Importance of calcium and magnesium in water - water hardening

D Barloková¹, J Ilavský¹, O Kapusta² and V Šimko³

¹Department of Sanitary & Environmental Engineering, Faculty of Civil Engineering STU, Radlinského 11, 810 05 Bratislava, Slovakia
²The Central Slovak Water Company, Partizánska cesta 5, 974 01 Banská Bystrica, Slovakia
³Water Progress, Račianske mýto 10990/1C, 831 02 Bratislava, Slovakia

Email: danka.barlokova@stuba.sk

Abstract. Basic information about importance of calcium and magnesium in water, about their properties, effect to human health, problems what can cause under the lower (< 1 mmol/L) and higher (> 5 mmol/L) concentrations in water supply distribution systems, the most commonly used methods of water hardening are presented. The article contains the water hardening results carried out during the pilot plant experiments in WTP Hriňová and WTP Turček. For water hardening, treated water at the end of the process line, i.e., after coagulation, sedimentation and filtration, saturated with CO₂ and filtrated through half-burnt dolomite material (PVD) was used. The results show that the filtration rate is 17.1 m/h in the case of WTP Hriňová and 15.2 m/h in the case of WTP Turček to achieve the recommended concentration of Ca and Mg in the treated water after the addition of CO₂ and filtration through PVD. The longer the water contact time with PVD (depending on the CO₂ content), the more water is enriched with magnesium, but the calcium concentration has not so much increased.

1. Introduction
Drinking water is an important source of minerals and trace elements that are necessary for a person's life, because the body can’t create them themselves and must be received by food and water. Drinking water contains essential macro elements (e.g. calcium, magnesium), as well as trace elements (e.g., chromium, cobalt, copper, zinc, selenium, manganese, iron, sodium, potassium, iodine) necessary for the proper function of the individual organs of the human body. Drinking water comes naturally from the geological base through which water passes or is added to water to increase its concentration in water wherever it is needed. In drinking water they are usually in ionic form, perfectly dissolved and therefore easily absorbable and usable (compared to foods).

The drinking water supplied to the water supply network has to comply with the legal regulations, currently it is Government Regulation No. 354/2006. There are 81 parameters (excluding radiological indicators) with precisely defined limit values. These are based on EU Directive No. 98/83/EC, as well as data from the World Health Organization (WHO) [1].

In GR No. 354/2006 are determined only recommended values (table 1) for calcium more than 30 mg/L, for magnesium more than 10 mg/L. Some areas of Slovakia comply with legislation, Ca and Mg values in water are exceeded and water softening (especially Western Slovakia) is required, but in other areas the Ca and Mg concentrations are low and water needs to be hardened. Such areas include, for example, the whole area of the High Tatras, Central Slovakia between Zvolen and Tisov.
Slovak Ore Mountains and the north-eastern part of Eastern Slovakia. Large surface water reservoirs such as Turček, Hriňová, Málinec, Klenovec, Bukovec, and Starina have been built in these regions. This is due to the hydrogeological composition of the substrate, which is made up of rocks of magmatic origin, deficient in calcium and magnesium content. Such water causes health and technological problems.

Table 1. Values of Water hardness and concentrations of Ca and Mg in drinking water by the Government Regulation No. 354/2006.

| Parameter                  | Symbol | Unit    | Drinking water |  |
|----------------------------|--------|---------|----------------|---|
| Calcium + Magnesium        | Ca + Mg| mmol/L  | 1.1 - 5.0      |   |
| Calcium                    | Ca     | mg/L    | > 30           |   |
| Magnesium                  | Mg     | mg/L    | 125            | 10 - 30 |

The term of water hardness is used in relation to calcium and magnesium contents. In general, the water hardness is understood as a sum of material concentrations of Ca, Mg, Sr, and Ba or just the sum of Ca and Mg.

Table 2 contains water “hardness” scales used both in the domestic and foreign literature. Expressing hardness in degrees (e.g. German, French) has already been abandoned; in the Anglo-Saxon literature we can find hardness expressed as the equivalent of CaCO₃ (mg/L) or, more rarely, of Ca (mg/L).

Table 2. Water hardness scales.

| Scale of hardness | Ca + Mg [mmol/L] | Hardness [°dH] | Hardness Ca [mg/L] | Hardness CaCO₃ [mg/L] |
|-------------------|------------------|----------------|--------------------|-----------------------|
| Very soft         | 0 - 0.71         | 0 - 4          | 0 - 20             | 0 - 50                |
| Soft              | 0.71 - 1.42      | 4 - 8          | 20 - 40            | 50 - 100              |
| Medium hardness   | 1.42 - 2.14      | 8 - 12         | 40 - 60            | 100 - 150             |
| Higher hardness   | 2.14 - 3.20      | 12 - 18        | 60 - 80            | 150 - 200             |
| Hard              | 3.20 - 5.40      | 18 - 30        | 80 - 120           | 200 - 300             |
| Very hard         | > 5.40           | > 30           | > 120              | > 300                 |

Both extremes of hardness are undesired from both the health and technological points of view; it is complicated to determine optimal concentrations of Ca and Mg in drinking water and the health requirements need not necessarily comply with the technological ones.

