

Leaching of brasses in long-term direct contact with water

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Abstract

Copper-zinc alloys (alfa-beta brasses) are currently used to produce house water piping and further parts, that might be in direct contact with drinking water. Lead is added to these alloys in order to improve their machinability. It is well known that lead is unhealthy for humans and, according to EU Council Directive 98/83/EC on the quality of water for human consumption, the admissible Pb content in drinking water has to decrease during the next years because of its high toxicity. The interest in improving public health evocated the need of developing new ecological materials for application on water piping and systems because extensive research indicates that the occurrence of increased Pb content in drinking water can be due to the release (leaching) of Pb from leaded copper alloys. As a consequence of such findings, the dissolution /erosion behaviour of a commercial sanitary brass tap, submitted to a dynamic test simulating the service conditions, has been studied. For that purpose an equipment that enables a long – term direct contact with water has been designed and developed. The chemical composition of the tap and of the final residue produced during the test have been determined by XRF spectrometry and the solutions analysed by atomic absorption spectrometry. Results concerning metal values dissolution have been compared with the limit values established by the legislation. For the experimental conditions, results show that Pb level in leaching solution is lower than the admissible value indicated for the quality of water for human consumption.

Introduction

Many of the products that can be in direct contact with drinking water, namely plumbing fixtures, taps, fittings, valves and connection systems, are made of leaded brasses. The addition of lead to brasses has two purposes: to improve machinability and to ensure pressure tightness [1,2,3,4]. As a consequence of its low solubility on these copper alloys, lead appears in the microstructure as globules and acts as solid lubricant, decreasing involved forces in turning operations, increasing the surface quality and promoting short and discontinues chips, reasons why leaded brasses are currently named free cutting brasses [1,2,3,4]. Besides all the advantages promoted by lead addition to sanitary brasses, its presence must be controlled not only to avoid shrinkage and hot tearing [5] but mainly to fulfil legislation. In fact, as a consequence of its high toxicity and unhealthy effects for humans [1,6,7], new regulations have been developed in order to limit lead content in public drinking water supplies and, in some countries, to limit lead content in brass products used on water distribution, in order to prevent the risk of Pb release, by leaching, of the alloys in long-term direct contact with water [1,6]. According to Council Directive 98/83/EC [8], of November 3th, 1998, on the quality of water for human consumption, Pb content in drinking water must be limited to 10 µg/l after December 25th, 2013, and 25 µg/l from December 25th, 2003 to December 25th, 2013. Pb content restrictions cause technical and economical problems to brass manufactures because it implies changes on the production processes, namely on machining operations. As a solution to this problem, the use of new alloys, inorganic and organic coatings, chemical removal of lead from

products surface, and composites of copper alloys with graphite particles, have been proposed [6,7,9]. However, the most promising alternative seems to be the Pb substitution by Bi and Se [7,9]. Some of these alloys are already patented and commercially available, such as SeBiloy I and SeBiloy II [7,9] with 1%Bi - 0.5%Se and 2%Bi - 1%Se, respectively. These alloys exhibit machinability behaviour and mechanical and casting characteristics similar to traditional leaded brasses [7,9], but are about 50% more expensive [9]. The purpose of this work was to verify that would it be really necessary to substitute leaded brasses in products that are in long term direct contact with water, as consequence of lead dissolution.

Experimental procedure

In order to evaluate the dissolution behaviour of a brass tap, namely the Pb amount that can dissolve in drinking water as a result of leaching, a commercial sanitary brass tap (figure 1) has been submitted to a dynamic test that simulates the service conditions at which it currently operates. Its chemical composition (table 1) and the chemical composition of the produced final residue have been determined by XRF spectrometry.



Fig 1 - Sanitary brass tap tested.

Table 1 - Chemical composition of the brass tap tested

Cu (%)	Pb (%)	Sn (%)	Fe (%)	Al (%)	Ni (%)	Si (%)	Zn (%)
60.32	2.04	0.51	0.59	0.55	0.22	0.10	REM

An equipment was designed and developed to ensure a test with a long term direct contact with water, using the same pressure and flow conditions of the drinking water network (3kgf/cm² and 0.1L/s). This equipment, presented on figure 2, consists of a closed circuit in which water flows continuously and where the unique metallic component is the brass tap (the only that can provide metallic elements to water). The equipment is composed by a 50 L tank in which drinking water of public network was introduced, a pump, flow and pressure regulators, a flow meter, a pressure indicator and a funnel. Test run for 180 days.

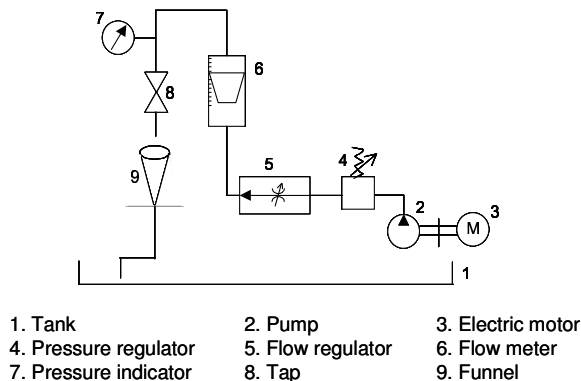


Figure 2 – Scheme of the equipment used for test the leaching of a sanitary brass tap in long term direct contact with water.

