Increasing of drinking water quality at real water treatment plant by recarbonization process

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Abstract: According to the World Health Organization, chemical and microbial contaminants in drinking water will continue in the interest of suppliers of drinking water. The review establishment of new knowledge for drinking water including the potential benefits of the mineral content is necessary. The paper is focused on an assessment of the quality of water from surface source for drinking water preparation and quality of drinking water produced at the real plant. The lab-scale verification of water recarbonization with lime and carbon dioxide was chosen based on the results of full scale plant data analysis. Recarbonization tests were carried out with the raw water and the impact of recarbonization on coagulation process at different coagulant doses was studied. The results show that water recarbonization had adverse influence on the water treatment processes.

Keywords: drinking water, recarbonization, surface source, water quality, water treatment

Introduction

The main aim of water treatment and drinking water distribution is the protection of health. Another important aim is to ensure access to the high-quality drinking water. Epidemiological studies also suggest that drinking water can be significant source of calcium. Calcium-rich mineral water provides over one-third of the recommended dietary of this mineral in adults. However receiving calcium is important at all ages, but the need for Ca²⁺ is higher during childhood, fetal growth, pregnancy and lactation (Azoulay et al., 2001). Upwards of 99 % of total calcium is found in bones and teeth, where operate like important structural component. Others calcium's functions belong to metabolic processes, where serve as signal for basic physiological processes, for example vascular contraction. It influences on blood coagulation, because cooperation in transformation fibrinogen on fibrin. Calcium ions influence muscles contractions and nervous transmission. Calcium ions also are very important on activation and elimination of various hormones secretion (e.g. insulin), as well various enzymes (Melicherčík and Melicherčíková, 2010).

Based on the World Health Organization (WHO) findings, next to fluoride, for calcium and magnesium are evident the strongest health benefits associated with their presence in drinking-water (Cotruvo *et al.*, 2009, Nordin 2010).

The importance of Ca and Mg in drinking was already known before World War II. Direct evidence on the health benefits of various hard waters appeared at the end of the 50-ies. Japanese chemist Kobayashi described the relationship between water hardness and the incidence of vascular diseases in 1957. His claims were based on epidemiological analysis. Higher mortality rates from cerebrovascular diseases in the areas of Japanese rivers with more acid (i.e. softer) water were compared to those with more alkaline (i.e. harder) water used for drinking purposes (Kožíšek, 2000).

The contributions of drinking water to nutritional status also depend on water consumption. It is highly variable depending on behavioural factors and environmental conditions. Individuals with the greatest relative consumption of water include infants, residents in hot climates, and individuals engaged in strenuous physical activity. Consumption of moderately hard water containing typical amounts of calcium and magnesium (1.6-2.2 mmol.l-1) provides an important incremental percentage of their daily intake. Moreover, hard water (>2.2 mmol.l⁻¹) can reduce the losses of calcium, magnesium and other essential minerals from food during cooking. If low mineralized (0-1.6 mmol.l⁻¹) water is used for food and beverage production, reduced concentrations of Ca and Mg, and other essential elements would also occur in those products (Monarca et al., 2009, Poláček et al., 2010).

The reason of low mineral content in source water is that water is formed in the poor soluble mineral geological structures. If the content of dissolved inorganic salts in nature water is very low, it is necessary to supplement them in the process of water treatment technology. Water treatment can affect the content of minerals, and thus the total intake of calcium and magnesium. Recarbonization process aims to increase water hardness (calcium and magnesium content increases) and is appropriate for very soft water treatment. Very soft water is corrosive to plumbing resulting in the damage of the systems and potentially increases content of metals such as copper and lead in drinking water. Endurance of water facilities is determined by their resistance to corrosion. In order to limit the corrosion of steel and concrete pipes, it is desirable to acid neutralizing capacity must be reached 1.4 to 2.1 mmol.l⁻¹. In this value is applied inhibitory effect of calcium, bicarbonate and carbonate ions, which means that the inner surface of the pipe begins to create protective carbonate layer (Cotruvo *et al.*, 2005; Yang *et al.*, 2002; Olejko, 1999).

