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Possibility of Water Purification from Soluble $CaCO_3$ Admixture with the Help of Recrystallization at −17 °C

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Abstract

It is demonstrated experimentally that the application of freezing – unfreezing procedure for the purification of water from soluble amounts of $CaCO_3$ under the conditions recommended for obtaining water from melted ice (freezing ~0.2 l of water at −17 °C) is ineffective. An explanation is the fact that salt freezes into the ice. It is concluded that changes in the concentrations of inorganic impurities cannot be a decisive physicochemical factor for distinguishing between the melted water and the initial one.

INTRODUCTION

The phenomenon of melted water, which is obtained immediately after the ice melts, is well known [1]. This phenomenon means that, as a rule, the use of melted water brings about more positive results that the use of usual water. For instance, the positive effect of melted water was observed in special experiments on growing agricultural plants: the growth rate and productivity increase [2]; a noticeable increase in fertility of different animal species was observed in biological experiments [3].

Physicochemical properties of melted water have not been investigated systematically. Only sporadic information was published about measurements of permittivity [4], concentrations of oxygen and carbon dioxide [2]. Finally, an increased hydrogen peroxide content of melted water has been reported recently [5].

One of physicochemical parameters by which melted water can differ from usual one could be noticeable decrease in the concentration of dissolved inorganic impurities, because the solubility of impurities in ice is much lower than in water. However, it was demonstrated in [6] that under the conditions usually recommended for obtaining melted water (volume: 0.2–0.5 l; temperature: −17 °C) water purification from NaCl occurs only by 15–20 % within one cycle of freezing-unfreezing.

It should be noted that the problems connected with obtaining and properties of melted water are directly related to the problem of obtaining pure drinking water, which is one of the central problems of modern civilization; its urgency is undeniable. Because of this, a separate task within this problem is that concerning the efficiency of water purification with the help of freezing [7, 8].

Theoretically, the mechanism of water purification by freezing is as follows. At first, the ice crystal phase is formed under freezing; it displaces impurity molecules into the non-frozen water. Correspondingly, in the case of incomplete freezing, the concentration of impurities in water obtained by unfreezing the ice (that is, in melted water) should be lower than in the initial water, and of course lower than in the non-frozen water.

One can easily see that the proposed procedure of water purification is similar in its essence to the directed crystallization procedure [9]. A difference from the generally accepted methods is only in the direction of movement of the crystallization front. In the standard recrystallization procedures, this motion occurs mainly in one direction, while during freezing in usual vessels the crystallization front moves simultaneously top-down, bottom-up, from edges to centre, *etc.* It was shown experimentally that freezing allows one, though not very efficiently, to purify water from the particles of the dispersed phase (insoluble impurities) [10].

The goal of the present work is to obtain information about the efficiency of freezing at a temperature of −17 °C to purify water from $CaCO_3$ salt. In order to solve the formulated problem, we carried out a direct experiment: comparison between $CaCO_3$ concentrations in melted and non-frozen water in the case of incomplete freezing of $CaCO_3$ aqueous solution at −17 °C.

The choice of this salt, which is always present in any kind of water, is due to the fact that the information on its concentration is one of the most important parameters for the analysis of drinking water; the importance of obtaining the quantitative data on the possibility of water purification from this impurity with the help of any method is of high practical significance.

EXPERIMENTAL

The initial water was twice distilled one; limestone (chalk) was used as $CaCO_3$. The $CaCO_3$ powder ground and crushed in agate mortar was mixed with water (~300 ml). The dissolution process lasted for several days without intensive mixing. Experiments were carried out with the solution filtered three times. A half of the filtered solution (~150 ml) was a reference sample. No precipitation was observed in the reference solution for 7 days.

Aqueous solutions of $CaCO_3$ were placed in thin-wall non-calibrated glass beakers (initial beaker). The mass of beakers m_b was 39.7 to 41.6 g. Weighing was carried out with analytical balance of ADV 200 type (accuracy of weighing according to certificate was ±0.1 mg). The mass of the solution to be frozen was ~100 g, which corresponded to the solution volume ~100 ml. After weighing, the solution under investigation was placed in the freezer (at a temperature of −17 °C) and kept there until ~50 % of water turned into ice (it is generally accepted that in order to obtain high-quality water it is necessary to freeze less than 50 % of its initial volume). Time within which such a state was achieved was ~2.5 h. After 2.5 h, the beaker was taken out, unfrozen water was poured into another glass beaker, which was also weighed preliminarily, and the mass m_w^{n-f} of this water portion was determined by weighing. The glass with the remaining ice was weighed and the mass of ice was determined: m_w^m : $m_w^{m,n-f} = m_e^{m,n-f} - m_{gl}$, where $m_e^{m,n-f}$ is the measured mass of the beaker with the samples of melted and non-frozen water, respectively.

