Copper Alloys for Drinking Water Application

Challenges and Opportunities

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Abstract

Currently many components of drinking water installations are made from copper alloys, which are established and proven materials. Changing regulatory requirements led to continuous modifications of their composition. In the last two decades, developments of these materials were focused on the reduction of lead leaching into drinking water while maintaining corrosion resistance and machinability. Hygienically suitable materials are listed on 4MS und German UBA positive lists.

In 2018, considerable turbulences were triggered by the discussion about the reduction of the parametric value of lead from 10 to 5 µg/l in the draft European Drinking Water Directive, the identification of lead as a substance of very high concern (SVHC) and its addition to the REACH Candidate List for authorization by ECHA. Many leaded materials, including newly developed ones, would be removed by a parametric value of 5 µg/l in drinking water.

Both decisions were severe challenges on copper alloys as plumbing materials. Furthermore, manufacturers are put under pressure by tough competition with other and cheaper alternative plumbing materials (for example plastic materials).

1 Requirements for drinking water quality

The requirements for drinking water at the tap are laid down in the European Drinking Water Directive and in the national regulations based thereon [1, 2]. Components and materials of drinking water installations must not unduly alter the quality of the drinking water.

1.1 European Acceptance Scheme (EAS)

In 1998, the European Commission promoted the development of a European Acceptance Scheme (EAS). The intention was to install a standardized European approval system for products in contact with drinking water to replace individual national approval systems and to remove trade barriers within the EU. In 2006, the EAS project was abandoned without having achieved substantial results [3, 4].

1.2 4MS cooperation

In December 2010, France, Germany, the Netherlands, and the United Kingdom declared their intention to establish a co-operation in the field of approval of products in contact with drinking water concerning hygienic requirements [5].

In the last years, an accepted system for the evaluation of materials for their suitability in drinking water has been developed and installed. The legal basis for this was the Drinking Water Directive especially article 10 "Quality assurance of treatment, equipment and materials".

1.3 Testing and assessment procedure for metallic materials

Tests of metallic materials are carried out according to the European Standards EN 15664-1 and EN 15664-2 [6, 7]. It is a long-term test with duration of 26 weeks. The experimental setup simulates a dead end line in the kitchen. The operating conditions are characterized by a daily sequence of successive 22 short flow periods (1 and 2 min) and 22 stagnation periods of different lengths (0.25 h to 8 h) and a maximum temperature of 25 °C. 5 test specimens are installed in a test line. Wetted surface area of the test specimens is 12 % of the total wetted surface area of the test line.

Assessment of copper alloys for fittings, valves, water meters etc. is based on a wetted surface area of 10 % of a drinking water installation. Measured concentrations are normalized to that ratio. Calculated mean values from 8 normalized values of a complete sampling procedure (0.5 h to 16 h stagnation) and normalized concentrations after 4 h stagnation are compared with the so-called reference concentrations (RC). The reference concentrations are derived from the parametric values of the Drinking Water Directive regarding possible geogenic pollutions. Copper and zinc: 90 %, all other components: 50% of the respective parametric value. After 16 weeks of operation, reference concentrations must not be exceeded. The advantage of this experimental setup (model) is that the results can be taken directly. No additional theories and assumptions have to be put into it apart from the consideration of the surfaces in contact with the water.

Assessment is carried out according to the procedure defined in the 4MS document “Acceptance of metallic materials used for products in contact with drinking water – Part A – Procedure for the acceptance” [8].

The composition of metallic materials is not prescribed by law unlike in the United States, where the lead content in components used in drinking water systems is regu--lated in the Safe Drinking Water Act Section 1417 in all states since January 2014 [9]. The weighted average lead content in pipes, fittings, fixtures, and other components must not exceed 0.25 percent by weight. In consequence the lead content of these components is limited to a maximum of 0.25 %.

The 4MS approach assumes that either materials themselves react only slightly with the water or that protective scales are formed during operation, which reduce both corrosion reactions and release of corrosion products into the water to an acceptable level.

The test results are decisive. The candidate materials are tested and evaluated. Accepted materials are listed in the 4MS Common Composition List including their compositions and areas of application; (Group A: pipes, surface area 100 %; group B: fittings etc., surface area 10 % and group C: small parts, surface area 1 %). It has to be noted that only the hygienic suitability is assessed [10]. Further requirements such as corrosion resistance are not subject of that procedure. The previously frequently used dezincification resistant copper alloy CW602N does not meet the requirements due to the high lead release and is therefore not listed.

