



THEORETICAL ASPECTS OF DISPOSAL OF LIQUID MINERAL WASTE*

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Abstract

The study is devoted to the substantiation of the possibility of isolating valuable components from highly mineralized natural-man-made waters, which are simultaneously exposed during the development of oil, gas fields and solid minerals. In modern conditions, these waters become waste. Moreover, they have all the characteristics of hydromineral raw materials. To effectively involve them in secondary use, it is necessary to identify potentially possible conditions for the selective separation of components from a multicomponent system, including using the climatic features of the territories that allow the use of cryotechnology.

Keywords: brines, freezing, structure of solutions,

1. Introduction

Recently, the problem of protecting the environment from the harmful effects of liquid waste from field development, which is groundwater, in particular, containing high concentrations of dissolved salts, that is, water of brine mineralization, becoming increasingly urgent. In essence, highly mineralized groundwater is the richest source of various kinds of mineral compounds of both industrial and balneological importance.

At present, the brines that are broken up during the development of various mineral deposits in Eastern Siberia are liquid waste and are not processed. The theoretical and practical feasibility of processing brines is reflected in the research results of leading specialists – A.A. Dzyuba, P.I. Trofimuk, E.V. Pinekker, B.I. Pisarsky, G.M. Speizer, etc. The high content of industrially valuable components in brines predetermines the economic

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efficiency of their processing, provided that complex technological schemes are used. A large list of marketable products can be obtained from brines; moreover, this raw material has a number of advantages over solid mineral nodules.

One of the main directions of solving the problem of effective processing of brines is the theoretical substantiation of the possibility of selective extraction of the maximum number of components and the introduction of complex technological schemes into production. Currently, the issues of extracting valuable components from dilute solutions have been worked out. So for the processing of brines in Eastern Siberia, the sharply continental climate of the region can be very useful. The freezing process is known mainly for the desalination of solutions. Its use for the separation of phases of highly mineralized systems, in particular, brines, is not known. The basic mechanisms governing the behavior of water systems at negative temperatures are also not clear enough.

2. Study purpose

The main goal of this study is to theoretically substantiate the possibility of efficient processing of highly mineralized waters with the extraction of valuable components from them, including the use of natural and climatic resources of the brine bedding area. The theoretical aspects of the selective isolation of components from concentrated multicomponent solutions using cryotechnology have not been sufficiently studied.

3. Materials and methods

The efficiency of freezing is influenced by the temperature regime, the initial concentration of the solution, the final volume of the concentrate, the concentration of inorganic ions in the solution, the pH of the aqueous solution, the ionic strength of the solution, and the structural characteristics of the liquid phase. The study of the characteristics of brines and the freezing process was carried out using atomic absorption analysis and the method of inductively coupled plasma to determine the quantitative content of components, conductometric analysis to determine the electrical conductivity of solutions, cryotechnical methods, planning and processing the experimental results using statistical methods and the Microsoft Excel application package.

4. Results and discussion

The freezing method is one of the methods of fractional crystallization. Fractional crystallization is widely used in chemical, coke-chemical, petrochemical, metallurgical, pharmaceutical, food and other industries.

Using this process, the following tasks are solved:

- separation of technological mixtures into fractions, enriched with one or another component;
- isolation of various substances from natural and technological solutions;
- deep cleaning of substances from impurities;
- concentration of dilute solutions by freezing out the solvent;
- separation of valuable or harmful components from gas mixtures.

For brines of the Siberian platform, which are of industrial value due to the high content of micro- and macrocomponents (Table 1), the first and second tasks are the most important: separation of technological mixtures into fractions enriched with one or another component; isolation of various substances from natural and technological solutions (Ulanova et al., 2019).

The freezing process is accompanied by phase transformations and consists in the fact that at a temperature below the freezing point of water, pure water turns into a solid state, forming crystals of fresh ice, and the brine with salts dissolved in it is placed in the cells between these crystals.