The main aim of this contribution was to analyse raw surface source water quality and prepared drinking water quality. The procedure of lab-scale verification of recarbonization process using lime and carbon dioxide was chosen. The lime reacts with CO_2 to form calcium bicarbonate. Another aim was to investigate the influence of recarbonization process on efficiency of water treatment processes in lab-scale.

Materials and methods

Raw water quality

Raw water and prepared drinking water samples were collected at real water treatment plant at weekly intervals during December 2010 to January 2011 for the purpose of chemical analysis. Chemical analysis were focuses on the follow indicators: $Ca^{2+} + Mg^{2+}$, Ca^{2+} , Mg^{2+} , acid neutralizing capacity (ANC_{4.5}), base neutralizing capacity (BNC_{8.3}), dissolved oxygen, oxygen saturation, free CO₂ and pH, and were performed according to Slovak technical standards. The results was evaluated and compared with legislative limits (Regulation of the Government, 2010). Figures 1–4 show calcium and magnesium concentrations and ANC_{4.5} values in these water samples.

Recarbonization process in lab scale

The suspension for recarbonization was prepared from lime milk (2 % suspension of hydrated lime in water) and water with carbon dioxide. Recarbonization was performed by mixing of prepared concentrated suspension with raw water according to mass balance in order to achieve desired ANC_{4.5} value. Recarbonization process was controlled by chemical analysis performance focussing on pH, ANC_{4.5}, Ca²⁺ + Mg²⁺, Ca²⁺ and calcium-carbonate equilibrium parameter. Aggressive carbon dioxide was analysed by Heyer test. In this test, aggressive CO₂ dissolves CaCO₃ (marble) forming hydrogen carbonate and thus increases the total alkalinity of water. The increase in alkalinity is commensurable to the originally dissolved aggressive CO_2 amount.

Jar testing

The jar test is a common laboratory procedure used to determine the optimum operating conditions for water treatment procedure. A jar test simulates the coagulation and flocculation processes. Coagulation is the process by which colloidal particles and very fine solid suspensions initially present in water are combined into larger agglomerates that can be separated via sedimentation, flocculation, filtration, centrifugation or other separation methods. Coagulation is commonly achieved by adding different types of chemicals (coagulants) to the wastewater to promote destabilization of the colloid dispersion and consequently to agglomerate the resulting individual colloidal particles (Bratby, 2006).

Jar testing apparatus containers were filled with sample water. Subsequently the coagulant was added to each container and stirred at approximately 100 rpm (revolutions per minute) for 2 minutes. Applied coagulant dose was 5.5 ml.l⁻¹, which corresponds to 4.3 mg.l⁻¹ Fe. After completing of this phase the stirring speed was reduced to 25 to 35 rpm and mixing was maintained for 10 minutes. This slower mixing speed helps to promote floc formation by enhancing collisions of particles and thus creating larger flocs. Afterwards the mixing was turned off and the containers were allowed to settle for 40 minutes. Supernatant was sampled at 1 cm below the water surface after sedimentation and samples were filtered with a filter paper. The residual coagulant content was measured in the sample taken from each container.



Fig. 1. Scheme of jar testing device.

Results and discussion

Raw water and drinking water quality

The values of calcium and magnesium concentrations measured in raw water as well as in drinking water samples taken at the real water treatment plant and performed by chelatometric method were very low in comparison with recommended values for calcium and magnesium by Government Decree No 496/2010, the value 1.1 to 5.0 mmol.l⁻¹ (Fig. 2., Fig. 3.).



Fig. 2. Time dependence of the sum of calcium and magnesium concentrations in raw water at real water treatment plant.



Fig. 3. Time dependence of the sum of calcium and magnesium concentrations in drinking water at real water treatment plant.

The low values of the total water hardness were similar as low calcium concentrations in raw and drinking water measured by chelatometric method. The concentrations were very low considering in recommended values for calcium, which is >30 mg,l⁻¹.

Similarly, magnesium concentrations were below the recommended value for magnesium (10–30 mg.l⁻¹). Results show that distributed water from this real water treatment plant can be considered as very soft water.



