Development of technological modes for preparation of mineral water for sports drinks

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Abstract

Introduction. Conducted research study is devoted to development of technological modes of desalination of natural mineral medical-table sodium chloride water for water treatment technologies in the production of beverages for athletes.

Materials and methods. Samples of initial water and water that has been desalinated using the experimental installation with different modes were investigated. Measuring of temperature mode of crystallizer was carried out using temperature sensors and digital thermometer. Quality indicators of the water samples using Photometer Palintest 7500 and standard techniques were determined.

Results and discussion. The influence of different factors of the process of freezing on the quality of desalinated natural mineral medical-table sodium chloride water "Kuyalnik" was investigated. The patterns of distribution of components of initial water between the frozen solid phase, and a concentrated solution in the process of freezing are identified. For the majority of the investigated factors order of traffic was such: $Ca^{2+} > HCO^{-}_3 > (Na^+ > Cl^-) > (Mg^{2+} > SO^{2-}_4 > K^+)$, and with a decrease in water salinity so: $Ca^{2+} > SO^{2-}_4 > (Na^+ > Cl^-) > (HCO^{-}_3 > Mg^{2+} > K^+)$.

Summary of the study results allowed to recommend the following technological parameters of the carrying out the process of desalination of natural mineral sodium chloride water by freeze: operating temperature mode of crystallizer, which is changing in the process from -2 to -4 ° C, the concentration of carbon dioxide in the water at the beginning of the process of freezing - 3,7 g/dm^3, duration of the desalination process (process without cooling) - 60 minutes, one step of freezing, melting of solid phase under ambient conditions without prior separation of the frozen solid phase. With such technological modes of the carrying out the process of freezing it is possible to obtain water with mineral composition, mainly with existing relevant recommendations to the mineral composition of beverages for athletes.

Conclusion. As a result of scientific research an improved method for organizing the process of desalination by freeze was suggested.

Note. * Kurchevich I.V. – maiden name Kovalenko I.V.

Introduction

While an overall reduction in the rate of growth in demand for traditional soft drinks the today demand for beverages for special purposes with certain functional properties is growing. Significant market volume of such beverages makes drinks for athletes. Its share of the total consumption of soft drinks in the world is 2 % and of the consumption of functional drinks – 37 %. A forecast of the global sales for such beverages provides an increase of 39,08 % from 2011 up to 2016 [1,2]. For Ukraine, the beverage market for athletes is new and at the same time is promising. The main reasons for the growth of the interest to sports drinks is associated with the following: firstly, they are necessary for the diet of professional athletes. After all, the purpose of these drinks is effective replenishment of fluids lost in body, providing of the body with "quick energy" in the form of carbohydrates, as well as micro-, macro- and other substances that are necessary for the effective activities, for example, during physical activity, and after it, as well as for build muscle [3]. In addition, such drinks are correctional food for adherents of a healthy lifestyle. Indeed, in Ukraine, followed by Europe, the number of people who are actively involved in fitness, physical therapy, and lead a healthy lifestyle is constantly growing. Ukraine also participates and organizes the holding of various sports competitions at international level, and therefore the presence of domestic products of drinks for athletes will have a positive impact on the image and economics of the country.

For today, there is no consensus regarding the most effective formula of sports drinks. But it is known that such drink have to taste good, and its consumption has to make a contribution for increasing of organism's efficiency. It should be noted that the known formulas of sports drinks are simple. The basis of sports drinks is a carbohydrate-saline solution, and their characteristic is increased compared with conventional soft drinks, the content of salts of sodium, potassium, and other components. For changing of the physiological properties of sports drinks in its chemical composition it is necessary primarily to adjust carbohydrate concentration and the type of content of the electrolyte, solution osmolality and content of flavoring substances. Most beverages for athletes regarding their chemical composition are approximately the same. Osmolality of isotonic beverages usually is 280-340 mosmol/kg, the content of carbohydrates is 6-8% (glucose, fructose, sucrose and maltodextrin), while the concentration of sodium and potassium amounts to 20-30, and 5 mmol /l, respectively [4, 6].