The efficiency of freezing is largely determined by the equilibrium of phases in the "liquid – crystalline phase" system. For systems "water – solute", the diagram of phase equilibrium of the eutectic type is typical. The maximum degree of concentration is determined by the position of the eutectic point on the phase equilibrium diagram.

A feature is the high salinity of brines, and concentrated solutions cannot be described using the theory of Bernal and Fowler relating to a dilute solution. There are different theoretical views on the behavior of components in concentrated systems. The structure of concentrated solutions is similar to the structure of the corresponding water salt – hydrate, that is, water molecules are located among the ions that form the structure of the salt. With an increase in the concentration of the investigated solutions, the distribution of ions tends to the distribution characteristic of crystal hydrates, which are released from saturated solutions. Near the composition corresponding to pure water, the structure of the solution is determined by the structure of the water; near the composition corresponding to the crystalline hydrate – the structure of the crystalline hydrate.

Table 1. Content of elements in the studied brines

<i>Element</i>	<i>Sample № 1</i>	<i>Sample № 2</i>	<i>Sample № 3</i>	<i>Sample № 4</i>	<i>Sample № 5</i>
Li	308.31	368.62	193.55	164.66	170.55
B	186.78	282	175.71	129.73	131.25
Na	21500	22200	25978.38	28160.18	29745.48
Mg	11470.34	12595.94	13092.2	12375.85	12573.16
S	34.85	50.37	36.93192	41.32	42.6
Cl	203745.9	257671.7	240514	220447	200631
K	13500	13200	17942.71	14986.07	15262.68
Ca	73551.21	88062.6	86879.18	78284.41	77516.93
Ti	0.37	0.37	0.032	0.029874	0.049
V	0.95	0.97	0.00072	0.0012	0.0035
Mn	11.31	6.9	4.59	3.88	4
Fe	0.27	1.42	0.52	1.85	0.48
Co	0.065	0.082	0.017	0.013	0.014
Ni	0.066	0.18	0.52	0.26	0.26
Zn	11.75	1.99	0.51	0.36	0.43
Cu	0.153	0.096	0.023	0.021	0.026
As	0.17	0.21	0.0054	0.033	0.056
Se	1.48	1.82	0.15	0.064	0.01
Br	162774.4	165218.6	16280	16300	15100
Rb	7.72	8.77	15.02	12.07	12.2
Sr	974.45	1073.54	1497.42	1224.16	1254.23
I	49.64	59.58	0.016	0.011	0.013
Cs	0.24	0.27	0.49	0.32	0.31
Ba	0.58	0.61	0.997	1.39	1.36

The concept of the total solvation boundary (Mishchenko and Poltoratsky, 1976), introduced by KP Mishchenko and AM Sukhotin, is useful. It is clear that ions distort the structure of water, which is due to the difference in the nature of the interaction of ions with water molecules, on the one hand, and water molecules with each other, on the other hand.

The authors (Pavlova and Chizhik, 2005) It was determined that when studying the microstructure of electrolyte solutions, it is important to separate the effect of anions and cations on the structure of the solution, however, this is a very difficult task.

The structure of the solution is the statistical ordering of a complex equilibrium system "solvent – solute – products of their interaction" in an elementary volume under given conditions, characterized by certain near and far environments relative to the selected solution particles of different nature, the type of intra- and interparticle interactions, and the degree of their cohesion. The structure and structure of solutions, as well as their properties, depend mainly on the nature of the solvent and solute, its concentration, on the temperature and pressure at which the solution is located, on the addition of non-electrolytes (Rodnikova, 2003).

There are two approaches to describing the structure of solutions. The first approach is based on the idea of the dominant influence of the structures of the components of the solution. In this case, several regions are distinguished, where the structure of the solution is determined either by the structure of pure components or by the structure of their mixture. The second approach is based on a model concept of the structure of a solvated particle in solution.

