

ANALYSIS OF THE POSSIBILITY OF USEFUL IONS CONTENT INCREASING IN DRINKING WATER BY THE METHOD OF PARTIAL FREEZING

Currently, the level of man-made load on the environment, and, consequently, the number of pollutants in soil, water and air has reached catastrophic proportions and values. The environment components state is determined and characterized by the main physical and chemical indicators, the normal values of which are specified in the normative documents. The changes in the basic physical and chemical indicators of soil and groundwater are so significant that in most cases their spontaneous recovery is no longer possible [1–5]. Land resources of Poltava region are in intensive use of active oil and gas production complex and highly developed agro-industrial complex. Undoubtedly, the significant negative impact on the region's water resources is the result of irrational activities of the agro-industrial complex [1–5]. In most rural settlements of Poltava region there is no water of centralized water supply [1, 4, 5]. Therefore, the rural population is forced to use decentralized water. This is the water of private mine wells and wells, which contain water of the first and second aquifers [3–5]. According to most quality indicators, this water does not meet the standards, so it is dangerous to health [6–8]. Deaths among infants have occurred repeatedly due to the consumption of water with increased nitrate ion content [1, 4, 5, 9–11].

The water quality of the centralized water supply of Poltava city in terms of basic physical and chemical indicators meets standards [6–8, 12], but the content of some macrocomponents, such as Calcium and Magnesium ions, does not correspond to the physiological needs of the human body [13, 14]. An insufficient amount of reliable information and, as a result, a lack of public awareness is often the reason for the unjustified use of purification filtering devices to reduce or completely remove vital macrocomponents and, conversely, the complete lack of water purification where it is needed.

Therefore, the search for opportunities to improve the drinking water quality at household conditions is extremely relevant.

The authors carried out a patent search for the availability of methods for increasing the macrocomponents concentration useful for physiological human needs by a water sample partial freezing treatment. There are patents for technical water purification by freezing [15–17]. It is impossible to improve the drinking water quality at household conditions by using

presented methods. Information from literature sources and Internet resources is insufficient because it does not contain investigated and scientifically proven methods of freezing process using for water purification. Therefore, the idea to investigate the possibility of improving the drinking water quality by partial freezing, to experimentally substantiate it arose.

The work consisted of two parts. The purpose of the first part was to experimentally investigate and evaluate the possibility of improving the drinking water quality at household condition by freezing. The aim of the second part was to develop and test methods for improving the drinking water quality by freezing at household conditions and providing appropriate recommendations.

It was necessary to perform a number of tasks to achieve these goals:

- to find out the influence of HCO_3^- -ions, Ca^{2+} and Mg^{2+} ions on the physiological functions of the body;
- to investigate the content of HCO_3^- -ions, Ca^{2+} - and Mg^{2+} -ions concentration for determination the total, Calcium and Magnesium water hardness;
- to prove experimentally that the solid phase is not distilled water, but contains water-soluble salts (refutation of "myths");
- to study experimentally the dependences of the ions content on different parameters values of the freezing process, such as water volume, temperature, holding time, the ratio of frozen and unfrozen parts of the water sample;
- to perform an analysis of the results;
- to develop and work out a method of improving the quality drinking water by increasing the concentration of useful ions for physiological human needs by freezing.

The object of the research is untreated and treated (unfrozen and frozen (melted) parts of water) drinking water of the centralized water supply of Poltava, Sacco street. Water samples have taken according to [18–20].

The subjects of the study were the Calcium- and Magnesium-ions, hydrogen carbonate concentrations in untreated and treated (melted and unfrozen) water samples.

Natural water, including drinking water, is a solution. Main macrocomponents are Hydrogen carbonate ions, Calcium- and Magnesium-ions, Sodium-, Sulfate- and Chloride ions. The values of the main physical and chemical indicators of drinking water quality, including macrocomponents have mentioned in National standard of Ukraine (DSTU) [6]. We have determined the hydrogen carbonate ions, Calcium-

and Magnesium-ions content, taking into account the main problems of water quality of centralized water supply of Poltava region [5, 6, 12]. These macrocomponents have a significant effect on the human body.

