brass B was around 100 µm.
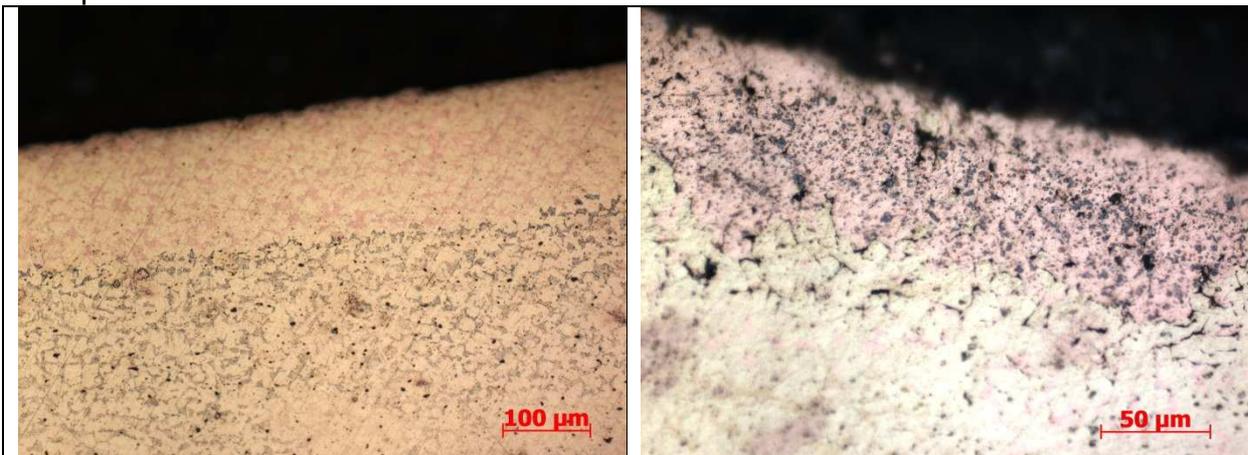

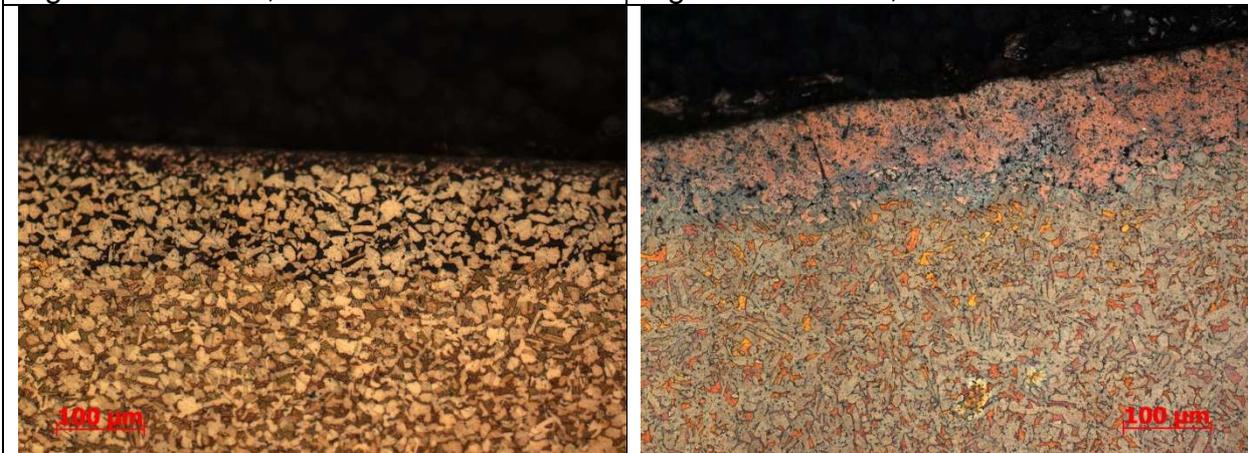Figure 1: Brass A, not etched

Figure 2: Brass B, not etched

Figure 3: Brass A, etched

Figure 4: Brass B, etched

Brass A shows selective attack of β phase of microstructure, whereas α phase remains un-attacked. In this case, as it can be seen from the Figures 1 and 3, Zn probably did not yet leached out – parts of microstructure are not missing (black holes) but just copper coloured. In the case of brass B, localized parts of surface are already leached out (Figures 2 and 4).