The main source of information on the change in the structure of the solution is the analysis of the concentration and temperature dependence of the test solution. In this case, a change in the course of the concentration dependence or a change in the nature of the temperature dependence of the structure-sensitive property upon going from one concentration region to another is interpreted as evidence of differences in the structure of the solution in these regions. The interpretation significantly depends on the selective sensitivity of the method and the model developed to relate the measured parameter to the molecular kinetic characteristics of the solution.

The points of view of different authors about the influence of these factors differ significantly. For example, it is suggested that the high salt background of the solution being frozen out promotes the extraction of organic compounds into the liquid phase due to the salting-out effect. There is also an opposite opinion that the presence of significant amounts of inorganic salts in the solution leads to a decrease in the extraction efficiency (Chen and Chen, 1996).

4.1. Influence of temperature conditions on salt crystallization

The temperature regime determines the rate of the freezing process. Temperature in the range of positive and negative values affects the rate of reactions, the solubility of compounds, the rate of dissolution, coagulation, as well as the concentration of undissociated ion pairs. There are several types of temperatures in solutions: structural, freezing point, temperature of the beginning of solution crystallization. The temperature of the beginning of crystallization (freezing point) is the temperature at which, as a result of cooling the solution, crystals begin to form. Lowering the freezing point ΔT_z is the difference between the freezing point of a pure solvent and a solution. The freezing point of the brine is always lower than the freezing point of pure water and depends on the concentration of dissolved salts. This dependence for brines can be expressed by the equation:

$$\Delta T_z = KC, \tag{1}$$

where

K —is the coefficient of proportionality;
 C —is the concentration of the solute in the solution.

For less dilute solutions, the crystallization onset temperature is determined from the phase diagram of the corresponding system. Since the freezing temperature of sea waters and highly mineralized natural brines will be different, we assume that this temperature should be calculated using different formulas.

For validation our results we have carried out a measurement of the freezing temperature for sodium chloride and sea-water in dependence on salinity. Figs. 1-2 show comparison of our experimental data on the sodium chloride and sea water with the well-known equations. It is clearly seen that our results are in a very good agreement with the data of other researchers.

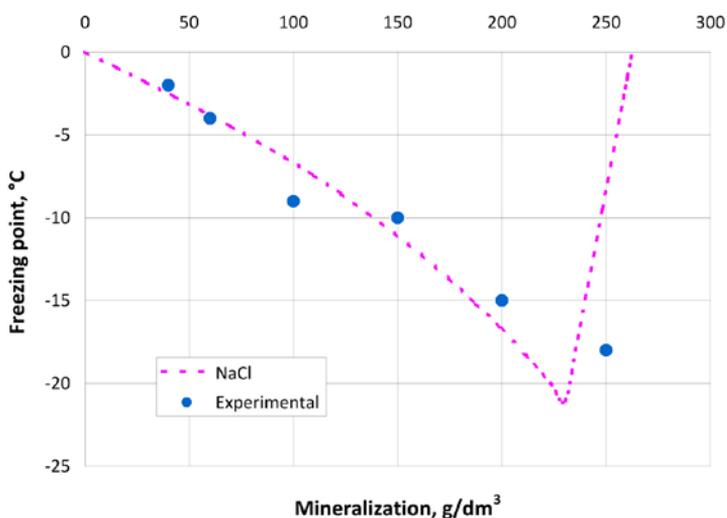


Fig. 1. The dependence of the freezing point on the salinity of the sodium chloride solution