1.4 Legal status the 4MS Common Composition List

The 4MS Common Composition Lists have no legal status as such. Only national regulations can give a legal status to them. In Germany, accepted metallic materials are listed by the German Federal Environment Agency (UBA) in the document “Evaluation criteria for metallic materials in contact with drinking water (Metall-Bewertungsgrundlage)”, which is legally binding since 10th April 2017 [11]. In consequence, in Germany only products with listed metallic materials may be used for drinking water installations and conformity procedures.

Furthermore, the 4MS material list for metallic materials is recognized in many states by regulators and industries. It is advantageous for manufacturers and users because it promises legal certainty and fewer efforts in the certification process. Within the specified areas of application, listed copper alloys can be used without restrictions in all drinking waters. Product tests as required by plastic materials according to “Bewertungsgrundlage für Kunststoffe und andere organische Materialien im Kontakt mit Trinkwasser (KTW-BWGL), Allgemeiner Teil” of German UBA are not required for products made of listed metallic materials [12]. As proof of hygienic compliance, test certificates 2.2 or inspection certificates 3.1 according to EN 10204 of the materials are sufficient [13]. Also this procedure represents an important contribution to consumer protection.

2 Revision of the Drinking Water Directive 98/83/EC

The revision of the Drinking Water Directive started at the beginning of 2018.

2.1 Proposal of the European Commission

On 1st February 2018, the European Commission submitted a proposal for the revision of the Drinking Water Directive [14, 15]. The reduction of the parametric value of lead from 10 µg/l to 5 µg/l (after a transition period of 10 years) in Annex I part B “Chemical parameters” caused fierce discussion and turbulence. No less problematic were the intended deletion of the current definition of the limit value as so-called “weekly average value” for the elements lead, copper and nickel and the deletion of Article 10 “Quality assurance of treatment, equipment and materials”. Random daytime sampling should be the only accepted sampling procedure.

2.2 Proposal of the European Parliament

On 23rd October 2018, the European Parliament's plenary adopted its amendments to the proposal of the European Commission [16]. The reduction of lead to 5 µg/l and the deletion of the definition of the limit value as “weekly average value” were adopted and confirmed unchanged. However, an equivalent replacement for Article 10 was requested.

2.3 Proposal of the European Council of Environment Ministers

On 5th March 2019, the European Council of Environment Ministers adopted the Commission's draft of 1st February 2018 as modified and improved version with the so-called "General Approach" [17].

In Annex I PART B “Chemical parameters”, the requirements for lead were easily mitigated: “This maximum value (10 µg/l) is accompanied by the minimisation measures according to Article 10 of this Directive. Member State should use their best endeavors to achieve a lower aspirational value of 5 µg/l by 15 years after the entry into force of this Directive”.

The deleted definition of the limit value as “weekly average value” was not resumed. In addition to the random daytime sampling method, fixed stagnation time methods and the determination of the average weekly intake by consumers are allowed [18].

The deleted Article 10 was resumed as extended Article 10 a “Minimum requirements for materials that come into contact with water intended for human consumption”. The Council's recast proposes to harmonise test methods for products in contact with drinking water through standardization under the Construction Products Regulation (CPR). A standardization mandate to be issued under the CPR would define technical specifications and methods to test products in contact with drinking water for compliance with hygiene and safety requirements [19].

The discussion and the process are still ongoing. This proposal will be the basis for the trialogue negotiations between Commission, Parliament and Council in autumn 2019 to achieve an agreement on a common version.

3 Consequences

The changes in the proposal of the European Commission would have undermined the accepted 4MS system.

The reduction of the parametric value of lead to 5 µg/l was contrary to the recommendation of the Regional Office for Europe of the World Health Organization (WHO), which had been tasked with reviewing the list of parameters and parameter values in Directive

98/83/EC. The WHO recommended to retain the current parametric value of lead, but remarked that lead is one of few substances known to cause direct health impacts, and concentrations should be therefore as low as reasonably practical [20].

The reduction of the parametric value of lead to 5 µg/l and the deletion of the weekly mean value would have serious consequences both for the operation of existing drinking water installations and for the building of new installations.

In the last years many of the lead-containing copper alloys for drinking water application had been developed to comply with the lead limit value of 10 µg/l. According to a statement of the German Federal Environmental Agency, a lead limit of 5 µg/l would mean the end of group B application for many lead-containing copper alloys especially for dezincification-resistant arsenic-copper alloys [21]. Changes would also apply to the current test procedure and to the 4MS assessment procedure.

The modification of accepted lead-containing alloys to comply with the 5 µg/l requirement will be difficult. Lead release depends on the lead content of the alloy, but it is not proportional to the lead content in the alloy. Lead release is also affected by other alloy elements (e.g. arsenic in brass materials). Relations are very complex. The art is to reduce lead release without adversely affecting corrosion resistance and machining.