The water introduced in the system was characterized according to reference analytical methods [10,11] concerning physical-chemical parameters as well as parameters related to toxic and undesirable substances.

Table 2 presents the evaluated parameters for water quality characterization, the analysis procedures used in its determination, the analysed values (AV) and the recommendable (RMV) and admissible (AVM) values indicated by the Portuguese legislation concerning drinking water quality [10]. All parameters fulfil the recommendable / admissible values indicated by drinking water quality legislation [10].

Table 2 –Water test quality characterization, analytical methods, recommendable and admissible values for each parameter.

Parameter	Method	AV	RMV	AVM
pH	Potentiometry	7.7	6.5-8.5	9.5
Conductivity [$\mu\text{S}/\text{cm}$], 20°C	Electrometric	90.5	400	-
Chlorides [mg/L]	Potentiometry	9.3	25	-
Sulfates [mg/L]	Turbidimetry	3.1	25	250
Hardness [mg/L CaCO ₃]	Potentiometry	19.2	-	500
Nitrate [mg/L]	Molecular absorption spectrophotometry	7.4	25	50
Free CO ₂ [mg/L]	Potenciometric titration acid-basic	0.42	-	-
Fe [$\mu\text{g}/\text{L}$]	Atomic absorption spectrometry	91.7	50	200
Cu [$\mu\text{g}/\text{L}$]	Atomic absorption spectrometry	7.0	3000*	-
Zn [$\mu\text{g}/\text{L}$]	Atomic absorption spectrometry	26.0	5000*	-
Al [mg/L]	Atomic absorption spectrometry	0.06	0.05	0.2
Pb [$\mu\text{g}/\text{L}$]	Atomic absorption spectrometry	2.0	-	50
Total alkalinity [mg/L CaCO ₃]	Potenciometric titration acid-basic	15.13	-	-

* After 12 hours of permanence in network distribution

To measure the dissolution of the tap, water samples have been regularly and systematically taken off for copper, zinc, lead and, in some cases, aluminium and iron dosage. These samples have been analysed by atomic absorption spectrometry on a Perkin-Elmer 1100B spectrometer, with a HGA-700 graphite camera under argon atmosphere.

Water circulation temperature, as well as room temperature, have been measured daily. pH and conductivity have been measured whenever one sample of water was taken off.

Results

Results of water analysis, conductivity and pH evolution during the test are presented on table 3.

Table 3 - Metals concentration in water, pH and conductivity for different test times.

Time [days]	Cu [$\mu\text{g}/\text{L}$]	Zn [$\mu\text{g}/\text{L}$]	Pb [$\mu\text{g}/\text{L}$]	Fe [$\mu\text{g}/\text{L}$]	Al [$\mu\text{g}/\text{l}$]	pH	Conductivity [$\mu\text{s}/\text{cm}$]
0	7.0	26.0	2.0	91.7	60.0	7.7	90.5
20	30.5	137.8	2.5	-	-	7.72	135.8
30	30.7	175.0	2.6	-	-	7.89	158.7
50	33.3	181.2	2.7	-	-	8.18	181.1
90	43.3	118.8	2.5	27.3	31.2	8.10	244.0
180	27.6	42.3	2.5	32.5	12.3	8.06	520.0

Figure 3 illustrates graphically the Pb, Cu and Zn dissolution as function of water contact time with brass tap.