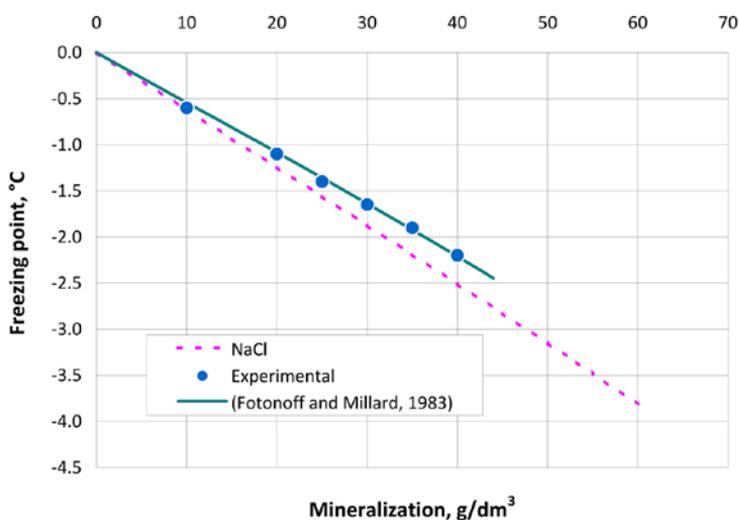


Fig. 2. Dependence of the freezing point of sea water on salinity (Fotonoff and Millard, 1983)

After the validation we have made an approximation of the experimental data on the freezing temperatures of brines solutions. Dependences of changes in freezing temperature in graphical and analytical forms are shown in Fig.3.

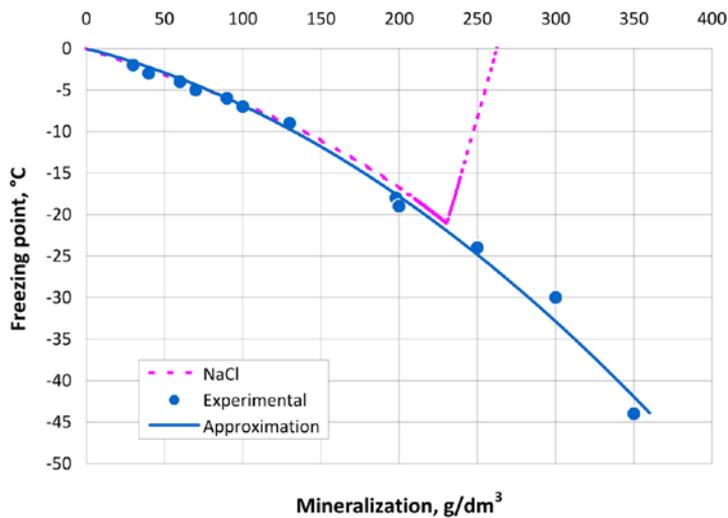


Fig. 3 Dependence of the freezing point of brine on salinity

The approximation equations for the Figs.1-3 are following:

NaCl (our approximation); $0 \leq M \leq 230.31 \text{ g/dm}^3$:

$$t_f = -6.2397 \cdot 10^{-2} \cdot M + 1.82 \cdot 10^{-5} \cdot M^2 - 6.2619 \cdot 10^{-7} \cdot M^3 \quad (2)$$

Sea water (Fotonoff and Millard, 1983); $0 \leq M \leq 44 \text{ g/dm}^3$:

$$t_f = -5.75 \cdot 10^{-2} \cdot M + 1.7105 \cdot 10^{-3} \cdot M^{3/2} - 2.1550 \cdot 10^{-4} \cdot M^2 \quad (3)$$

Brine (our approximation):

$$t_f = -4.8059 \cdot 10^{-2} \cdot M + 2.0513 \cdot 10^{-4} \cdot M^2 \quad (4)$$

Coefficient of determination for equation (3) is $R^2 = 0.991$

The analysis of the plotted graphical dependencies presented in Figs. 1-3 showed that the freezing temperature decreases with an increase in the total salinity of the solution. The other conclusion we can make is that for the multi-component solutions an increase in the number of components included in the system being frozen also leads to a decrease in the freezing temperature.

Studies have shown that the freezing of individual salts from desalinated water occurs at different temperatures. So, at a temperature of $-2 \text{ }^\circ\text{C}$, calcium carbonate precipitates. At $-3.5 \text{ }^\circ\text{C}$, sodium sulfate. When the temperature drops to $-20 \text{ }^\circ\text{C}$, table salt precipitates, to $-25.5 \dots -26 \text{ }^\circ\text{C}$, magnesium chlorides, and at very low temperatures $-40\text{-}55 \text{ }^\circ\text{C}$, potassium and calcium chlorides fall out.