Random daytime sampling might be suitable to assess the quality of the drinking water within a supply zone, but gives no adequate information about the situation of a single drinking water installation [22].

4 Lead free copper alloys

In the last decades, some new lead free copper alloys were developed with alternative chip breakers and are available on the market. However, it is not easy to replace lead on a technical level. Depending on the elements added to the breaker function, different families have emerged. These are copper alloys with silicon either with high or low zinc content, copper alloys with sulfur and copper alloys with bismuth or bismuth/selenium addition. A number of copper alloys with additives silicon and sulfur are on the 4MS lists.

The newly developed materials differ significantly in their properties, their production and machining procedure from conventional copper alloys. Only little experience and publicly available information on metal release and corrosion resistance behavior existed. For this reason, the American Water Research Foundation commissioned a study to compare these materials with the hitherto commonly used material C83600 (CuSn5Zn5Pb5) [23]. For this purpose, a representative from each material family was examined. At that time the sulfur-containing material was not yet on the market and could not be tested. Test lines with the materials were installed in a number of water works with test waters representative to main water qualities in the United States.

As expected, lead release was significantly reduced compared to the lead containing material C83600 (CuSn5Zn5Pb5). Furthermore, all tested lead free materials would have met the 4MS requirements. Concerning corrosion resistance (dezincification, stress corrosion cracking and erosion) materials with standardized composition behaved equally to or better than the comparison material C83600 (CuSn5Zn5Pb5).

5 Reach

On 27th June 2018, the European Chemicals Agency (ECHA) and Member State Competent Authorities have identified lead (EC 231-100-4, CAS 7439-92-1) as a substance of very high concern (SVHC) and added it to the REACH Candidate List for authorization [24].

The objective of the European Chemical Regulation REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) is to ensure a high level of protection of human health and the environment [25]. Candidate List substances are deemed a significant risk to human health and the environment and might eventually be added to the authorisation list. Once substances are on the authorisation list, users and sellers of these substances may need to apply to European Chemicals Agency ECHA for permission to sell and use these substances within the European Economic Area [26].

Lead may damage fertility or the unborn child, cause cancer, and harm breast-fed children. It also damages organs through prolonged or repeated exposure and is very toxic to aquatic life with long lasting effects. Lead has been banned from consumer electrical and electronic equipment supplied to the European Economic Area (EEA), but some industrial uses have so far been exempted.

Lead has been subject to a number of substance regulations, including Restriction of Hazardous Substances (RoHS) [27]. Its inclusion on the REACH Candidate List will create more regulatory obligations for its users.

This means that suppliers in the European Economic Area (EEA) have to check their products according to Article 33 for components with a lead content greater than 0.1 % weight by weight to declare these and to inform the article’s customers about them. This information must be provided unsolicited to professional and commercial customers. Consumers have the right to be informed about SVHCs in articles upon request. Information duty is independent of whether the (sub-)products are drinking water related or not. Further requirements do not exist. Lead is not banned and may continue to be used. The regulatory process has just begun and can last till 2024. No final decision has been reached yet.

6 (New) Challenges

6.1 Corrosion resistance of newly developed copper alloys - Information and review of applied test methods

The older DVGW product standards contained lists of suitable corrosion-resistant copper alloys. These lists were based on many years of experience. However, little experience and information is available for materials that have been developed in recent years. Some information is provided on the homepages of the manufacturers. The German Gesamtverband Messing-Sanitär (GMS) has commissioned some studies about corrosion resistance of brass materials. GMS published their own material list, which is updated when necessary [28, 29]. In addition to the hygienic aspects, this list also takes into account the requirements for corrosion resistance, mechanical strength, impermeability, and economic efficiency.

German corrosion experts complain about the lack of information on the corrosion behaviour of newly developed copper alloys and demand the provision of this information and, if necessary, appropriate investigation programs. Another important task for the experts is the review of the applied test methods with regard to their suitability for the newly developed materials.

6.2 Hot water systems

Unresolved issues are the behavior of copper alloys in hot water systems and the transferability of test results according to EN 15664-1 to these supply facilities.

There are only a few studies on the behavior of copper alloys in hot water systems and sampling results of real hot water systems [30, 31]. Furthermore, suitable sampling methods for these applications are lacking and have to be developed. Also the transferability of test results to other operating conditions has so far been investigated only in isolated cases.

It might not be possible to adopt the results from EN 15664-1 tests one by one for other operating states. This is indicated by observed significant exceedances of the current lead limit value of 10 µg/l in some hot water circulation systems with components made from listed copper alloys. Further research is needed.