The basis of a sports beverage like any other soft drink is water, which is 85-95 % of the total mass. Technological scheme of water treatment is determined by initial chemical composition of water, which in turn depends on the source of water supply, natural and climatic conditions. For the beverage production the water from artesian wells is mainly used. Such water is hardly polluted with substances of human origin and longtime preserve physicochemical properties unchanged. However, the content of sodium and potassium in such water in not enough for making beverages for athletes based on it. In this regard, salts are added to water artificially [5, 6]. Precisely from this point of view the use of natural mineral waters is promising for production of beverage for athletes. It is also important that the minerals contained in mineral water, are better absorbed by the human body, in comparison with those that are made to drinks in the form of salts. In addition, certain health-giving properties of the mineral water allow reinforcing positive physiological effects on consumer beverage [6, 7].

In Ukraine, the most known natural mineral waters are found. For the beverage industry for athletes can be used sodium chloride mineral water that relate to table and medical-table kind of water with mineralization up to 5 mg/dm^3. Such water is close in composition to quality mineral composition of drinks for athletes. But as the concentration of certain minerals is above recommended one, it is necessary to reduce it. To solve this problem, the authors offer to use a method of desalination by freeze.

Analysis of the advantages and disadvantages of modern methods of water desalination showed that freeze desalination method is characterized by low energy costs for process, lack of scaling and lack of the need to use chemicals for regeneration of work surfaces. Moreover the unique properties of chilled water are known, through which it is better assimilated by the body and bring a healthy and rejuvenating effect on the human. At the same time, the practical use of the freezing desalination method of natural mineral water is hampered by lack of recommendations on effective technological modes of this process. In this regard, the following purpose was stated: to develop the technological modes of desalination by freeze of natural mineral medical-table sodium chloride water for water treatment technologies in the production of beverages for athletes. To achieve this goal following tasks were solved:

– An effective way to organize the process of desalination water by freeze was proposed;

– The influence of different factors of the process of freezing on the quality of desalinated of natural mineral medical-table sodium chloride water was studied;

– Certain patterns of distribution of components of initial water between the frozen solid phase and a concentrated solution in the process of freezing were determined;

– The results of experimental studies were summarized and rational technological modes of desalination process of natural mineral medical-table sodium chloride water were identified.

Materials and methods

To increase the effectiveness of water desalination by freeze it was suggested to conduct it at variable during the process temperature of coolant in the crystallizer. At the same time in the beginning of the process the coolant temperature was maintained at the level required for supercooling of water and formation of germ of ice crystal on the external surface of the crystallizer. Further coolant temperature was varied in accordance with the liquidus line of natural mineral water, with little difference in temperature (0,6 ... 1,5 ° C) between the temperature of coolant and cryoscopic water temperature. In addition, it was suggested to saturate the mineral water before freeze with carbon dioxide to produce gas hydrates. It is known that water molecules through hydrogen bonds form a crystal lattice, and the gas molecules are placed in the inner cavities of the lattice, wherein held by Van der Waals forces [8]. This prevents the inclusion of other molecules and ions dissolved in the water substances in the ice structure [9]. Therefore, it was assumed that the saturation of mineral water with carbon dioxide before the freeze would enhance the increase of degree of desalination.

For experimental studies the natural mineral sodium chloride water "Kuyalnik" with total mineralization 3... 4 g/dm^3 was used. When performing the experimental study the influence of temperature mode of the crystallizer, carbon dioxide concentration in the initial water ($C_{carb.d.}$), water pH, initial common mineralization and temperature of water, duration of separation of solid frozen phase on quality of desalinated water were investigated. In the initial and desalinated water the content of ions of sodium, potassium, calcium, magnesium, chlorides, sulphates and bicarbonates, dissolved carbon dioxide, the pH and other water quality were determined. For this purpose, standard techniques were used.

The total impact of these factors of the process of freezing on the distribution of ions between the frozen out solid phase and concentrated solution was evaluated by the magnitude of the coefficient of involving ions in the solid phase (K_i, %):

$$K_i = (C_{s.p.} / C_{i.w.}) \cdot 100\,, \qquad (1)$$

where $C_{s.p.}$ – ion concentration in the melt of the solid phase, mg/dm^3;

$C_{i.w.}$ – ion concentration in the initial water, mg/dm^3.