Hydrogen carbonate ions have a positive effect on the formation and secretion of bile by the liver, regulate the metabolism of proteins and carbohydrates, reduce the acidity of gastric juice, improve the absorption of micro- and macronutrients, increase diuresis, anti-inflammatory effect [13, 14].

Hydrogen carbonate therapeutic and therapeutic-table waters ("Borjomi", "Luzhanskya", "Polyana kvasova", etc.) contain increased hydrogen carbonate ions concentration. They are recommended for use in relevant diseases of the gastrointestinal tract and other abdominal organs [21].

The role of Calcium is significant for the human body. Calcium ranks fifth among macronutrients in the human body. Calcium accounts for about two percent of an adult's body weight [12, 22]. It is necessary for the normal formation of bones and teeth, to ensure their strength. Calcium plays an important role in the functioning of the nervous and cardiovascular systems, ensures the normal functioning of muscles and the process of blood clotting; activates a number of enzymes, increases the body's resistance to infections, has anti-inflammatory effects, removes excess fluid from the tissues; participates in many other physiological processes [13, 14, 22, 23]. It is necessary to eat foods that contain Calcium to maintain a sufficient amount of it. Dairy products are the largest source of Calcium. It is also found in dark green vegetables (spinach, broccoli, etc.), beans, soybeans, fish, nuts [23]. In addition, it is necessary that Calcium ions enter the human body with drinking water [22]. Getting the sufficient amount of Calcium-ions with drinking water is important for human body. A number of chemical elements needed, including Magnesium, for their assimilation [13, 14, 23].

Magnesium is one of the most important macronutrients, which is found in significant quantities in all body tissues. [13, 14, 24, 25]. The Magnesium content in the human body is about 0.05 % of body weight, an average of 22-25 mg. The most Magnesium quantity is in bone tissue, less – in the muscles and tissues of internal organs: heart, liver, kidneys, brain [13, 14].

The role of these ions is extremely important in the biochemical processes of the human body. Magnesium participates in most enzymatic reactions and maintaining the ionic balance of body fluids, ensures the normal functioning of the nervous system, controls the body's energy, activates carbohydrate metabolism, takes part in protein synthesis, is a universal regulator of physiological and biochemical processes in the body [24, 25].

In addition, it is indispensable in the metabolism of Calcium, Sodium, Phosphorus and vitamins C and A. It promotes bone strength by maintaining normal Calcium levels [13, 24–26]. Magnesium is involved in the processes of neuromuscular excitability, thus ensuring the normal functioning of the nervous system, regulating the heart muscle, lowers blood pressure; relieves gallbladder spasms, decreases blood cholesterol and bile [13, 14]. It is part of almost 350 enzymes. [12, 24].

Standard [6] allows insufficient content of Calcium and Magnesium ions in drinking water, but for the normal functioning of the human body it is important to use drinking water with sufficient content of these macrocomponents.

We used the method of volumetric (titrimetric) analysis in the experimental part of the work. The total and Calcium hardness was determined by the method of complexometric titration [26, 27]. We have discovered type of hardness, determining content of hydrogen carbonate ions by acid-base titration (neutralization method) [28–30]. To define the type of hardness, it is necessary to determine the content of hydrogen carbonate ions in water for further comparison with the value of total hardness. A methyl orange indicator was added to the flask with a selected aliquot of water and titrated with hydrochloric acid until the color changed from yellow to orange. The hydrogen carbonate ions concentration in the untreated water sample of the centralized water supply of Poltava is equal to 5.2 mmol-eq/dm³. This indicator determines the alkalinity of the water. In previous standards, its limits were regulated from 1.5 mmol-eq/dm³ to 6.5 mmol-eq/dm³. The current standard does not regulate this value [6]. As mentioned above, its determination is necessary to detect the type of hardness. It is obviously, according to this indicator, water quality meets the physiological needs of human body.