The ice in the initial beaker was melted, then water was evaporated from both beakers without allowing it to boil. After evaporation, the glasses were weighed and the mass of $CaCO_3$ was determined: $m_{CaCO_3}^{m,n-f} = m_e^{m,n-f} - m_{gl}$, where $m_e^{m,n-f}$ is the measured mass of the beaker with $CaCO_3$ formed as a result of evaporation of the melted or non-frozen water, respectively.

The efficiency of water purification from $CaCO_3$ was estimated suing the separation coefficient, which was calculated suing the relation $\alpha_{sep} = m^m/m^{n\text{-}f}$, where m^m and $m^{n\text{-}f}$ are the relative masses of $CaCO_3$ after evaporating from the glasses with melted and frozen water, respectively, which were determined using equations: $m^m = m_{CaCO_3}^m / m_w^m$, $m^{n\text{-}f} = m_{CaCO_3}^{n-f} / m_w^{n-f}$. Concentrations of the initial $CaCO_3$ solutions C_{in} were calculated using equation $C_{in} = m_{CaCO_3}^{in} / V_{sol}^{in}$, where $m_{CaCO_3}^{in}$ is the mass of $CaCO_3$ after evaporation from the initial solution with the volume V_{sol}^{in}.

RESULTS AND DISCUSSION

After evaporation, the presence of white powder was always clearly observed in all the beakers. Visually, its amount was about the same in the beakers with melted and non-frozen water. This was especially evident in the case of approximate equality of the volumes of melted and non-frozen water (Table 1, exp.

TABLE 1

Results of determinaiton of separation coefficient

Exp. No.	C_{in}, mg/ml	$m^{m}_{CaCO_3}$, mg	m^{m}_{w}, g	$m^{m}\ 10^{5}$	$m^{n-f}_{CaCO_3}$	m^{n-f}_{w}	$m^{n-f}\ 10^{5}$	$\alpha_{sep} = m^{m}/m^{n-f}$
1	0.048 ± 0.002	1.7 ± 0.2	50.435	3.4 ± 0.4	2.9 ± 0.2	48.244	6.0 ± 0.4	0.57 ± 0.1
2	0.039 ± 0.002	0.9 ± 0.2	39.143	2.3 ± 0.5	2.7 ± 0.2	57.523	4.7 ± 0.4	0.49 ± 0.14
3	0.060 ± 0.002	3.8 ± 0.2	56.780	6.7 ± 0.4	2.3 ± 0.2	40.281	5.7 ± 0.5	1.17 ± 0.17
4	0.052 ± 0.002	2.6 ± 0.2	48.224	5.4 ± 0.4	2.3 ± 0.2	46.228	5.0 ± 0.5	1.07 ± 0.19
5	0.056 ± 0.002	2.5 ± 0.2	45.193	5.5 ± 0.4	2.9 ± 0.2	50.109	5.8 ± 0.5	0.96 ± 0.15
6	0.042 ± 0.002	2.7 ± 0.2	59.081	4.6 ± 0.3	1.6 ± 0.2	39.472	4.1 ± 0.5	1.12 ± 0.21

No. 4, 5). So, visual analysis showed that there were no differences in $CaCO_3$ concentrations in melted and non-frozen water. His observation allows us to conclude that freezing at −17 °C is inefficient for water purification from $CaCO_3$ impurities.

Quantitative results of the determination of $CaCO_3$ mass after evaporation, the masses of frozen and non-frozen water, m^{m}, $m^{n\text{-}f}$ and α_{sep} values are shown in Table 1. In our experiments, $CaCO_3$ concentration in the initial solutions was 0.04–0.06 mg/ml, which does not exceed the reference data for the solubility of $CaCO_3$ in water at 20 °C – 0.065 mg/ml [11]. One can see that noticeable scattering of α_{sep} values is observed. The reason is likely to be random character of the inclusion of impurities into ice, which is conditioned by extemporaneous spatial shape of water crystallization front [9]. Fortuitousness of the spatial orientation of crystallization front, based on probabilistic (fluctuation) processes, causes a difference in the surface area of the formed ice polycrystal. It is fortuitousness of the spatial shape of crystallization front that provides the origin of its cellular-dendrite structure [9]. Additional illustration of the presence of fluctuation processes during freezing of water solutions is provided by the results of another independent experiment connected with measuring the ratio of intensities of pyrene luminescence for two identical initial samples of water solutions – in melted and in non-frozen water. Initial pyrene concentration C_{Py} was 10^{-7} mol/l, freezing conditions were similar to those described in the Experimental section. In these experiments, the error of measuring α_{sep} parameter was ±5 %. For the first solution, the ratio was 1.35 and for the second one it was 0.87. One can see that water crystallization conditions in different beakers (even under completely identical external conditions) can be substantially different, which leads to different α_{sep} values for two identical samples. So, both for organic and inorganic substances, variations of their distribution in ice and in non-frozen water take place.