3.2. Electrochemical examinations

From the potentiodynamic polarization curves (Figure 5) measured under the same condition, no significant difference between both materials was observed, only the lower corrosion potential for B brass was observed. The same behaviour was observed also during initial 3 h long "stabilization" period, where corrosion potential at the end of this period was for approximately 100 mV lower for B brass.
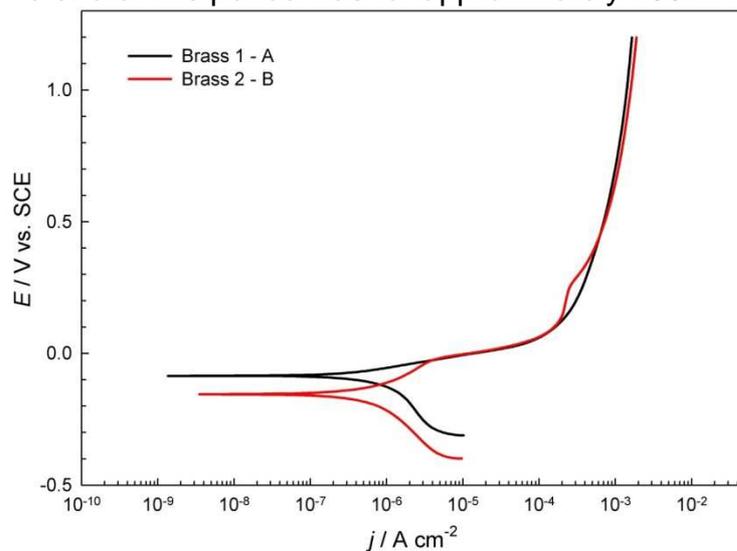

Figure 5: Potentiodynamic polarization curves for brasses A and B, scan rate 1 mV/s

The impedance spectra (Nyquist and Bode plots) for a good (brass A) and less good brass (brass b) are presented in Figure 6 after 1h, 14 days and 26 weeks of exposure in tap water.