For negative temperatures, the process of formation of crystalline hydrates, unstable at negative temperatures, is specific. For example, hydrohalite $\text{NaCl} \cdot 2\text{H}_2\text{O}$ is formed at -

0.15 °C, $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ stable at -15 °C, and $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ – below 0 °C, $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ is formed at -10 °C. KCl at 0 °C as KCl, at -6.6 °C two phases already coexist: KCl and $\text{KCl} \cdot \text{H}_2\text{O}$, at -10.6 °C is precipitated only $\text{KCl} \cdot \text{H}_2\text{O}$. At negative temperatures, individual crystalline hydrates are formed with the maximum possible number of molecules of crystallization water corresponding to the coordination numbers at a given value and their mixtures (but not mixed crystals). An abnormal decrease in the freezing temperatures of concentrated solutions should be noted.

4.2. Influence of the composition of solutions on the crystallization of salts

When systems freeze from water and salt, cryohydrates are formed – products consisting of water crystals and salt crystals that are not chemically bonded to each other. In such systems, the eutectic point is called the cryohydrate point. Of all the solutions located in composition to the left of the cryohydrate point, i.e. containing salt in a lower concentration, when cooled, first ice is released and only when the cryohydrate temperature is reached, both components crystallize. If the concentration of salt in the solution is greater than its concentration in the cryohydrate, then when the solution is cooled, salt crystals are first precipitated and only when the cryohydrate temperature is reached, both components crystallize.

With a further decrease in temperature, crystallization of pure ice occurs until the eutectic temperature is reached at which both components of the solution crystallize. This temperature is the temperature of its complete solidification, which is of great interest (table 3). Only electrolyte solutions with high solubility can have low eutectic temperatures. However, there can be no unambiguous connection between these values, since other factors also influence here.

Table 2. Eutectic temperatures of water-salt systems

<i>System</i>	<i>Crystallizing point, °C</i>	<i>Concentration, % (by weight) of anhydrous salt in solution</i>	<i>Solid phase composition</i>
$\text{CaCO}_3 + \text{H}_2\text{O}$	$-1.8 \dots -1.9$		Ice + CaCO_3
$\text{NaHCO}_3 + \text{H}_2\text{O}$	-2.3		Ice + NaHCO_3
$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	-2.1		Ice + $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$
$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$	-10.0		Ice + $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
$\text{K}_2\text{SO}_4 + \text{H}_2\text{O}$	$-1.55 \dots -2.9$		Ice + K_2SO_4
$\text{MgSO}_4 + \text{H}_2\text{O}$	-4.8		Ice + $\text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$
$\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	$-3.5 \dots -8.2$	3.86	Ice + $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
$\text{CaSO}_4 + \text{H}_2\text{O}$	$-15 \dots -17$		Ice + $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$
$\text{KCl} + \text{H}_2\text{O}$	-11.1	19.5	Ice + KCl
$\text{KCl} + \text{H}_2\text{O}$	$-34.2 \dots -36.8$		Ice + $\text{KCl} \cdot \text{H}_2\text{O}$
$\text{KBr} + \text{H}_2\text{O}$	-13		Ice + KBr
$\text{NaCl} + \text{H}_2\text{O}$	$-21.1 \dots -22.9$	22.4	Ice + $\text{NaCl} \cdot 2\text{H}_2\text{O}$
$\text{NaBr} + \text{H}_2\text{O}$	-24		Ice + NaBr
$\text{MgCl}_2 + \text{H}_2\text{O}$	-35.5		Ice + $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
$\text{MgCl}_2 + \text{H}_2\text{O}$	$-33.6 \dots -36$	21.6	Ice + $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$
$\text{CaCl}_2 + \text{H}_2\text{O}$	$-54 \dots -55$	$29.9 \dots 30.22$	Ice + $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

Table 2 shows that many electrolyte solutions completely solidify only with relatively deep cooling. Most of the above electrolytes are released in the form of crystalline hydrates, which, together with crystals of pure ice, form a cryohydrate.