Thus under stagnant conditions, the mass transfer of soluble corrosion products essentially occurs by diffusion while in circulation systems convection is also added. This leads to a thorough mixing and to a dilution of the migrated corrosion products in components. Concentrations of soluble corrosion products may increase to the solubility limit of possible solid products [32]. This can lead to a significant accumulation of corrosion products in the overall system. Accumulation of soluble corrosion products also depends on the residence time of the water in the circulation system. In addition, high temperatures generally accelerate the rate of corrosion reactions.

Investigations with copper pipes operated under different flow conditions had shown a significant influence of the flow regime on corrosion and on the formation of protecting scales [33, 34].

6.3 Effects of changing water quality

6.3.1 Dissolution of protecting scales

Changes of the water quality can effect corrosion reactions and the migration of corrosion products into the drinking water as could be seen at Flint water crisis [35, 36]. It was caused by the change of water supply from the Lake Huron and the Detroit River to the Flint River in 2014. Due to insufficient water treatment, lead leached from lead pipes into the drinking water exposing over 100,000 residents to elevated lead levels.

The Flint water crisis is an extreme case that cannot be compared with the situation in the European Union with today's installation materials, drinking water systems, and legal requirements on drinking water qualities. Nevertheless, there are open questions in copper alloys. One problem is the whereabouts of corroded lead from lead-containing copper alloys. Balance calculations with measurement data from corrosion tests according to EN 15664-1 showed that only a small part of the corroded lead passes into the water. The remainder must have been incorporated into the scales. The differences were up to 80 % for arsenic-free and up to 50 % for arsenic-containing alloys. Scales formed on the surfaces consist of low soluble corrosion products. These may be partially dissolved if water with a lower pH value than the former one is distributed and may temporarily cause an increase in lead concentrations.

6.3.2 Dezincification

Causes of dezincification are both the use of materials that are not suitable for the existing drinking water quality and changes in water quality by the supplier, which do not take into account the installed plumbing materials. The main influencing factor concerning water quality is the ratio of alkalinity to neutral salts. This ratio may change if water is softened by water treatment in water works. For this reason, the Turner diagram should be used for risk assessment before planning and conversion [37, 38].

The Turner diagram was developed at the beginning of the sixties for the copper alloy CuZN39Pb3 for the estimation of the risk for dezincification in warm water and its prevention. Later, the Turner diagram was extended for dezincification resistant brasses (DZR brasses) [39]. A continuation regarding newly developed materials is not known.

7 Reprocessing – Recycling

The extensive reprocessing of metal scrap and the use of the resulting alloys for products of the same quality is a unique selling proposition for metal alloys and an argument for their sustainability. Currently, large quantities of metal scrap are being recycled. In Europe, about 45 % of the recovered copper comes from recycling [40, 41].

The recycling of copper and copper alloys is a very effective way to return the valuable material back into the production cycle. In fact, copper production from secondary sources requires only a maximum of 20 % of the energy needed to extract primary copper from ore and concentrates.

In contrast to plastic materials, which can also be produced from renewable raw materials or synthetic raw materials, metals are not available endlessly, and the extraction and processing of the ores is often associated with heavy pollution of the environment.

7.1 Internal recycling

In most companies, chips resulting from machining and faulty products are returned either to the smelters in the factory or to the semi-finished product manufacturer. This procedure is effective as long as chips and scrap of incompatible alloys are not mixed and separate recycling cycles are operated.

Separation is necessary because even small amounts of impermissible impurities can lead to defective castings. For example silicon in copper-tin alloys is limited to a maximum of 0.02 %. Small amounts of silicon-containing materials make these melts unusable. Small amounts of bismuth lead to embrittlement of pure copper.

7.2 External recycling

It is more problematic to meet the required level of purity with reclaimed products after their lifetime cycle. Often, different materials are used for products but they are not separated during disposal. An important step towards separation is the labeling of the materials, which is already practiced by some manufacturers and required in DVGW standard W 421 for water meter housings [42].

7.3 Dilution

Most reclaimed materials from external recycling cycles contain significant amounts of lead, nickel, and other elements. Their contents often exceed the permissible values for accepted materials in the 4MS material list. This means that these alloys must be melted from new materials. Only small amounts of this metal scrap can be added. Calculations show that the dilution process takes decades if carried out in this manner [43].

A reprocessing of the metal scrap is required to speed up this process. In principle, copper alloys can be decomposed with electrochemical processes into their basic elements. However, this requires a lot of energy and is not always necessary. Alternative, appropriate and practicable procedures should be developed. Promising procedures such as the distillation are under development [44].

8 Literature

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