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UNCOMPRESIVE REQUIREMENTS FOR DRINKING WATER HARDNESS: CONSERVATION INDICATORS

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Abstract

Although drinking water hardness and alkalinity have little sanitary significance, economic disadvantages make them important characteristics to be considered in taking decision in obtaining suitable conditions for a proper quality of water intended for human consumption. Soap-consumption, scaling problems, corrosive aspects are the most challenging to the engineers and other persons involved in water science. Disparities in water quality parameters related to hardness have been observed with the Romanian and European legal acts. Romanian Laws 458/2002 and 311/2004 do not contain any provisions for softened water, calcium and magnesium maximum admissible concentrations and for minimum admissible residual hardness of water after the appliance of softening process. The minimum hardness value of 5 German Degree fixed by the Law 458/2002 was not compatible with the values indicated in the repealed European Directive 80/778/EEC and replaced by CD 98/83/EC.
After several years of intensive work, EU parliamentarians on 15 December 2020 adopted the new Drinking Water Directive (DWD), bringing with it a variety of changes. Within two years of its entry into force, Romania, like the other member states will have to make the necessary changes to comply with the new DWD 2020/2184.To this end the Law 458/2002 and the Law 311/2004 are proposed to be revised.

Keywords*: Total hardness; Temporary hardness; Permanent hardness; Soften water*

Introduction

The Council Directive 98/83/EC of 3 November 1998 on water intended for human consumption laid down the essential water quality parameters directly relevant to health, leaving Member States free to add parameters if they see fit [1]. This Directive replaces Council Directive 80/778/EEC that had the validity date 25 December 2003. The Directive 98/83/EC does not include many parameters which had been considered in the first drinking water quality Directive 80/778/EEC, although those parameters are important for establishing water treatment technology [2].

According to Article 7 of the Council Directive 80/778/EEC related to the quality of water intended for human consumption Romania, like the other Member States, had fixed

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values applicable to potable water for the parameters shown in the Annexes of the respective legal act.

A new Drinking Water Directive 2020/2184 had entered into force on 12 January 2021. This new DWD contains the strict minimum quality standards of water intended for human consumption [3].

In fixing the values, Romania has taken in most of the cases as a basis, the values appearing in the "Guide level" column of the Annexes included in the Directive. The Laws no. 458/2002 and no. 311/2004 are the Romanian Legal Acts in which the established quality values of drinking water parameters are indicated [4]. Water hardness is one of the parameters which is not clearly fixed.

Unconformities, lack of clear explanations leads to confusions and sometimes the designers hardly know their way about establishing technical solution for water treatment technology for removing hardness from natural water sources.

There is no health hazard, but economic disadvantages of hard water include increased soap / detergent consumption and higher fuel cost. Water hardness removal (water softening) is an expensive process from the standpoint of capital investment and daily operating costs [5].

Water hardness significance

Hardness is due mainly to the metallic divalent cation's calcium (Ca^{2+}) and magnesium (Mg^{2+}), although Iron (Fe^{2+}) and Strontium (Sr^{2+}) are also responsible. The metals are usually associated with bicarbonates (HCO_3^-), sulphate's (SO_4^{2-}), chlorides (Cl^-) and nitrates (NO_3^-). Hardness is expressed in terms of CaO or $CaCO_3$ [6], as it follows:

- one German Degree - 1°d = 10 mg Ca/L;
- one French Degree = 10 mg $CaCO_3$/L;
- one English Degree = 10 mg $CaCO_3$/0.7L;
- one American Degree = 1 mg $CaCO_3$/L;

Romania expresses water hardness in German Degrees (noted °d).

Hardness is divided into two forms: i) "Temporary hardness", or "Carbonate hardness" – metals associated with HCO_3^- and ii) "Permanent hardness", or "Non-carbonate hardness" – metals associated with $SO4^{2-}$, Cl^-, and NO_3^- [7]. Carbonate hardness plus noncarbonate hardness makes "Total hardness". If high concentrations of Na and K salts are present, the Non-carbonate hardness may be negative since such salts could form alkalinity, without producing hardness (so called "pseudo-alkalinity").