The next step in experimental research was to determine the water total hardness. To do this, ammonium buffer mixture, dark blue acid chromium indicator was added to the flask with the selected aliquot and titrated with Trilon B solution until the cherry-red color of the solution turned blue. It turned out that the water samples taken in different periods have different values of total hardness, ranging from 0.31 mmol-eq/dm³ to 0.48 mmol-eq/dm³. This is probably due to soil processes and hydrological features of this aquifer. Such processes occurs permanently and change groundwater ions concentration.

Analyzing the obtained results, the values of hydrogen carbonate ions content and the values of total stiffness were compared. The value of the hydrogen carbonate ions content is greater than Calcium- and Magnesium-ions content, so the carbonate hardness is equal to the total ($H_C = H_T$).

Since the value of the hydrogen carbonate ion content is greater than the content of Calcium and Magnesium ions (total hardness), the conclusion is the fact that the carbonate hardness is equal to the total hardness.

In addition, we can conclude that this indicator of water does not meet the physiological needs of the human body [6]. Moreover, after boiling such water, calcium and magnesium carbonates precipitate, ie the hardness of the water (Calcium-ions and Magnesium-ions content) become zero.

To determine the calcium and magnesium components of the total hardness, the content of Calcium-ions was determined experimentally, and the content of Magnesium ions – by difference. To do this, a 10 % solution of sodium hydroxide, crystals of a dry murexide with sodium chloride mixture were added to the flask with the selected aliquot, titrated with a solution of Trilon B until the color of the solution changed from crimson to purple. The values of calcium hardness also had different values (from 0.072 mmol-eq/dm³ to 0.300 mmol-eq/dm³) depending on the time of water sampling. Based on the results obtained, it can be concluded that when consuming 2 dm³ per day a person can receive only 6 mg of Calcium-ions, which does not meet the physiological needs of the human body [22].

Magnesium hardness was found as the difference between total and calcium hardnesses:

The value of magnesium hardness ($H_{Mg^{2+}}$) varies within

$$H_{Mg^{2+}} = 0.48 - 0.30 = 0.18 \text{ mmol-eq/dm}^3.$$

$$H_{Mg^{2+}} = 0.310 - 0.072 = 0.238 \text{ mmol-eq/dm}^3.$$

The daily physiological requirement of Magnesium is 6 mg/kg human body weight, ie 300-350 mg for an adult [25]. According to the results of the experiment, it is obvious that the required ions are not enough in drinking water.

Since the aim of the work was to develop a method of improving water quality at household conditions, the freezer of a Samsung refrigerator was used for water treatment by freezing. Technical characteristics of the refrigerator: refrigerator type – two-compartment; total refrigerator's volume – 510 dm³; useful freezer's volume – 194 dm³; freezing capacity –10 kg/24 hours. We kept the water in the refrigerator at a temperature of -16°C during different times to obtain different volume ratios (frozen:unfrozen).

Water samples with a volume of 0.5 dm³ were kept in the freezer at different intervals to obtain the ratios of the volumes of water parts (frozen

(melted) and unfrozen) approximately 1:1, 1:3 and 3:1. The ratios of the obtained water volumes are presented in table 4.2.1.

Table 4.2.1

The ratios of the investigated water samples volumes

Sample, №	Volume of water, dm ³					Volume ratio (M:UF)
	V _{initial} , dm ³	Melted (M) (cm ³)	Unfrozen (UF) (cm ³)	Conversion to 10 dm ³		
				Melted (M)	Unfrozen (UF)	
1	2	3	4	5	6	7
1	0.5	0.365	0.135	7.3	2.7	1:0.37
2	0.5	0.245	0.255	4.9	5.1	1:1.04
3	0.5	0.235	0.265	4.7	5.3	1:1.13
4	0.5	0.11	0.39	2.2	7.8	1:3.55

To work out water treatment techniques, each sample of water with a volume of 0.5 dm³ was kept at -16°C for different time intervals: 2.5; 3.5; 4.5; 5.5; 6.5 and 7.5 hours. To minimize the influence of various factors, in the first place possible temperature gradient, each water sample was placed in the same place of freezer chamber. Water samples numbers, time of their freezing and obtained volumes of melted (frozen) and unfrozen parts are presented in table 4.2.2.

