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INFLUENCE OF ICE STRUCTURE ON VITABILITY OF FROZEN SAND-WATER AND SAND-CLAY MIXTURES

Purpose. To establish influence regularity of sand, water and clay preparation conditions on vitability of frozen mixtures made from combinations of these components and to increase the castings quality in foundries, as well as to improve technologies for artificial freezing of soils for underground constructions.

Methodology. In this research, sand, clay, and water are used. Ice quality is estimated visually after water freezing at –15 °C in glass tubes. Frozen mixtures' vitability at –15 °C is studied on beam-type samples. As indicators of survivability, the time to 1 mm bending of samples on supports and the time to their destruction are accepted. The time is recorded with a stopwatch, the temperature with an alcohol thermometer, the mass with electronic scales and the deflection arrow with a clock-type indicator.

Findings. The presence and amount of water-soluble impurities in rare water significantly influence the nature, size and distribution of gas bubbles in ice, as well as frozen sand-water mixtures vitability. Frozen mixtures' survivability increases with water content in them increasing, and, for sand + water mixtures, survivability is maximum if ice has a homogeneous structure. Among mixtures with clays, the mixture with non-swollen kaolin clay has the greatest vitability. Regarding survivability, recommendations for manufacturing products from frozen foundry mixtures have been developed.

Originality. For the first time, deformation change kinetics (bending arrows) under the influence of beam-type samples' self-mass from mixtures of quartz sand and water and quartz sand, clay and water frozen at –15 °C, which have been previously prepared in different ways, have been investigated. Insights into the influence of various factors and ice quality on the vitability of frozen mixtures have been further developed.

Practical value. The obtained results can be useful for expanding ideas about natural frozen soils' behavior during their cyclic temperature changes, soils artificially frozen during mine shafts elaboration, escalators' and junctions' tunnels, etc. when constructing subways. In foundries, the developed recommendations will reduce technological losses and will improve casting quality made using frozen casting molds and cores from sand-water or sand-clay-water mixtures, castings' patterns and their pouring systems from sand-water mixtures.

Keywords: *water, sand, clay, freezing, vitability, ice, gas, impurities, destruction*

Introduction. Any artificially created frozen mixture of quartz sand and water or quartz sand, clay and water, in its physical properties, is similar to frozen natural soils, which have a certain freezing temperature (structuring), strength, gas permeability, etc. [1, 2].

The main binding substance of frozen artificially created wet mixtures and natural soils is ice. As a rule, ice of natural origin appears when fresh water reaches 0 °C. When soluble salts are present in water, its freezing (crystallization) temperature decreases with their concentration in water increasing. In particular, sea water, which contains a large amount of sodium, magnesium, potassium, calcium, and other salts, on average, crystallizes at a temperature of –1.9÷–2.1 °C. At the same time, some salts dissolved in water are emerged in crystal-hydrates form from ice at temperatures below –5 °C. That is, in seawater, where NaCl is a major part of soluble minerals, at temperatures below –13 °C, aquamarine hydrates of sodium chloride appear which are in equilibrium with seawater [3]. At the same time, as a result of selective crystallization of salts dissolved in seawater, pickle concentration and its volume in cells, as well as the volume of ice solid phase, continuously change in accordance with temperature changes. Therefore, with temperature changing part of such pickle freezes out or part of ice turns into pickle. This gives such ice instability in terms of its physical properties.

The crystalline structure of ice from fresh and distilled water at atmospheric pressure is stable in temperature range from 0 to –80 °C. Fresh water of natural origin contains small amounts of soluble (salts, gases, etc.) and insoluble (mechanical) impurities. At the same time, with temperature increasing, most salts' solubility in water increases, for gases – decreases and mechanical impurities mass remains unchanged [4].

Natural ice is solid, colorless, transparent, vitreous, noncleavable, brittle, optically positive substance with low refractive index, low hardness (1.5 on Mohs scale), and density of 931 kg/m^3. It means that after water crystallization its ice has larger volume than water itself. At the same time, due to the fact that molecule (atom) sizes of most gases located in water exceed ice channel sizes, after crystallization completion only hydrogen, helium and neon can remain dissolved in ice [5, 6].

Ice of natural origin is one of 17 known water crystalline modifications, which under certain conditions also has 3 amorphous modifications [6]. Each modification of ice differs from others in relative molecule arrangement and, accordingly, in properties level (Yao H., lee I., Robinson G.W., 1990). At the same time, unlike natural ice, which crystallizes in hexagonal syngonia, its other modifications occur only at very low temperatures and ultra-high pressure. That is, very low temperature and ultra-high pressure can change the angles between hydrogen bonds in water molecules and, accordingly, ice's structure and properties [7].