Alkalinity is related to Hardness because it is due to the presence of bicarbonate – HCO_3^-, carbonate – CO_3^{2-}, or hydroxide – OH^-. Alkalinity is useful in waters in that it provides buffering to resist changes in pH. It is normally divided into "Caustic alkalinity" above pH 8.3 (presence of OH^- and CO_3^{2-}) and "Total alkalinity" above pH = 4.5 (presence of HCO_3^-).

Carbonate hardness is called also "temporary hardness" because the bicarbonate and carbonate ions which it is associated with tends to precipitate this portion of the hardness at elevated temperatures such as occur in boilers or during the softening process with lime. Noncarbonate hardness is also called "permanent hardness" because it cannot be removed or precipitated by boiling.

As far as it is known, the alkalinity of a water has a little health influence significance. Hard waters are as satisfactory for human consumption as soft waters. Highly alkaline waters are usually unpalatable, and consumers tend to seek other supplies. For potable supplies, soft

waters must have about 4 - 5°d, whereas very hard groundwaters may have hardness more than 17°d.

The need for softening a potable water depends on reasons of convenience and economy rather than of health since except at very high concentrations, namely more than 50°d hardness is quite harmless and may indeed make a water more palatable.

Alkalinity and Hardness are often expressed in mg $CaCO_3$/L. If alkalinity and hardness are both expressed in terms of $CaCO_3$, the carbonate hardness (temporary hardness) can be deducted as follows:

- if alkalinity is lower than total hardness, carbonate hardness (in mg/L) is equal to alkalinity (in mg/L);
- if total hardness is lower than alkalinity, carbonate hardness (in mg/L) is equal to total hardness (in mg/L).

Disparity between the requirements of the European and Romanian legal acts related to water hardness and alkalinity.

The values of the water quality parameters given in CD 80/778/EEC must be less than or the same as the values shown in the "Maximum admissible concentration (MAC)" column. For magnesium, MAC is 50mg/L. For calcium only G (Guide level) value is mentioned, namely, maximum 100mg/L. Guide levels are taken as a basis in fixing the values for MAC. The "G" values are: Ca^{2+} = 100mg/L and Mg^{2+} = 30mg/L. The maximum total hardness is deducible:

$$\text{Total hardness ("G" value)} = \frac{100\text{mg}Ca^{2+}/\text{l}}{20\text{mg}Ca^{2+}/\text{meq}} \cdot \frac{28\text{mgCaO/meq}}{10\text{mgCaO/°d}} + \frac{30\text{mg}Mg^{2+}/\text{l}}{12.16\text{mg}Mg^{2+}/\text{meq}} \cdot \frac{28\text{mgCaO/meq}}{10\text{mgCaO/°d}} = 21\text{°d} \quad (1)$$

$$\text{Total magnesium hardness (CMA value)} = \frac{50}{12.16} \cdot \frac{28}{10} = 11.52°d \quad (2)$$

$$\text{Total calcium hardness (Guide value)} = \frac{100}{20} \cdot \frac{28}{10} = 14\text{°d} \quad (3)$$

Apparently, the DWD does not consider other quality parametric values than those mentioned in its Annexes. But in the preamble, indent (13) is saying: "Safe water intended for human consumption means not only the absence of harmful micro-organisms and substances, but also the presence of certain amounts of natura minerals and essential elements, taking into consideration that long-term consumption of demineralised water, or water very low in essential elements such as calcium and magnesium can compromise human health".

Romanian legal acts Law 458/2002 completed and modified by Law 311/2004 do not mention any limitative values for Ca^{2+} and Mg^{2+} concentrations. So, no deducible maximum values of hardness are available to be considered for designing the proper water treatment technology. On the contrary, the Romanian Laws provide the minimum value of hardness for drinking water, 5 German degree, that is, 50mg CaO/L, that is, 35.7mg Ca^{2+}/L. This is the first confusion: EU Directive is referred to the softened water intended for human consumption, whereas Romanian Law – to the drinking water, in general [8].

The second noncompliance with EU Directive concerns the minimum value of hardness specified by Law 458, namely 5 German degrees which means 35.7 mg Ca^{2+}/L. This value is lower than 60 mg Ca^{2+}/L mentioned in the Directive. Article 7, intend 4, says that for the parameters appearing in Table F of Annex I in the Directive 80/778/EEC the values to be fixed

by Member States must not be lower than those given in the "Minimum required concentration" column for softened water intended for human consumption.