1.1. Calcium and magnesium - effects to human health

Calcium and magnesium are necessary for healthy growth and protection of bones from decalcification, they reduce nerve-muscle excitability, stress, and fatigue, support immunity, and affect blood coagulation [2]. Water from the water main is thus the simplest every-day source of calcium and magnesium for our organisms (we can absorb almost 60% of magnesium contained in water compared to only 30-40% of magnesium contained in the food).

If the calcium supply is insufficient for a longer period of time, a continuous osteoporosis and pain of joints can occur with a consequent more frequent fragilitas ossium. Lack of calcium is demonstrated by headaches, migraine, and brittle nails; you can experience eczemas. If the calcium supply is excessive for a longer period of time (especially in the form of artificial preparations with excessive
content of calcium), formation of uratomas or kidney stones and faster vessel calcification could occur, especially when vitamin D is not co-administered [3].

Magnesium together with calcium Ca$^{2+}$ represents one of the main controllers of muscle contraction including tension of smooth muscles and lack of it could result in cramps, heartbeat, hypertension, nervousness, caprice, sleep disorders, and improper functioning of the nervous system or endocrine glands (digestive system, kidneys, thyroid). Excessive content of magnesium in our organism is very rare, since magnesium can be easily excreted in urine. That is why a sufficient, not excessive supply of both minerals for a healthy human provides not only optimal mineralization of skeleton and prevention from osteoporosis, but also the ability of a human to cope with active physical performance, regular exercises, and increased daily stress, and provides proper functioning of almost every metabolic or enzymatic process running in the organism as well as proper functioning of the nervous system.

The health significance of water hardness (calcium and magnesium contents) should be taken into account not later than when selecting a water source for drinking water supply (the health significance should be preferred to the technical point of view, so the water hardness treatment should only be accepted at a significant excess of the recommended values). From the health point of view, we prefer harder waters. Statistical results show that in the regions with drinking-water containing higher concentrations of calcium and magnesium, the number of inhabitants suffering from cardiovascular diseases and the risk of sudden cardiac death is lower [3, 4].

1.2. Calcium and magnesium in the distribution network
From the technological point of view, neither too soft water being aggressive and causing pipelines corrosion nor hard water reducing service life of pipelines and basins due to formation of incrustations are appropriate. It is reported that, in dependence on the interaction with other factors such as pH and alkalinity, incrustations are caused by water with hardness (as equivalent of CaCO$_3$) higher than 200 mg/L (WHO, 1993). When water contains hydrogen carbonates, water warming will cause elimination of CO$_2$ and transformation of hydrogen carbonate onto (calcium) carbonate to be precipitated on the walls of boiling utensils, pipelines, and boilers in the form of firm water scale. Due to these reasons, calcium and magnesium are removed from water.

1.3. Water hardening (recarbonization)
Hardness is increased at water deacidification and stabilization. Remineralization is performed by filtration through appropriate materials (marble, dolomite, half-burnt dolomite, magnesite, and others) or by direct dosing of calcium compounds (lime). From the hygienic point of view, the troubleless situation will be when wholesome raw materials approved for getting in contact with drinking water are used, when the recommended ratio Mg:Ca is adhered to, and when water is acceptable from the sensory point of view. Since solubility of the raw materials used is low, it should be increased by adding CO$_2$ in water.

Poorly mineralized water (water with the value ANC$_{4.5}$ < 0.8 mmol/L) is not suitable either from the health point of view for its potential of washing up mineral substances from the organism in the volume greater than its own supply [6] or from the technological point of view. When treating such waters, concentrations of Ca$^{2+}$ and Mg$^{2+}$ in the technological procedure should be increased for minimizing its corrosive or aggressive impacts.

The most frequently used procedures of water recarbonization include recarbonization using lime and carbon dioxide, carbonates and carbon dioxide, carbonates and strong acids and PVD and carbon dioxide [5]. Each of the aforementioned possibilities of recarbonization has negative and positive aspects (such as clogging of pipes at the lime dosing, cleanliness of used raw materials, sufficient contact time with the filtration materials, temperature and pH effects, presence of Fe and Mn, organic substances, filters washing). The chosen recarbonization technology is affected by the amount of water to be treated and its mineralization, operating costs, treatment plant equipment, and so on.
2. Experimental part

The pilot-plant experiments were aimed at checking the possibility of enriching water of magnesium in the water treatment plant (WTP) Hriňová. Currently, the contents of calcium and magnesium in water at the outlet from the WTP Hriňová are 27 mg/L of Ca and 4 mg/l of Mg; the average value of Ca + Mg is 0.84 mmol/L.