Under its own weight influence, regardless of temperature, ice (except snow and hoarfrost), which occurs in nature, acquires plastic properties and fluidity. From investigations on frozen soils' mechanics and frozen mixtures' properties, it is known that their strength increases with temperature decreasing and moisture content increasing in them, influence on their mechanical properties of pore water viscosity, dissolved salts content in it, etc. (Tsytovich N.A., 1957).

Despite significant amount of fundamental and applied research on water and ice properties, there are still a great number of questions regarding their influence on frozen mixtures' properties, in particular those which are used for manufacturing casting molds and cores.

Literature review. Casting molds and cores from freezing mixtures are used to produce small castings for general machine-building purpose in foundries. Such mixtures are two-component (sand + water) or three-component (sand + clay + water) systems. At the same time, regardless of components number in above-mentioned systems, their properties are mainly determined by initial temperature, ice content and structure in them. This regularity is due to the fact that:

- ice in such systems is only one binder;
- foundry enterprises conduct water crystallization in mixtures at atmospheric pressure and temperatures from –10 to –73 °C;
- in ice structure there always exist mechanical impurities (any random solid particles, salts concentrated solutions drops, crystal hydrates, etc.), as well as gas bubbles;
- mixtures' strength is affected by imperfection of grains morphology and their fractional composition.

Any origin ice's structure is characterized by impurities and gas bubbles selective accumulation in it. This is devoted to the fact that ice crystals during their growth in water, like crystals in any other liquid substance, always displace extraneous substances from their structure as much as possible [8].

As mentioned above, water used for technical purposes always contains mechanical impurities, dissolved salts, and gases (O_2, N_2, H_2, CO_2, CO, H_2S, CH_4, etc.).

Due to the fact that gases solubility in water at 0 °C is greater than in ice at negative temperatures, ice structure may contain gas bubbles [9], whose nature of location in ice depends on:

- water crystallization front movement velocity;
- direction and water solidification front shearing speed;
- water movement intensity and direction ahead of solidification boundary;
- mineral impurities in water quantity, properties and nature;
- the amount and nature of gases dissolved in water;
- atmospheric pressure values during water crystallization period, etc.

That is, as a result of soluble impurities liquation and insoluble in water segregation, after its crystallization, most "dirty" ice (in terms of impurities and gas bubbles) is located in places where freezing water crystallizes last. An example of this nature of impurities location is ice, which, for example, forms in test tube, where water crystallization front movement passes from test tube walls to its middle. At the same time, ice in icicles is the cleanest in terms of impurities and absent gas bubbles according to film flowing over icicle surface mode. In this case water crystallizes from inside out – from icicle surface to outer water layer surface on it. That is, during icicles growing, water crystallization front moves from icicle to outer surface of water film on it, which leads to gases dissolved in it removal from the water into surrounding air.

Among water impurities, from obtaining ice with high strength point of view, the most undesirable are gases dissolved in water, as well as salts that form crystal hydrates in ice (Richard L. Pitter, William G. Finnegan, 1990; Eric W. Wolff, 1996).

Gases solubility in liquids is described by Clapeyron-Clausius and Henry-Dalton laws, according to which: gases solubility decreases with temperature increasing, which, in particular, follows from analysis of dependences in Fig. 1; at constant solution temperature, gas solubility in it is proportional to this gas above it pressure; in the case of gases mixture dissolving in liquid, each of them dissolves in proportion to its partial pressure.

But Henry's law applies only to those gases, which solubility is low and which, at the same time, do not form chemical compounds with liquid. At the same time, gases solubility in liquid largely depends on concentration of other substances dissolved in it, which, in particular, is taken into account in the Sechenov's formula.

When using this or that water for freezing, Mpemba paradox should also be taken into account, according to which boiling water in severe frost crystallizes faster than cold water (Mpemba E.B., Osborne D.G., 1969). The reason for this paradox, according to the authors' [10] opinion, is hydrogen bonds in water, which increase as its temperature increases, and presence of strongly connected clusters in it, which together ensure rapid appearance of ice with hexagonal structure in water upon sharp cooling of boiling water.