In Table F the minimum value of alkalinity of 30 mg HCO_3^-/L for softened drinking water is required, whereas in Romanian Laws the alkalinity is not specified at all.

The alkalinity value of 30 mg HCO_3^-/L corresponds to a hardness of 1.37 German degree so, this value can be justified by being under the value of hardness corresponding to solubility product $[Ca^{2+}] \cdot [CO_3]$.

If the raw water has the total hardness over the corresponding maximum values of calcium and magnesium softening process by $CaCO_3$ precipitation (in most of the cases by lime) is applied:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow CaCO_3 + 2\ H_2O \quad (4)$$

The solubility product at the temperature of 25°C is:

$$[Ca^{2+}] \cdot [CO_3^{2-}] = 5 \times 10^{-9} \quad (5)$$

If this solubility product is above 5 x 10^{-3}, the respective water will become oversaturated with $CaCO_3$ and will become chemically unstable.

At normal temperatures $CaCO_3$ saturation corresponds to the concentrations of 20 – 40 mg/L. Let us take, for exemplification, this concentration, 30mg $CaCO_3$/L.

Calcium concentration is:

$$\frac{30\ mg\ CaCO^3/l}{100\ mg\ CaCO^3/mmol} \cdot 40\ \frac{mgCa^{2+}}{mmol} = 12\ mg\ Ca^{2+}/l \quad (6)$$

The corresponding hardness is:

$$\frac{12\ mg\ Ca^{2+}/l}{20\ mg\ Ca^{2+}/meq} \cdot \frac{28\ mg\ CaO/meq}{10\ mg\ CaO/°d} = 1.68°d \quad (7)$$

If after treatment the carbonate hardness value is above 1.68°d that water will be oversaturated with $CaCO_3$ and we shall have scale deposition on the surfaces in contact with this water (chemically unstable).

If the carbonate hardness value is under 1.68°d this water will be chemically stable. In table "F" of the Directive 8 /778/EEC the minimum value of softened water alkalinity is 30 mg HCO_3^-/L which corresponds to a hardness of:

$$\frac{30\ mgHCO_{3-}/l}{61\ mg\ HCO_{3-}/meq} \cdot \frac{28\ mg\ CaO/meq}{10\ mg\ CaO/°d} = 1.37°d \quad (8)$$

Because this value is under $CaCO_3$ saturation value, this water will be chemically stable. So, this is the reason of establishing minimum values of total hardness and alkalinity for softened water intended for human consumption in the European Directive.

But the main reason is the compromising of human health with the longterm consumption of water very low essential elements like Ca and Mg.

Conclusions

Hardness (calcium and magnesium concentrations) and alkalinity are not taken into consideration with the appreciation of drinking water quality in Romanian specific legal acts. If these parameters are not to be included with their minimum and maximum admissible values the decision makers / title holders will not look for any water treatment unit operation requiring expenses. In consequence, the detergent consumption will be increased and the impact on natural water resources will be important requiring more money.

If some indicator values specified in CD 80/778/EEC are not included in CD 98/83/EC it does not mean that Member States must not keep the limitative quality values for water intended for human consumption.

The former European legal act provided 21 German degree as a Guide Level for total hardness (deduced from calcium and magnesium concentration), whereas Romanian legal acts do not have any value of this parameter established.

The MAC of magnesium hardness was indicated to be 11.5°d by the former, EU Directive, whereas Romanian Laws did not include any specific value of magnesium.

The Guide level value for calcium hardness was 14°d according to the Directive, whereas in Romanian Laws there was no specification about that.

There is a wrong minimum hardness value indicated by Law no. 458/2002 for drinking water quality. The natural hardness has no minimum limitation. But minimum value of softened water intended for human consumption was specified by the Directive 80/778/EEC which is now repelled, but, some parametric values could be still considered to reduce any possible negative health impact, as well as to reduce corrosiveness or aggressivity of water and the improve taste.

The minimum value of drinking water hardness indicated by Law 458/2002 is under the minimum level indicated by the Directive 80/778/EEC for soften water.

Minimum concentration of Ca and Mg or total dissolved solids in softened or demineralized water is to be established considering the characteristics of water that enters those processes.

In consequence, the provisions of Romanian legislation acts are proposed to be revised and harmonised according to the European legislation.

In order to have a unitary way to express water hardness measurements milliequivalent per litre is proposed to be used instead of German, French, English, American Degrees.

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