If the original solution contained less water than is necessary for the corresponding crystalline hydrate, then complete curing will end at a higher temperature and the product will not contain ice crystals.

Unlike two-component solutions (solvent and salt), eutectic points shift mainly towards low temperatures due to the presence of many ions in water at the same time, that is, when solutions of complex composition freeze, the eutectic points of readily soluble salts change. It can be concluded that in a multicomponent system, such as seawater, the liquid phase – salt in the form of a solution – is preserved to lower temperatures (and in a multicomponent concentrated brine system even to lower temperatures) than in a two-component system. Salt precipitation occurs not at a fixed temperature value, but in a certain temperature range.

Brines are characterized by a complex chemical composition. The precipitation of salt from a complex solution upsets the ionic equilibrium in the brine. For this reason, the crystallization of an individual salt occurs unevenly, at different rates, and at some stages part of the crystalline hydrate can pass back into the brine. With a decrease in the temperature of the liquid, the translational motion becomes less intense, the mobility of the particles decreases, the influence of the interaction energy between the particles increases, the viscosity increases, the liquid gradually thickens and, finally, solidifies in the form of a glassy mass or crystallizes, if there are necessary conditions for this (Egorov et al., 2000).

We carried out experiments on freezing out brines from the Udachnaya pipe with a total salinity of about 400 g/dm^3 under natural conditions and when the brine is placed in a cooling mixture (acetone + liquid nitrogen). It was revealed that with artificial cooling, the brine freezes after 30 minutes at a temperature of $-40 \dots -45 \text{ }^\circ\text{C}$ throughout the entire volume. Under natural conditions, a gradual decrease in temperature when keeping the brine at $-5 \text{ }^\circ\text{C}$ and after creating a temperature difference by bringing the solution into the room, salt falls out of it. We have studied the composition of the salt. Most of the sediment is hydrohalite ($\text{NaCl} \cdot 2\text{H}_2\text{O}$). Further, it was noticed that at an air temperature of $-30 \dots -33 \text{ }^\circ\text{C}$, a small amount of salt falls out in the cold. It is noted in (Li et al., 2020) that the nucleation of ice crystals in calcium chloride brine with a mineralization of 320 g/dm^3 occurs at a temperature of $-37 \text{ }^\circ\text{C}$, and cooling to $-55 \text{ }^\circ\text{C}$ does not lead to complete freezing and the brine is a loose mushy mixture (the space between filled with ice crystals with a solution with a salinity of 360 g/dm^3). At a temperature of $-37 \dots -45 \text{ }^\circ\text{C}$, salt $\text{NaCl} \cdot 2\text{H}_2\text{O}$ precipitated from the brine, the crystallization temperature is affected by other components that make up the brine. Thus, by acting on the brine with clearly defined negative temperatures, it is possible to extract certain salts from them, which can be directly used in industry. In addition, the precipitated salts reduce the total mineralization of the initial solution to be frozen, thereby facilitating the extraction of other components from it that does not precipitate out of salts.

4.3. Influence of hypothermia rate (fast and slow) on ice formation

Interphase and intraphase interactions between solid salts and their eutectics, on the one hand, and dissolved substances in the unfrozen part of the solution or contained in liquid cells, on the other, are important for the formation of ice composition when highly mineralized waters freeze at sufficiently low negative temperatures. If the temperature decrease is slow, needle ice forms with a vertical arrangement of relatively large crystals, which contributes to better drainage of brine and obtaining fresh water with lower mineralization. With the rapid course of the freezing process of water, the resulting ice crystals are much smaller and are located haphazardly. Studies have confirmed that the resulting ice has a spongy structure, and this complicates the separation of intercrystalline

brine and the resulting desalinated water in this case has an increased mineralization. Taking into account this circumstance, it is advisable to carry out desalination of saline waters by freezing in conditions of their slow supercooling.