Investigation of the process of water desalination was carried out on experimental installation made in the Odessa National Academy of Food Technologies. Installation is equipped with modern control and measurement instrumentation. In the installation a freezing out of water was carried on the outer smooth surface of a seven vertical tubular crystallizers with an outer diameter of 12 mm and height 337 mm [10]. To study the influence of temperature modes on quality of desalinated water the following temperature modes of crystallizer (TX) were used: I - variable in the process, t_x = -2 ... -4 ° C, II - variable in the process, t_x = -3 ... - 5 ° C; III - a constant in the process, t_x = -5 ° C. For these temperature modes provided freezing of solid phase up to a thickness of 9 mm in all experiments the duration of the freezing process (excluding the duration of the water cooling process to onset temperature of its crystallization) was 60 min for the mode I, 45 min for mode II and 36 minutes for mode III. In modes I and II the creation of conditions for the water crystallization at the cooling surface was achieved by reducing the temperature of intermediate coolant in the beginning of the process of minus 5 °C. Since the first crystals on the surface of crystallizer the temperature of the coolant increased, and then changed automatically in the above ranges. In all experiments, the initial mass of desalinated of water was 2,32 kg.

Measuring of temperature mode of crystallizer was carried out using temperature sensors TCM – 002 and digital thermometer DS18B20, measurement of volume of water was carried out using measuring cylinders (PJSC "Steklopribor"), thickness and height of frozen out solid phase - with calipers L-150.

To investigate the influence of carbon dioxide concentration on the quality of desalinated water the packaged mineral water was degassed. Degassing of water was conducted by heating up to t = 90 ° C (for obtaining water samples $C_{\text{carb.d.}}$ = 0,27 g/dm^3), and by heating it to the boiling point and holding at that temperature for 9...10 min (for obtaining the water samples $C_{\text{y.r.}}$ g/dm^3 = 0).

In experimental studies were also used the water samples, which were not subjected to degassing. In water samples before degassation the carbon dioxide concentration was equal to 3,7 g/dm^3.

For processing and analysis of obtained experimental data modern mathematical packages, in particular the "Excel", were used.

Results and discussion

Analysis of the experimental data obtained during the investigation of the influence of temperature modes on the quality of desalinated water, showed that the best degree of desalination is achieved at a temperature mode of crystallizer I, regarding both ions and other physico-chemical parameters of water quality. For example, at a temperature range I the sodium cations are involved in the solid phase by 10...12 % smaller than when temperature conditions II and III (Fig. 1). At the variable temperature mode t_x = -2...-4 °C (mode I) the best degree of desalination also of other ions is achieved. Therefore, in the course of further studies of the influence of other factors of the process of desalination on its quality temperature regime I was used. It should be noted that at this stage of study water samples, which were completely degassed were used.

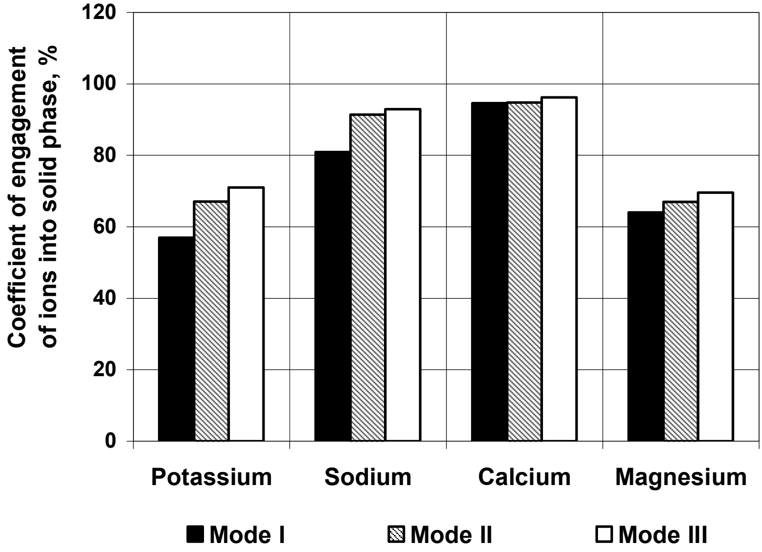

Fig.1. Influence of temperature mode of the process of freezing on the cationic composition of desalinated water

In course of experimental study of the influence of the carbon dioxide content in the mineral water before desalination on the quality indicators after freezing out the water samples with an initial value of dryness equal to 3280 mg/dm^3 and carbon dioxide contents equal to 0; 0,27 and 3,7 g/dm^3 were used. At the specified concentrations of carbon dioxide water pH was 8,32; 5,9 and 4,88 respectively.