Table 4.2.2

Water samples numbers, time of their freezing and obtained volumes of melted (frozen) and unfrozen parts

Sample, №		5	6	7	8	9	10	
Freezing time, hours		2.5	3.5	4.5	5.5	6.5	7.5	
Water volumes, cm ³	Water part type	Melted	100	160	230	290	180	340
		Unfrozen	400	340	270	210	320	160

After water treatment, the concentration hydrogen ion carbonate was determined in each sample. Numbers of water samples, types, water aliquot volumes, chloride acid solution concentration as well as its volumes spent on titration and content values of hydrogen carbonate ions are presented in table 4.2.3. The melted and unfrozen parts of the samples are marked with symbols M and UF, respectively.

Table 4.2.3

Numbers of water samples, types, water aliquot volumes, chloride acid solution concentration as well as its volumes spent on titration and content values of hydrogen carbonate ions

Sample, №	Water type	V _A , cm ³	V _{HCl1} , cm ³	V _{HCl2} , cm ³	V _{HCl3} , cm ³	V _{HCl} , cm ³	C _{HCl} , mmol-eq/dm ³	X _{HCO₃⁻} mol-eq/dm ³
1	M	50	1.25	1.20	1.15	1.20	0.1	2.4
	UF	50	4.00	4.00	4.00	4.00	0.1	8.00
2	M	50	1.80	1.75	1.85	1.80	0.1	3.60
	UF	50	3.40	3.40	3.40	3.40	0.1	6.80
3	M	50	1.90	1.90	1.90	1.90	0.1	3.80
	UF	50	3.25	3.35	3.30	3.30	0.1	6.60
4	M	50	2.30	2.30	2.30	2.30	0.1	4.60
	UF	50	2.90	2.95	2.85	2.90	0.1	5.80
5	M	50	2.20	2.30	2.25	2.25	0.097	4.37
	UF	50	2.75	2.85	2.80	2.80	0.097	5.43
6	M	50	1.90	1.95	1.90	1.92	0.097	3.72
	UF	50	3.15	3.15	3.15	3.15	0.097	6.11
7	M	50	1.60	1.60	1.55	1.58	0.097	3.07
	UF	50	4.25	4.25	4.25	4.25	0.097	8.25
8	M	50	1.35	1.35	1.30	1.33	0.097	2.59
	UF	50	4.40	4.40	4.40	4.40	0.097	8.57
9	M	50	1.10	1.20	1.15	1.15	0.097	2.23
	UF	50	5.15	5.15	5.15	5.15	0.097	10.02
10	M	50	1.00	0.95	0.90	0.95	0.097	1.85
	UF	50	6.35	6.30	6.40	6.35	0.097	12.3
Completely melted		50	6.50	6.50	6.50	6.50	0.1	5.20

According to the experiment results there is gradual increasing of hydrogen carbonate ions concentration as function of increasing of freezing time for unfrozen water parts. In a completely frozen water sample, and then a fully molten the hydrogen carbonate-ions content is identical to which was determined in the untreated water sample.

The total hardness was determined in all water samples. Water sample numbers, type of sample parts, water aliquots volumes, concentration of Trilon B solution as well as its volumes spent on titration and values of total hardness are presented in table 4.2.4.