Fig. 4. Time dependence of $ANC_{4.5}(\blacklozenge)$ in raw water, recommended values: > 0.8 mmol.l⁻¹ (–).



Fig. 5. Time dependence of ANC_{4.5}(♦) in drinking water, recommended values: > 0.8 mmol.l⁻¹ (–).

Acid neutralizing capacity was below the recommended value for $ANC_{4.5}$ related to water chemical stability > 0.8 mmol.l⁻¹ (Decree, 2004). Results are shown in the Fig. 4. and in Fig. 5.

Raw water recarbonization in lab scale

The parameters of calcium-carbonate equilibrium during recarbonization process performance were studied. Also coagulation tests at different coagulant dosage were carried out. Coagulation processes were performed with raw water without recarbonization and raw water after recarbonization process under the same conditions. Iron concentrations were measured in water after sedimentation as well as in water samples after filtration. Calcium concentration, hardness, ANC_{4.5} and pH were evaluated also water samples after filtration.

Recarbonization process was accomplished by the use of lime and CO_2 . The lime reacts with CO_2 to form calcium bicarbonate. The mixture of suspen-

Tab. 1. The parameters of calcium-carbonate equilibrium in the raw water measured by Heyer test.

Experim.	pH 1 st day	pH 5 th day	$\begin{array}{c} \mathrm{ANC}_{4.5} \\ \mathrm{(mmol.l^{-1})} \\ \mathrm{l^{st}~day} \end{array}$	$\mathrm{ANC}_{4.5}$ (mmol.l ⁻¹) $5^{\mathrm{th}}\mathrm{day}$	$\begin{array}{c} \mathrm{Ca}^{2^{+}}\\ \mathrm{(mg.l^{-1})}\\ \mathrm{1^{st}~day} \end{array}$	$\begin{array}{c} \mathrm{Ca}^{2^{+}}\\ \mathrm{(mg.l^{-1})}\\ 5^{\mathrm{th}}\mathrm{day} \end{array}$	Ca + Mg (mmol.l ⁻¹)	Fe after sediment. (mg.l ⁻¹)	Fe after filtration (mg.l ⁻¹)
E1	7.22	7.83	0.80	0.85	21.00	22.00	0.67	4.01	2.20
E2	7.29	8.30	1.00	1.05	23.20	26.00	0.74	4.04	2.32
EO	6.29	8.32	0.18	0.50	6.40	11.00	0.30	1.50	0.20

Luptáková A. et al., Increasing of drinking water quality at real water treatment...

sion for recarbonization and raw water was applied in order to increase $ANC_{4.5}$ from 0.1 mmol.l⁻¹ to 0.8–1.0 mmol.l⁻¹ in two experiments (E1, E2). Also experiments with untreated raw water (without recarbonization) were performed in parallel (E0) (Table 1).

Tab. 2. Aggressive CO_2 in the raw water measured by Heyer test.

Experiment	Aggressive CO ₂ (mg.l ⁻¹)
E1	1.1
E2	0
EO	7.04

Small coagulation flocks were formed in untreated raw water. Very low water temperature (2 °C) seems to be one of the reasons. Coagulation flocks formed in water after recarbonization were difficult observed by naked eye.

Tab. 3. Conditions of coagulation tests.

Raw water					
Temperature	2 °C				
Fe (mg.l ⁻¹)	0.08				
Coagulant	Preflock – 40 % $Fe_2(SO_4)_3$				

The next coagulation tests at different coagulant doses have subsequently been carried out.

The efficiency of the first step of water treatment technology, i.e. coagulation and sedimentation processes, was evaluated based on mass balance of coagulant (Fe^{3+}) dosage and comparing the residual coagulant concentration in water samples after sedimentation and filtration. The results of the coagulation test are summarised in Table 5.

Recarbonization was obtained the increase concentration of total hardness from original 0.3 mmol.l⁻¹ to 0.7 mmol.l⁻¹ performed by lab-scale experiments

Tab. 4. Results of coagulation tests.