Analysis of the obtained experimental data has shown that water, pre-saturated with carbon dioxide at a concentration of 3,7 g/dm^3 is better desalted. Under these conditions of carrying process in the solid phase less than 20 % of potassium ions, less than 12 % - sodium ions, less than 15 % - calcium ions, less than 6 % - magnesium ions are involved when compared with a process when desalted water is pre-saturated with carbon dioxide not (Fig. 2). Increasing efficiency of the process of water desalination in this case is explained by obtaining hydrates of carbon dioxide and ousting more impurities from the water from crystallization front.

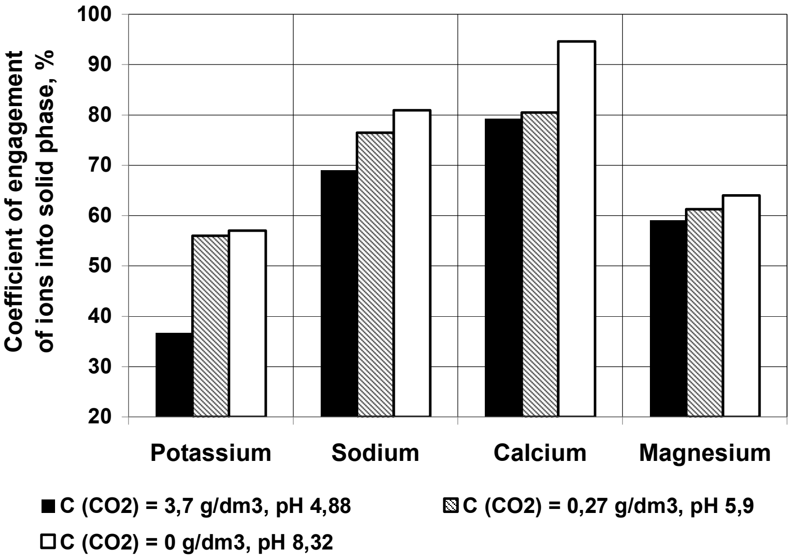

Fig. 2. Influence of the initial amount of carbon dioxide on the cationic composition of desalinated water

Adding of carbon dioxide to the initial water has reduced its pH, and there is very few published data on the patterns of influence of this factor on the quality of desalinated water by freeze. Therefore further studies have been conducted about the influences of content in water of ascorbic acid as a substance adding of which lowers the pH. It was added to the initial degassed water to a pH value that is equal to 4,88 (similar pH at $C_{carb.d.}$ = 3,7 mg/dm^3). Results of investigation were compared with the results obtained in the desalination of water samples with the same pH, but obtained by saturating water with carbon dioxide. It is found that the addition of ascorbic acid in water before freeze affects specifically on variation of its quality in the desalination process: at a solid phase at 39,3% involvement of magnesium ions is increased and involvement of potassium ions and calcium sulfate by 11,1; 40 and 15,1 % respectively is decreased. At the same time the effectiveness of freezing process (for total mineralization) is deteriorated by 15 %. Thus, it was found that the decreasing of pH of the water before desalination, in particular by the addition of ascorbic acid in it, is impractical.

Natural mineral water at the outlet from borehole has a temperature 8...12 ° C, but depending on the ambient temperature can be heated up to 20 ° C or higher. Therefore the influence of water temperature before freezing (in the range 8...20 °C) on its quality after desalination was investigated. In studies the samples of water with $C_{carb.d.}$ = 3,7 g/dm^3 were used. Analysis of the study's results has shown that the lowering of the initial temperature of the initial water improves the quality of desalinated water. With that, this improvement at all indicators of water quality did not exceed 5%, so further cooling of the water before freezing is not necessary.

Also the influence of initial common salinity of water on changing the quality of the desalination process is studied. For studies water with a salinity of 3,22 g/dm^3 and 2,37 g/dm^3 was used. As the samples with a lower concentration of salts desalinated water after the first stage of freezing was used.

It has been stated that reducing of the mineralization of the initial water affect on the distribution character of ions between liquid and solid phases during desalination. At the same time the involvement of the solid phase of chloride for 4,4%, potassium – 14,4% Sodium - 4,9%, sulfates - for 22,1% increases and reduced the involvement of calcium ions at 6,9%, magnesium - 22,3%, hydrocarbons - 16,1%.