The total impedance of a good brass increases with time of exposure. Bode diagrams show the changing mechanisms of detected corrosion layer growth during the observed time (Figure 6 a). Different behaviour was observed for a less good bronze (Figure 6 b), where total impedance decreases with time and has lower values of estimated polarization resistance (discussed below).
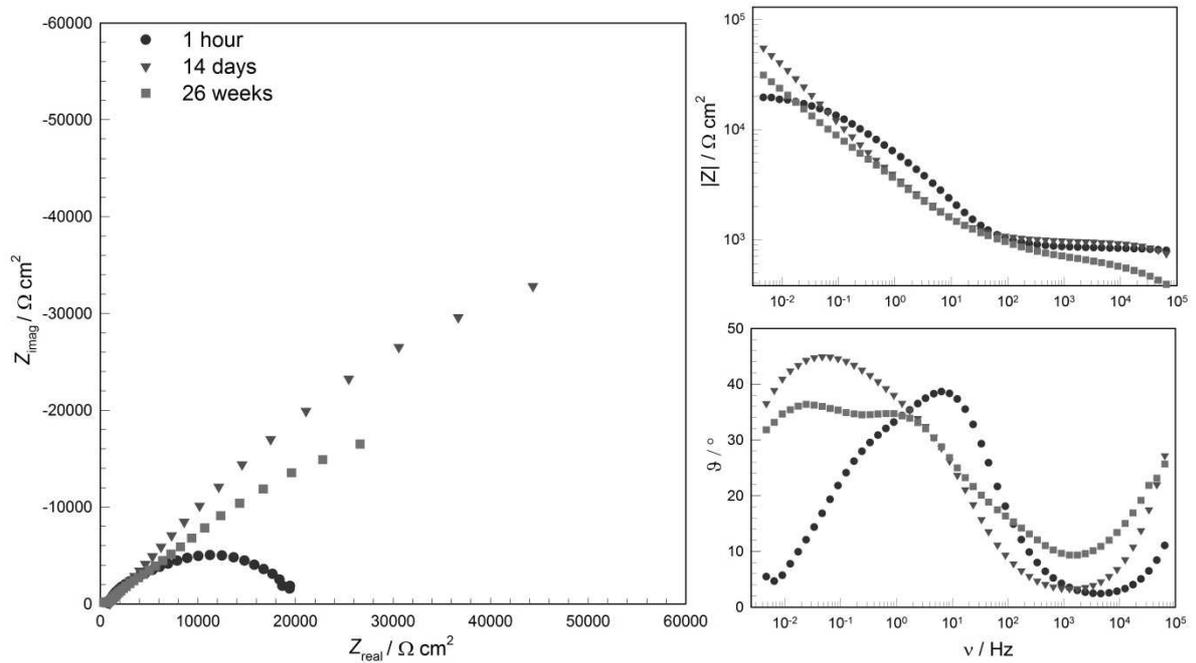
a)
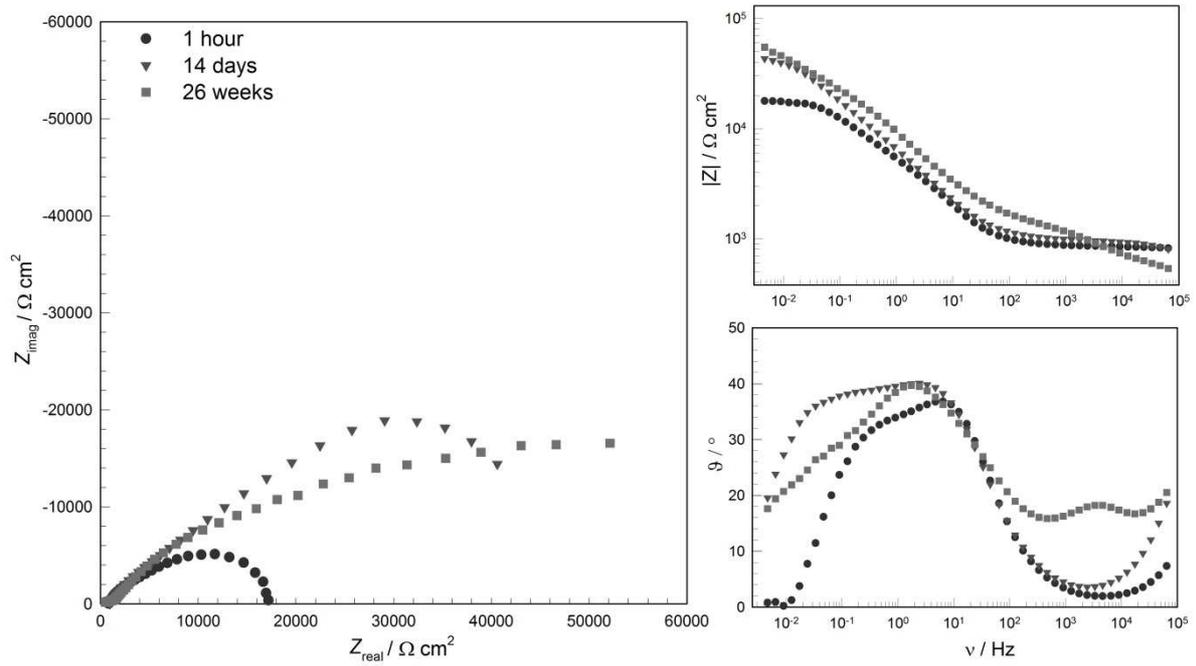
b)

Figure 6: Impedance spectra presented as Nyquist and Bode plots for different brasses after different exposure time in tap water: brass A and brass B