Thus, variability of the obtained α_{sep} values is natural and explainable. We conclude, basing on the fact that no noticeable difference between α_{sep} and 1 is observed with an accuracy of the factor of 2, that concentrations of $CaCO_3$ in melted and non-frozen water are approximately the same. Thus, conclusions made from visual and quantitative analysis coincide: freezing at −17 °C and volume of frozen water about 50 % does not allow efficient purification from the soluble amount of $CaCO_3$. (However, it should be noted that randomly a small α_{sep} value can perhaps be obtained in some experiments, which will mean substantial degree of purification.)

The mechanism of impurity insertion (for $CaCO_3$ molecules, Ca^{2+} and CO_3^{2-} ions) into water during freezing can involve their inclusion into cavities of cellular-dendrite structure of the crystallization front, which are formed due to high freezing rate [9] and attachment of these particles to the smooth ice surface (adsorption). The first reason is likely to be the determinant one, since sorption of impurities occurs at any time, nevertheless, one may succeed in obtaining ice single crystals from the aqueous solutions of inorganic salts under freezing [13]. The condition of the formation of dendrite structures in the absence of mixing can be written as [14]:

$$(\mathrm{d}T/\mathrm{d}x)_{x=0}V^{-0.5} \leq AC_\mathrm{L} \qquad (1)$$

Here $(\mathrm{d}T/\mathrm{d}x)_{x=0}$ is the temperature gradient in the cooled liquid; V is the rate of crystallization front movement; C_L is the concentration of an impurity near the crystallization front; A is the constant slightly depending on the kind of the system. When condition (1) is fulfilled, the $CaCO_3$ molecules, Ca^{2+} and CO_3^{2-} ions get into the formed cells of the interdendrite space and stay there. Really, in order to obtain high-quality ice single crystals during directed crystallization of aqueous solutions of salts, the rate of crystallization front movement should be less than 0.05 cm/h [13], while in our experiments it was about 0.5 cm/h.

So, inefficiency of purification of the aqueous solution of $CaCO_3$ with the help of freezing is explained by the formation of cellular dendrite structure of crystallization front accompanying the applied freezing rate.

It was noted in the Introduction on the basis of the data reported in [6] that purification of the aqueous solution of NaCl by means of freezing is inefficient, too. Similar results involving inefficiency of the purification of $CaCO_3$ and NaCl aqueous solutions by freezing, in our opinion, allow one to note carefully that the rate threshold of the formation of cellular dendrite structure during water freezing, indicated in [14] as approximately 0.05 cm/h is likely to be too low and can easily be overcome. This may be due to the structural features of ice: water molecule forms four H bonds in it, that is why the probability of dendrite formation is high. It is the formation of the cellular dendrite structure during water freezing that explains the fact that water obtained from the melted sea ice is salty. (Salt content of ice is due mainly to the concentration of sodium chloride molecules which is about 30 g/l in seawater [15].) Really, in this natural experiment, perhaps due to very large amount of freezing water, and corresponding intensive heat transfer to the crystallization front, the rate of freezing is very small; in addition, there is always rather intensive mixing due to various convective fluxes and flows. (The absence of substantial temperature and concentration gradients at the crystallization front is the necessary condition for efficient purification with the help of directed crystallization [9].) So, the nature is likely to have almost ideal conditions for water crystallization and therefore for obtaining almost salt-free ice. However, this does not happen in reality. This means that either the rate of crystallization front in seawater is higher than 0.05 cm/h or some other factors exist that distort the conditions of obtaining salt-free ice (for example, seawater gets onto the ice surface and gets frozen there). Because sea ice is salty, various projects aimed at obtaining salt-free water from icebergs are connected with their transportation from the Antarctic (continental ice) rather than from the Arctic (where ice is composed mainly of seawater).

CONCLUSION

Thus, the freezing procedure used to purify water from the dissolved $CaCO_3$ is ineffective. Thus means that unusual properties assigned to melted water, which is recommended to be obtained from water frozen in a froster, are likely to be not determined by changes in the content of inorganic impurities.

It follows from our data that a single freezing procedure has no sense for purification of water containing $CaCO_3$ with the help of freezer. The same conclusion about inefficiency of freezing procedure for the purification of salty water (for example, in the region near the Azov sea) follows from the data reported in [6].

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