4.4. Study of the effect of mineralization on the involvement of ions in the ice and liquid phases

The amount of substances involved in ice depends to a greater extent on the rate of ice formation. The concentration of Cl^- , SO_4^{2-} , HCO_3^- ions in ice increases with an increase in their concentration. The dependence of the content of ions in ice on their content in the initial solution is linear within limited limits. For Cl^- and SO_4^{2-} this is the concentration of 5-6 g/dm^3 , for HCO_3^- – 500 mg/dm^3 . When the concentration of chloride and sulfate ions in the initial solution is 6 g/dm^3 and higher, their involvement in ice begins to decrease, and at a concentration above 500 mg/dm^3 , it increases (Izutsu et al., 2011).

We investigated the process of freezing brines of two different genetic types: chloride-sodium-potassium and chloride-calcium-magnesium. It turned out that the degree of involvement in the ice phase for different components of the brine is different. From the diagrams for two elements – calcium and magnesium (Fig. 4-5) – it can be seen that the distribution of these elements between the ice and liquid phases becomes noticeable with increased salinity of the frozen solution, in our case – for brine with $M_{\text{tot}} = 200 \text{ g/dm}^3$. It was found that for saline waters with a low total mineralization (up to 16 g/dm^3), elements – calcium and magnesium – are equally involved both in ice and in the unfrozen brine phase. And the higher the total salinity of the solution, the more efficient the distribution of elements between the ice and brine phases; the concentration of the element in the brine phase increases, and the ice is desalinated with an increase in the total brine salinity.

With ice formation in natural conditions, in addition to the ice phase, crystallization of other phases is possible, mainly salts, the formation of colloidal sediments (cryocoagulants). In a simplified form, co-precipitation with ice includes adsorption, occlusion, and the formation of solid solutions (isomorphic compounds). In both cases, electrical phenomena at the water-ice interface play a role.

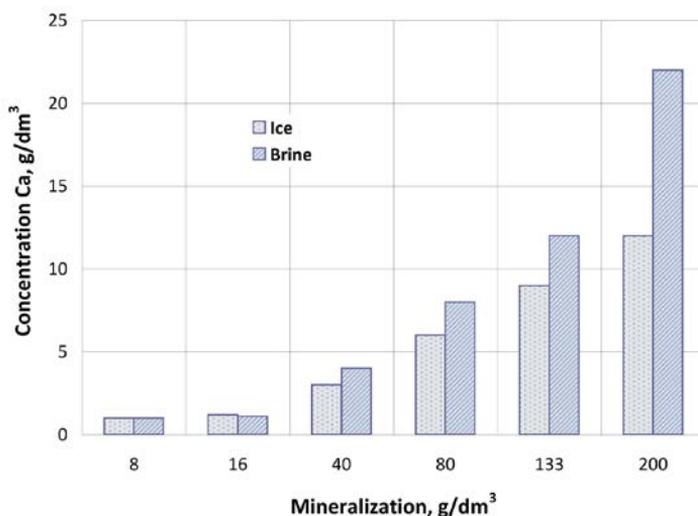


Fig. 4. Dependence of the involvement of calcium ions in the ice and liquid phases on the initial salinity of the frozen brine

Cations of alkali and alkaline earth metals interact with the ice surface electrostatically (physical adsorption), chemisorption is established for anions. The value of the ionization potential of such ions lies in the range of 9-10 eV and is close to 9.6 eV – the ionization potential of water molecules. Probably, therefore, of the anions, the most selectively sorbed Cl^- – ion, the ionization potential of which is 9.15 eV, F^- , Br^- , J^- – ions (10.0; 9.1; 8.9 eV – respectively, their ionization potentials). The adsorption of cations by ice is associated with their effect on the structure of water. The least influence, and, consequently, the least ability to be incorporated into ice, is possessed by ions in which the value of the hydration constant is close to zero. Therefore, potassium should be best sorbed from alkaline ions. Ions of alkaline earth metals have a very weak adsorption interaction with ice.