Table 4.2.4

Water sample numbers, type of sample parts, water aliquots volumes, concentration of Trilon B solution as well as its volumes spent on titration and values of total hardness

Sample, №	Water type	V _A , cm ³	V _{TB1} , cm ³	V _{TB2} , cm ³	V _{TB3} , cm ³	V _{TB} , cm ³	C _{TB} , mol-eq/dm ³	H _T , mmol-eq/dm ³
1	M	50	1.10	1.10	1.10	1.10	0.01	0.22
	UF	50	3.75	3.65	3.70	3.70	0.01	0.74
2	M	50	1.45	1.55	1.50	1.50	0.01	0.30
	UF	50	3.30	3.30	3.30	3.30	0.01	0.66
3	M	50	1.60	1.65	1.55	1.60	0.01	0.32
	UF	50	3.25	3.15	3.20	3.20	0.01	0.64
4	M	50	2.00	2.00	2.00	2.00	0.01	0.40
	UF	50	2.80	2.85	2.75	2.80	0.01	0.56
5	M	50	9.25	9.25	9.25	9.25	0.00098	0.18
	UF	50	17.05	17.00	16.95	17.00	0.00098	0.33
6	M	50	7.55	7.45	7.50	7.50	0.00098	0.16
	UF	50	21.00	20.95	21.05	21.00	0.00098	0.41
7	M	50	6.00	6.00	6.00	6.00	0.00098	0.123
	UF	50	24.50	24.5	24.45	24.50	0.00098	0.48
8	M	50	5.05	4.95	5.00	5.00	0.00098	0.10
	UF	50	30.05	29.95	30.00	30.00	0.00098	0.59
9	M	50	3.50	3.50	3.50	3.50	0.00098	0.069
	UF	50	33.00	33.00	33.00	33.00	0.00098	0.65
10	M	50	2.55	2.45	2.50	2.50	0.00098	0.049
	UF	50	35.55	35.45	35.50	35.50	0.00098	0.70
Completely melted		50	6.00	6.00	6.00	6.00	0,01	0.48

It is obvious that the value of the total hardness of water increases in the unfrozen part of the water with increasing ratio of water parts F: UF in the direction of unfrozen. Also, an increase in the value of the total water hardness in the unfrozen part of the sample is observed when processing time is longer. As in case with hydrogen carbonate-ions the hardness water value in a completely frozen water sample, and then a fully molten is identical to which was determined in the untreated water sample.

The Calcium hardness was determined in all water samples too [27]. Water sample numbers, type of sample parts, water aliquots volumes, concentration of Trilon B solution as well as its volumes spent on titration and values of Calcium hardness are presented in table 4.2.5.

Table 4.2.5

Water sample numbers, type of sample parts, water aliquots volumes, concentration of Trilon B solution as well as its volumes spent on titration and values of Calcium hardness

Sample, №	Water type	V _A , cm ³	V _{TB1} , cm ³	V _{TB2} , cm ³	V _{TB3} , cm ³	V _{TB} , cm ³	C _{TB} , mol-eq/dm ³	H _{Ca²⁺} , mmol-eq/dm ³
1	M	50	0.60	0.60	0.60	0.60	0.01	0.12
	UF	50	2.45	2.40	2.35	2.40	0,01	0.48
2	M	50	0.95	0.85	0.90	0.90	0.01	0.18
	UF	50	2.15	2.05	2.10	2.10	0.01	0.42
3	M	50	1.00	1.00	1.00	1.00	0.01	0.20
	UF	50	2.00	2.00	2.00	2.00	0.01	0.40
4	M	50	1.35	1.25	1.30	1.30	0.01	0.26
	UF	50	1.70	1.75	1.65	1.70	0.01	0.34
5	M	50	0.00	0.00	0.00	0.00	0.00098	0.00
	UF	50	8.00	7.96	8.05	8.00	0.00098	0.078
6	M	50	0.00	0.00	0.00	0.00	0.00098	0.00
	UF	50	10.55	10.45	10.50	10.50	0.00098	0.10
7	M	50	0.00	0.00	0.00	0.00	0.00098	0.00
	UF	50	13.50	13.45	13.55	13.50	0,00098	0.123
8	M	50	0.00	0.00	0.00	0.00	0.00098	0.00
	UF	50	17.50	17.50	17.50	17.50	0.00098	0.172
9	M	50	0.00	0.00	0.00	0.00	0.00098	0.00
	UF	50	20.45	20.50	20.55	20.50	0.00098	0.20
10	M	50	0.00	0.00	0.00	0.00	0.00098	0.00
	UF	50	24.55	24.45	24.50	24.50	0.00098	0.24
Completely melted		50	3.75	3.75	3.75	3.75	0.00098	0.30