The values of the absolute impedance IZI, measured at the lowest used frequency, i.e. 1 mHz, are compared on the Figure 7, for the both brasses, measured sequentially from the beginning of exposure in the environment, up to 26 week.
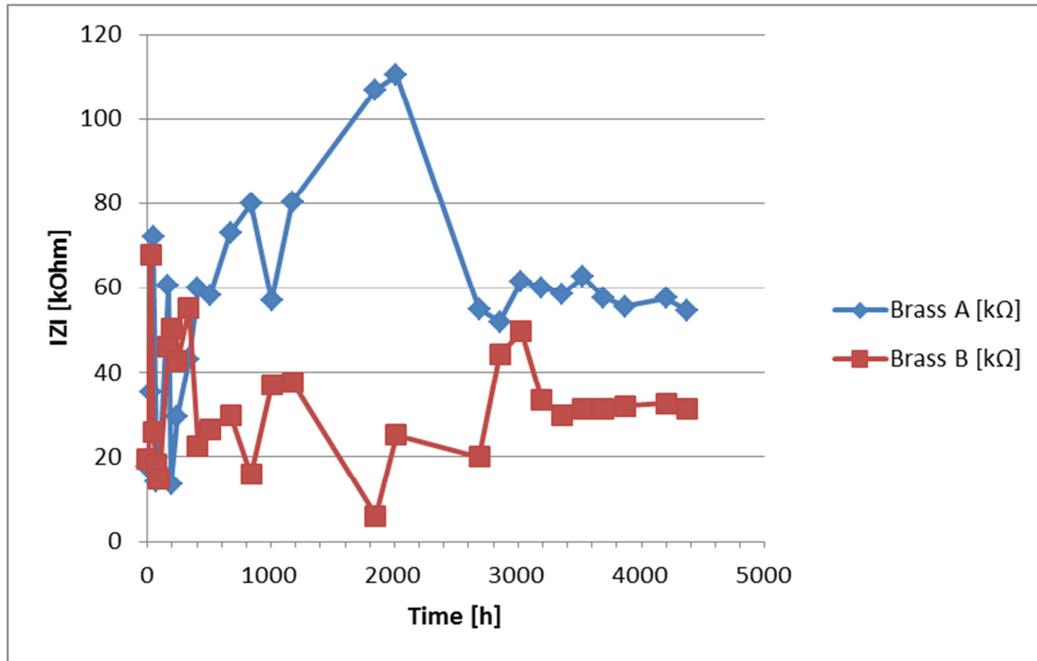
Figure 7: Values of absolute impedance |Z| at the lowest used frequency, i.e. 1 mHz, at different times of exposure

After the initiation period of approximately 100 hours, where somehow random fluctuation of |Z| are observed for both brasses, the |Z| values stabilizes. Better brass (A) reaches approximately 30 kΩ higher values than less good brass (B). It is well-known [7] that, in the case of lowest observed frequency, absolute impedance can be correlated to the polarization resistance, R_p, of the observed alloy in a conductive solution. The higher the polarization resistance of an alloy in a corrosive solution, the more resistant it is to corrosion, and the lowest corrosion rate may be expected.

3.3. Raman and SEM/EDS investigation

After 14 days of exposure morphology of corrosion products that formed on the two different brasses were studied. The surface of a good brass is very even, a thin layer of cuprite was formed, as observed from Raman spectrum (Figure 8 – A). The peaks at 419, 530 and 643 cm^{-1} denote formation of cuprite. The surface of the less good brass was different, it was covered with a thin layer of cuprite and different morphologies of corrosion products, among them also carbonates, as proved by EDS analysis where excessive amounts of carbon and oxygen was detected. Raman analysis showed the presence of cuprite and carbonate, with most pronounced bands for carbonate at 206, 704 and 1085 cm^{-1} (Figure 8 – B).
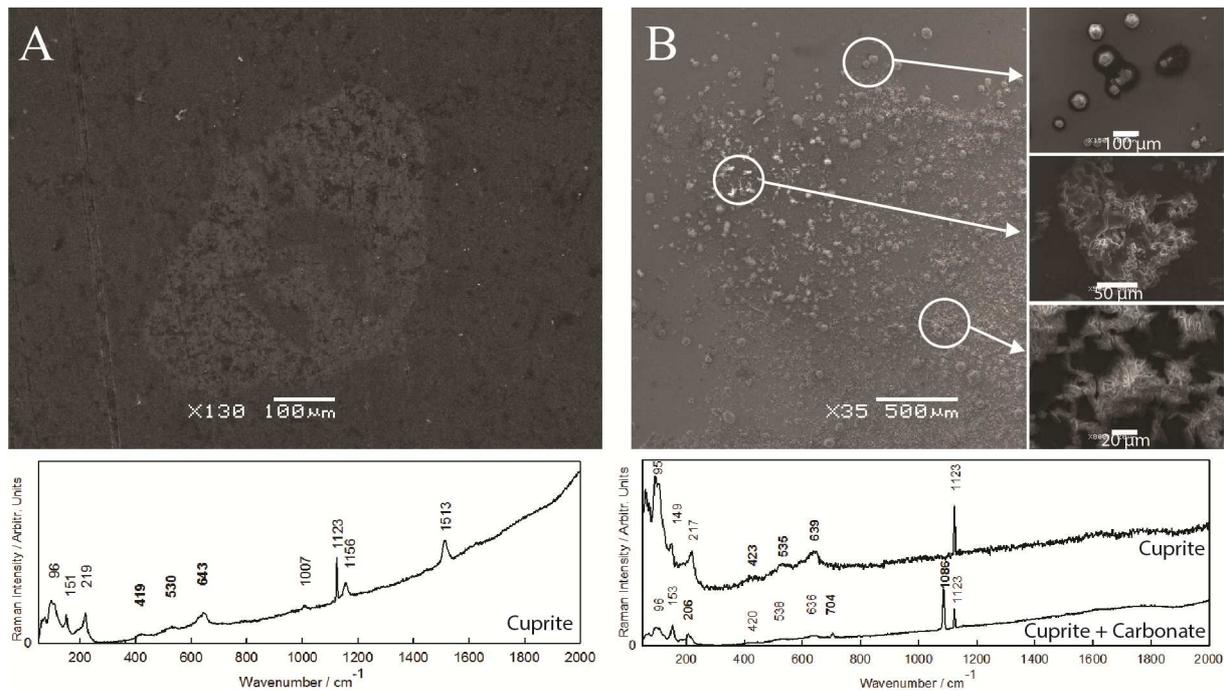
Figure 8: SEM images of a good brass A) and a less good brass B) with corresponding Raman spectra