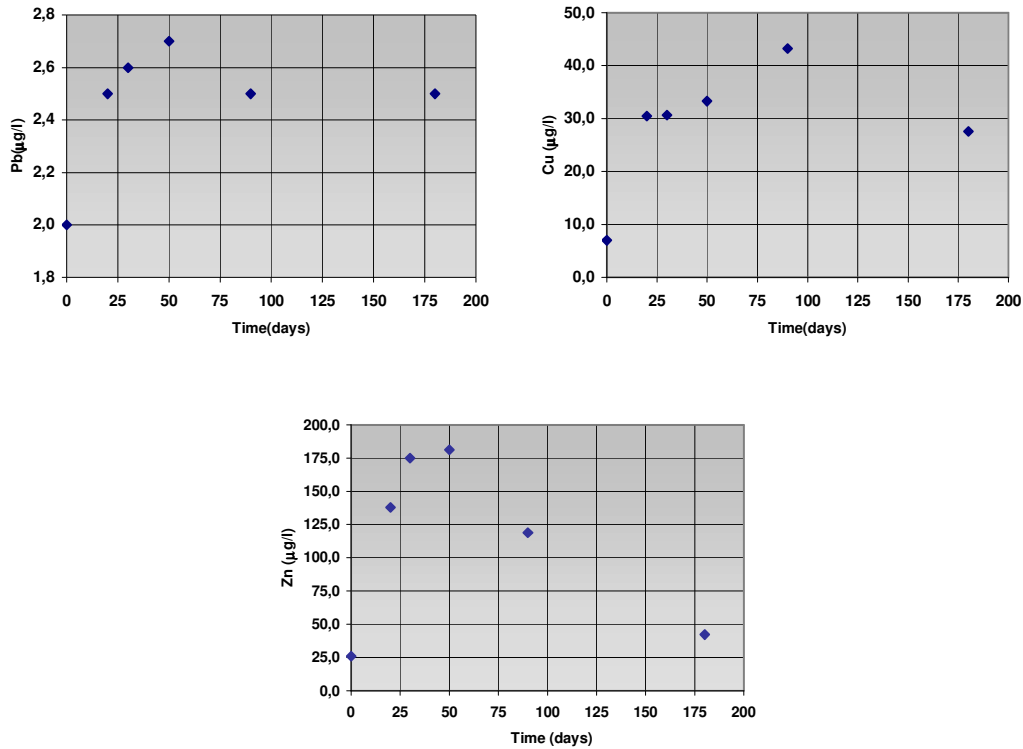


Figure 3 – Lead, copper and zinc dissolution as function of water contact time with brass tap.

Results presented on table 3 and figure 3 show that water circulation inside tap promotes Cu, Zn and Pb dissolution. The greater dissolution rate is obtained for zinc, with a maximum value of 155.2 µg/L after 50 days of non-stop water circulation. Comparing the results of metals dissolution (table 3) with allowed (AVM) and recommended (RVM) values (table 2), it can be seen that any of the three studied elements exceeds those values. This is more relevant for Pb dissolution because of the toxicity associated to this element. In fact, these test shows that after a water circulation of 180 days, at an average temperature of 39°C, the maximum Pb content in water is of 2.7µg/L, obtained after 50 days of test, of which 2.0µg/L corresponds to Pb content in the water originally introduced in the system. Thus, Pb dissolution value is significantly lower than the allowed value stipulated by legislation, and even lower than the value allowed after 2013 (10µg/L).

For the mentioned elements, the concentration in water increases during an initial period and then starts to decrease (figure 3). This fact might be a consequence of a precipitation phenomenon caused by pH changes during the test, with water becoming more alkaline (figure 4). However, relationship between conductivity and time (figure 5) suggests the promotion of ionic species in solution. For this reason, search for other elements that could result from tap dissolution, namely Fe and Al were also performed, but their concentration, measured after 90 and 180 days, was lower than the initial values. This suggests that these ionic species are also not responsible for the conductivity increase, which could be explained by a water reaction with the atmosphere (CO₂ and O₂ absorption for example).

Analysis of the final residue from tank bottom and walls reveal the presence of Cu, Zn, Fe, Al, Ni, Si and Ca. Zinc and copper weight has been estimated in 1.84 mg and 0.22 mg respectively. Pb has not been detected in the residue. The presence of other elements in the circuit could be a result of dust as a consequence of contaminations with atmosphere air.

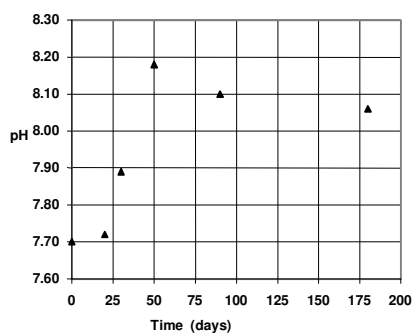


Figure 4 - pH evolution with time

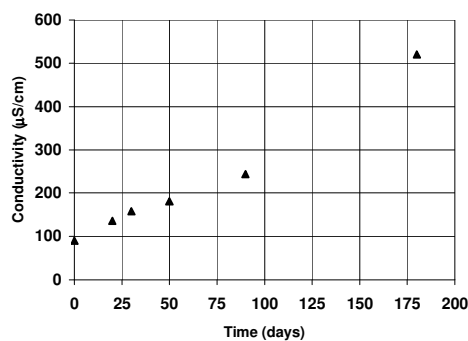


Figure 5 – Conductivity evolution with time

Conclusions

Unlike what would be expectable, the dissolved lead content resulting from leaching of brasses in long term direct contact with drinking water is much lower than the officially authorized by legal directives. That does not imply any toxic hazard to consumers, showing that there is no imperative to replace lead in brass taps. Chemical analysis shows that copper and mostly zinc are dissolved from brass tap and zinc dissolution has been estimated in 1.1×10^{-3} mg/(mm² of brass surface) at a rate of 2.2×10^{-5} mg/mm²/day or 2.6×10^{-6} mg/mm²/(mm³ of water). Water quality parameters could be influence by CO₂ and O₂ absorption.

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