It should also be noted that although a two-stage freezing allows to reach a greater degree of initial desalination of mineral water, but the efficiency of the process of separation on the desalinated water and the concentrate of impurities in the second stage of desalination is lower than in the first one. In addition, deeper desalination of natural mineral water "Kuyalnik" in case it is used for the production of beverages for athletes is impractical. It is explained by the fact that after one-step freezing of initial water, which is pre-saturated with carbon dioxide at a concentration of 3,7 g/dm^3, and when a temperature mode I the quality of desalinated water needed for sports drinks production is reached.

Based on calculations according to the experimental data of coefficients K_w the nature of the influence of factors of the freezing process to the order of motion of ions in the solid phase is defined:

- change of temperature mode of crystallizer, carbon dioxide concentration in original water, pH and initial temperature of water does not influence the order of motion of ions in the solid phase. In all experimental studies performed it was as follows: Ca^{2+} > HCO_3^- > (Na^+ >Cl^-) > (Mg^{2+} > SO_4^{2-} > K^+). It was found that the ions listed in brackets may be interchanged with one another due to insignificant difference in their percentage;
- change of initial salinity of water affects the order of ions motion in the solid phase. For example, when reducing the initial mineralization of natural sodium-chloride water from 3,22 to 2.37 g/dm^3 the motion order of ions in the solid phase chznge from said above to the next: Ca^{2+} > SO_4^{2-} > (Na^+ > Cl^-) > (HCO_3^- > Mg^{2+} > K^+).

To confirm the stated order of ions motion, there were conducted a study of influence of separation duration of the solid phase (spontaneous runoff of concentrated solution from the surface of frozen phase under action of gravity in the environment conditions) on the quality of desalinated water. It was found that separation of the solid phase for 60 min allow to reduce the content of ions of dissolved salts in desalinated water on 28...62,4 %, and separation of the solid phase for 100 min - on 36...69,7 % in contrast to desalinated water, which was obtained without separation of the solid phase. However, during separation water purification from magnesium ions and sulfates was most efficient. And most chelated ion, which was the least extracted from the solid phase during separation, was calcium.

In the course of experimental study performance there were also received dependences reflecting the influence of temperature of crystallizer, concentration of carbon dioxide in initial water, pH, temperature and salinity of initial water to such kinetic characteristics of desalination by freeze as changing with time of height and thickness of the solid phase, as well as water temperature. Peculiarity of changes the kinetic characteristics is that adding carbon dioxide to the initial water significantly affected the height of the frozen solid phase. At the same time increasing of the height of solids was equal to 6 mm, compared with the solid phase obtained from the sample of degassed water.

Summary of the study results allowed to recommend the following technological parameters of the carrying out the process of desalination of natural mineral sodium chloride water by freeze: operating temperature mode of crystallizer, which is changing in the process from -2 to -4 ° C, the concentration of carbon dioxide in the water at the beginning of the process of freezing - 3,7 g/dm^3, duration of the desalination process (process without cooling) - 60 minutes, one step of freezing, melting of solid phase under ambient conditions without prior separation of the frozen solid phase [11, 12]. With such technological modes of the carrying out the process of freezing it is possible to obtain water with mineral composition, mainly with existing relevant recommendations to the mineral composition of beverages for athletes (Table 1).

Table 1

The electrolyte content in sports drinks and in desalinated water, prepared on the claimed process

Ions	**Recommended mineral composition of drinks for athletes, mg/dm^3** (Pat. RU 2375930 Composition non-carbonated sports drinks, non-carbonated sports drink and method for producing, 2009)	**Mineral composition of desalinated water on claimed method**
Na^+	230…1725	750…850
K^+	117…780	11…13
Mg^{2+}	12…364,5	15…45
Ca^{2+}	20…600	20…85

Lacking in water content of, e.g., potassium ions, will be compensated by the adding of carbohydrate compositions in water prepared in concentrated form.

Conclusion

1. As a result of performance of experimental studies the regularities of influence of such factors of freeze desalination process as operating temperature of crystallizer, pH, temperature and salinity of the initial natural sodium chloride water on quality indicators of prepared water, the order of the ion motion in solid phase, as well as changes in the characteristics of the solid and liquid phase were revealed.
2. The results of experimental studies are summarized and recommendations on the method and technological modes of desalination process by freeze of natural mineral medical-table sodium chloride water for technologies in the production of beverages for athletes are made.

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