Based on our investigations it is possible to conclude that identical regularity, as well as at definition of hydrogen carbonate ions and at definition of the total hardness is observed. That is, in the unfrozen part of water with an increase in its volume and duration of water treatment, the Calcium ions content increasing occurs.

The results of the Magnesium-ions content have calculated for samples № 1–4 presented presented in the table 4.2.6 and for samples № 5–9 – in the table 4.2.7.

Table 4.2.6

The Magnesium-ions content in samples of treated water

Sample, №	1		2		3		4		Completely melted
	M	UF	M	UF	M	UF	M	UF	
H _{Mg²⁺}	0.10	0.26	0.12	0.24	0.12	0.24	0.14	0.20	0.18

Table 4.2.7

The Magnesium-ions content in samples of treated water

Sample, №	5		6		7		8		9		10	
	M	UF										
H _{Mg²⁺}	0.18	0.26	0.16	0.31	0.12	0.36	0.10	0.42	0.07	0.45	0.05	0.46

In this case, similarly, in the unfrozen part of water with an increase in its volume and duration of water treatment, the Magnesium ions content increasing occurs.

Experimentally, we have confirmed that completely freezing of water sample cannot improve its macrocomponent composition, because the ions concentration remains unchanged.

We have proved experimentally the fact that the solid phase is not distilled water, but one that contains water-soluble salts.

It is possible to increase the concentration of hydrogen carbonate ions, Calcium- and Magnesium-ions in unfrozen water by partially freezing the water and removing its frozen part.

The concentration of hydrogen carbonate ions, Calcium- and Magnesium-ions in the unfrozen water part is directly proportional to the processing time.

Concentrations of calcium and magnesium in drinking water can be increased to the physiological needs of the human body by repeated partial freezing. The softer the water, the larger the volume of water you need to take for primary freezing.

Based on our investigations, we have made conclusions and recommendations for improving drinking water quality in the household conditions.

Conclusions

1. The physiological influence of HCO_3^- -ions, Ca^{2+} and Mg^{2+} ions, on the human body has studied.

2. We experimentally determined the HCO_3^- -ions, Ca^{2+} and Mg^{2+} ions content in untreated and treated waters.

3. The authors experimentally investigated the macrocomponent composition of all phases. It is confirmed that after complete freezing the macrocomponent composition of water does not change.

4. The solid phase (melted part of water) is not distilled water, and contains water-soluble salts.

5. We have developed and worked out a method of freezing water to increase the Calcium and Magnesium ions concentrations.

6. It has experimentally proven that the chemical water composition depends on the processing time.

7. It is necessary to disseminate information about the possibility of drinking water quality improving method in household conditions by means of freezing.

8. In further researches it is necessary to investigate efficiency of the method depending on the different macrocomponent composition of natural waters.

Increasing the useful ions concentration:

If need to increase Calcium- and Magnesium-ions and hydrogen carbonate ions, that it is necessary to freeze water to ratio of unfrozen water parts to melted as 1:1 and consume unfrozen part of water. Freezing of the unfrozen part can be repeated, because with each step the concentration of required ions in the unfrozen water part will increase.

The obtained results are important and should be brought to the general public, as they can be used in everyday life to improve the quality of drinking water at the household conditions.

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