Fig. 6. Calcium and magnesium concentrations as a function of $ANC_{4.5}$ after recarbonization process.



Fig. 7. Aggressive CO₂ concentrations as a function of ANC_{4.5} after recarbonization process.

(Fig. 6). Results of Heyer test show that the aggressive CO_2 content was reduced from value 7.0 mg.l⁻¹ to the value near 0 mg.l⁻¹ (Fig. 7). The maximum content of aggressive CO_2 is 5 mg.l⁻¹ with regard to "Requirements for Quality of Water in Piping Systems" (Slovak Technical Standard STN 75 7151).

The results show increase of calcium value (from 6.4 mg.l⁻¹ to 23.2 mg.l⁻¹) and increase of ANC_{4.5} value (from 0.18 to 1.0 mmol.l⁻¹) by recar-

Experimental dosage	1	2	3	4	5	6	7
Coagulant ml.l ⁻¹	2.88	3.20	3.52	3.84	4.16	4.48	4.80
Fe (mg.l ⁻¹)	4.50	5.00	5.50	6.00	6.50	7.00	7.50
After sedimentation							
Fe (mg.l ⁻¹)	3.85	4.32	4.82	5.05	5.69	5.31	5.05
After filtration							
Fe (mg.l ⁻¹)	0.78	1.23	1.03	0.62	2.11	2.76	0.81
$Ca^{2+}Mg^{2+}$ (mmol.l ⁻¹)	0.73	0.80	0.85	0.95	0.70	0.70	0.70

Tab. 5. Res	ults of coa	gulation tests.
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Fe dosage (mg.l ⁻¹)		5.0	5.5	6.0	6.5	7.0	7.5
Residual Fe in water samples after sedimentation (mg.l ⁻¹)		4.32	4.82	5.05	5.69	5.31	5.05
Residual Fe in water samples after sedimentation (%)		86.40	87.64	84.17	87.54	75.86	67.33
Treatment efficiency (%)		13.60	12.36	15.83	12.46	24.14	32.67



Fig. 8. Residual Fe after filtration.

bonization process performed with raw water. On the other hand iron concentrations also increased. The value of iron concentration was 4.0 mg.l⁻¹ after sedimentation (for comparison 1.5 mg.l⁻¹ was in untreated raw water) and after filtration it was 2.20 mg.l⁻¹(0.20 mg.l⁻¹ was in untreated raw water), see in Table 1.

However, recarbonization process was followed by significant deterioration of separation properties of produced suspended solids during the treatment process. High content of residual coagulant after sedimentation (3.8–5.7 mg.l⁻¹) and filtration (0.6–2.8 mg.l⁻¹) is given in the Table 4. Fe dosage 7.5 mg.l⁻¹ caused decrease of residual coagulant content. It seems to be that conditions for coagulation process were better. On the other hand, the content of residual Fe was 0.81 mg.l⁻¹ in water after filtration. However, recommended limit for iron in drinking water is 0.2 mg.l⁻¹ (Decree, 2010). It can be concluded that the treated water by applied processes does not follow recommended limit for iron in drinking water.

Conclusion

From the results of chemical analysis performed with the samples of drinking water follows that produced water can be characterized as a very soft. In particular very high aggressive properties are typical for such water (Büchlerová, 2002). Therefore, it is necessary to include recarbonization in the water treatment technology.

Recarbonization tests were carried out with the raw water and the impact of recarbonization process on sequential coagulation process at different coagulant doses was studied. The results show that recarbonization process was followed by significant deterioration of separation properties of produced suspended solids during the treatment process. Consequently, it means that it will be necessary to increase the coagulant dosage. Higher sedimentation time for efficient separation performance is also required. In addition significant increase in filter loading, i.e., shortening the filtration cycle, and higher washing water consumption can be expected.

The results of the paper suggest that further investigation should be focused on the study and optimization of the recarbonization process. Other possibilities of the process optimization could be operation of recarbonization process after coagulation, or sedimentation instead of pre-coagulation. The study aimed at the utilization of other recarbonization agents, for example half-calcined dolomite, could be also an option.

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