4. Conclusions

Different electrochemical and spectroscopic techniques were employed in order to study the differences between two qualities of bronzes: one approved for drinking water application, and the other which was withdrawn from the use due to harmful migrations of Pb and other elements into the water.

Electrochemical investigation showed that short term polarization curves do not indicate the different properties of the two brasses while electrochemical impedance spectroscopy revealed the different susceptibility to corrosion during long term investigation. Polarization resistance, which is proportional to corrosion resistance, was better for approved brass that the one which is not approved for use in the contact with drinking water.

SEM and Raman investigation showed the different corrosion products that formed on the surface of two different brasses. The approved brass was covered with a thin layer of cuprite only, while the less good brass was more corroded with areas covered with carbonates in the form of calcium carbonates and copper hydroxycarbonates.

After standardized fast dezinfication test, metallographic investigation showed slightly controversial observation regarding to the "status" of both materials for their use in plumbing systems. Both brasses are susceptible to dezinfication according to the results of fast test. However, the attack on approved brass is homogenuous along the surface, and the leaching of Zn was not completed; attack of not approved brass is local, and leaching of Zn was already observed.

Based on all results gained during this research it can be concluded that fast tests unfortunately do not offer to reliable results, therefore long-term electrochemical studies are recommended for the investigation of corrosion of brasses in drinking water.

5. References

1. Y. Zhang, Dezincification and brass lead leaching in premise plumbing systems: effect of alloy, physical conditions and water chemistry, master thesis, Virginia, USA, 2009
2. N.A.Murray-Ramos, Examining aspects of copper and brass corrosion in drinking water, master thesis, Virginia, USA, 2006
3. Internal corrosion of water distribution systems, AWWA Research Foundation, DVGW-Tehnologiezentrum Wasser, Denver, USA, 1996
4. Xiaohui Zhang, Simo O. Pehkonena, Nikolai Kocherginsky, Grant Andrew Ellis, Copper corrosion in mildly alkaline water with the disinfectant monochloramine, Corrosion Science 44 (2002), 2507-2528
5. 4 MS Common Approach, Acceptance of metal materials used for products in contact with drinking water, part B – 4 MS Common Composition List, 2nd Rev., 11th February, 2013
6. EN ISO 6509-1: 2014 - Corrosion of metals and alloys -- Determination of dezincification resistance of copper alloys with zinc -- Part 1: Test method
7. J. R. Scully, Polarization Resistance Method for Determination of Instantaneous Corrosion Rates, Corrosion 56 (2000) 199-218