The selective incorporation of ions into ice crystals is due to adsorption occlusion. This process is greatly influenced by all ions of the solution. One or another ion in the presence of one type of "interfering" ion can easily be incorporated into the ice, and with another, even in negligible amounts, it is introduced into it with great difficulty.

Potassium is involved in ice from dilute solutions more intensively than sodium, because as a result of an increase in the degree of hydration, it prevents the formation of ice-like structures, in contrast to sodium. The Na^+ / K^+ ratio in ice is greatly influenced by the potential difference at the ice-water interface, which, in turn, is formed under the influence of the mobility of ions and their associates.

Freezing of water at the interface causes electrical potentials and discharge currents. Their appearance is associated with the selective involvement of any of the ions of dissolved substances into the ice.

Thus, it has been shown that a decrease in the temperature of precipitation of salts in natural brines determines the possibility of selective extraction of salts from highly concentrated natural salt systems. The established patterns make it possible to implement the process of selective extraction of salts from natural brines in technological schemes of their processing based on the use of cryotechnological processes.

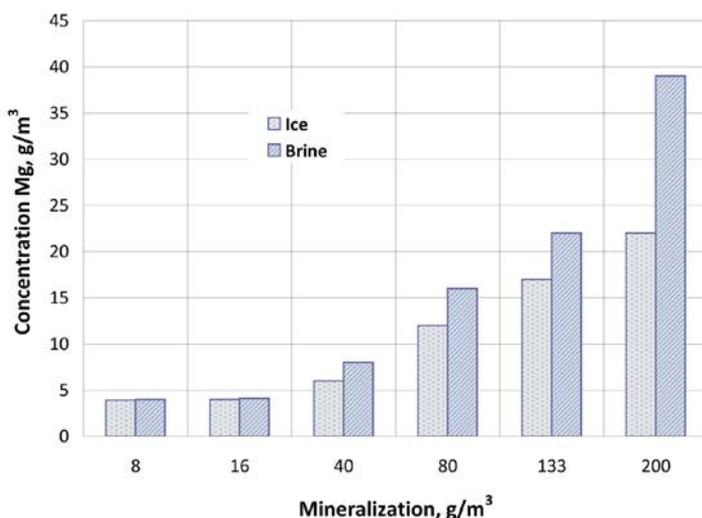


Fig. 5. Dependence of the involvement of magnesium ions in the ice and liquid phases on the initial salinity of the frozen brine

5. Conclusion

The development of mineral deposits in flooded areas, in particular, within the Siberian geological platform, the main influence is exerted by the following factors: temperature regime, composition and structural characteristics of solutions.

It was revealed that the freezing point of concentrated salt solutions is abnormally low, and it was found that up to a mineralization of 200 g/dm³ the temperature dependence of the freezing point is determined by the salt concentration, and above 200 g/dm³ the freezing point is determined by the polycomponent composition. The gradient of the freezing point decrease in a multicomponent system in comparison with a salt solution increases by 3.5 times. In natural brines and artificial multicomponent systems, with a decrease in temperature, cryohydrates are formed, precipitating. It was experimentally established that an increase in the number of components in the system reduces the eutectic temperature of the water-salt system, in particular, for NaCl + H₂O from -22.9 °C (for an individual solution) to -37 ... -55 °C (for brine).

It is shown that a decrease in the temperature of precipitation of salts in natural brines determines the possibility of selective extraction of salts from highly concentrated natural salt systems. The established patterns make it possible to implement the process of selective extraction of salts from natural brines in technological schemes of their processing based on the use of cryotechnological processes.

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