The experiments were performed on the model equipment for filtration speeds 17 m/h corresponding with the real needs in the case of implementation of this technological level during the planned reconstruction of the WTP Hriňová. For the experiments, we used water treated in accordance with the current water treatment technology (UV radiation, dosing of CO₂, dosing of coagulant PIX113, fast mixing using a hydro mixer, slow mixing, sedimentation, dosing of lime, filters with sand. The aim of the other pilot-plant experiments in WTP Turček was to verify the influence of different filtration rates on increasing the calcium and magnesium content in treated water in WTP Turček. For water hardening, treated water was used at the end of the process line, i.e., after coagulation, lamellar settling tanks and filtration, enriched with CO₂ and filtered through PVD. At present, the calcium and magnesium content in the water at the outflow from the WTP Turček district is about 21 mg/L Ca and 3.5 mg/L Mg, the average Ca + Mg value is 0.55 mmol/L.

The water from the filters was led through a control valve to the CO₂ injection reaction column and then led to the two columns with half-burnt dolomite (PVD). The columns contained filtration material Everzit dol from Germany (particle size 2-4 mm, height 110 cm, column area with PVD 95 cm², medium volume 10,454 dm³). Each column had a separate water outlet and a different flow rate was set in each column. Samples were collected before the reaction tank, after the addition of CO₂ through the reaction tank and the exit of the PVD columns. In table 3 shows the filtration conditions of the experiment and the contact time of the water with the PVD material.

| Experiment 1 | Experiment 2 | Experiment 3 | Experiment 4 | Experiment 5 |
|--------------|--------------|--------------|--------------|--------------|
| Filtration rate [m/h] | 6.1          | 7.2          | 8.0          | 12.9         | 15.2         |
| Water flow [l/min] | 0.96         | 1.14         | 1.267        | 2.042        | 2.407        |
| Contact time [min] | 10.88        | 9.17         | 8.25         | 5.12         | 4.34         |

3. Results and discussion

In figure 1 is presented the progress of water hardening and change of individual indicators during model tests at WTP Hriňová (at a filtration rate of 17.1 m/h).

![Figure 1](image-url)  
**Figure 1.** The course of changes of concentrations of Ca, Mg (left), Ca+Mg, ANC₄.₅ and BNC₈.₃ in particular water treatment processes during model tests in the WTP Hriňová.
Figure 2. The course of change of concentration of Ca and Mg (left), Ca+Mg, ANC_{A,5} and BNC_{8,3} in particular water treatment processes during model tests in the WTP Turček.

Figure 2 shows the results of the experiments for the different filter rates and change of concentration of Ca and Mg during the experiments in WTP Turček.

The results show that the filtration rate 17.1 m/h in the case of WTP Hriňová and 15.2 m/h in the case of Turček to achieve the recommended concentration of Ca and Mg in the treated water after the addition of CO_2 and filtration through PVD. At this rate, the total hardness value of Ca + Mg 1.2 and respectively, 1.52 mmol/L which is compared to GR No. 354/2006 which recommends 1.1 to 5 mmol/L. The longer the water contact time with PVD (depending on the CO_2 content), the more water is enriched with magnesium, but the calcium concentration has not so much increased.

4. Conclusion

The article shows the health significance of the presence of calcium and magnesium in drinking-water and the significance of water recarbonization from the health and technological points of view. Drinking water should only be softened when contents of calcium and magnesium significantly exceed the recommended upper hardness limit (5 mmol/L). In the case of soft waters, recarbonization should mainly be used for increasing the content of magnesium. Both in the distribution network and at the consumer, water should be in the balanced state without corrosive and incrustation properties. As shown by the pilot-plant tests, using half-burnt dolomite is suitable even in large water treatment plants. WTP Hriňová, Turček, Klenovec, and Málinec have the content of magnesium in distributed water 3.5-5.5 mg/l and it is a very low value as compared to the recommended value of 10-30 mg/l according to GR No. 354/2006 Coll. as amended.

Acknowledgements

The experimental measurements were performed with the financial support of the APVV-15-0379 and VEGA 01/0400/15 projects.

References

[1] WHO 2011 Guidelines for Drinking-water Quality (GDWQ) Geneva
[2] WHO 2009 Calcium and magnesium in drinking water – Public health significance Geneva p 194
[3] http://www.meda.sk/sk/Pacient/Terapeuticke-oblasti/Vyznam-horcika-pre-ludsky-organizmus.html
[4] Kožišek F 2003 The health significance of the “hardness” of drinking water National Institute of Public Health in Prague
[5] Olejko Š 2000 Technology of drinking water hardening The 4th Int. Con. Proc. Zlín pp 119-124