As per now, data about frozen sand-water and other similar mixtures properties in terms of their using in foundry industry for foundry molds and cores manufacturing are limited and are of exclusively fragmentary nature. In particular, Gruzman V.M. (1983) in his works determined sand-water frozen mixtures' mechanical and thermo-physical properties, their filtration characteristics. He showed impossibility of increasing solidification rate of foundry castings molds made from frozen sand-water mixtures, outlining conditions of destruction of frozen molds surface by molten steel flow and thermal radiation from its free surface, etc. N.I. Tarasevich with coworkers (2000) dealt with modeling the process of heat transfer in frozen mixtures. In works by Mynov Susumu and his colleagues (1980) and investigation [10], the authors established the fact that frozen mixtures strength increases with

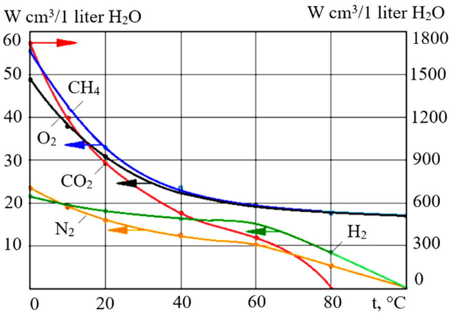


Fig. 1. Dependencies of maximum volume of gas dissolved in distilled water on its temperature (*Namiot A. Yu., 1991*)

their temperature decreasing. At the same time, one of the main factors that also significantly increases frozen mixtures strength is water content in mixture. Clay and quartz sand fraction reduction increase mixtures strength less effectively. At the same time, sand-water mixture frozen at –60 °C with 5 % water compressive strength can reach 8–11 MPa [11].

In a work by Solonenko L. I. (2018), it has been discovered that in order to increase strength and reduce crushability in mixture for manufacturing frozen casting molds, it is advisable to use 5 % (by mass) of fresh water and 5 % (by mass) of bentonite clay at freezing temperature not higher than –19÷ –20 °C. At the same time, clay nature, its content in molding mixture, as well as water and clay preparation method before molding have a decisive effect on frozen molds' strength and crushability. Quartz sand mixtures with 5 % boiled water and 5 % swollen bentonite clay have the greatest strength and the least crushability. Similar indicators are slightly lower in mixtures with non-swollen clays and CO_2 carbonated water. Sand mixture with 5 % of tap water and 5 % of swollen bentonite clay has average strength and one of the lowest crushability.

In order to accelerate sand-water mixtures' freezing time, the authors [12] have proposed a complex process of frozen casting mold production. In this case, low-temperature forming technology is combined with control of time and creation place of ultra-low temperature. The authors of [13] cooled sand in contact with cooling liquid, and then mixed it with wet suspension and mixture. The authors in [14] cooled water to freezing at least partially before or during mold forming process. For increasing frozen casting mold and cores strength and surface hardness, the authors [15] suggest putting additionally amide, carbon or polyether fibers with length of 1–4 mm into the mixture.

Technical and ecological attractiveness of obtaining castings in frozen molds process has contributed to various technologies that use frozen water development [16, 17]. In particular, version of containerless casting process, which is formed from frozen sand, is considered in [18]. Rapid prototyping casting technology branch includes the patent [19], where future casting mold working cavities are mechanically cut out from frozen sand-water mixture using a 3D-milling machine, etc.

Within development of the idea of making castings in frozen molds as such, other scientific and technological directions have been found. In particular, M. I. Zamyatin's research (2013) is devoted to elaboration of anti-burnt paint compositions for foundry molds from frozen mixtures. In his works, Doroshenko V. S. investigated possibilities and methods of quartz sand casting molds based on ice castings models [20, 21] manufacturing, etc.

A feature of any product made from frozen mixtures is limited time of their use at given air temperatures, that is, their vitability. Among the factors that determine frozen mixture vitability are water amount in it, initial freezing temperature, presence and nature of dust-like impurities in a mixture, ice structure in intergranular cuffs, etc. At the same time, ice structure largely depends on dissolved gas in water volume. That is, frozen mixture vitability should also depend on water used in mixture preparation method. But almost in all studies on these mixture types carried out today, authors do not take into account their ice structure – cuffs between sand particles. Such data absence does not allow giving an unequivocal answer about the influence of used water condition on one of the frozen mixture's most important properties – its vitability, as an indicator of maximum permissible mold or core delaying time from the moment of its freezing to mold filling with melt. At the same time, this allows one to enhance the understanding concerning possibilities of frozen mixtures in foundry production implementation and to develop reasonable recommendations for their use.

In this regard, study on influence of water preparation conditions on ice structure and frozen sand-water and sand-clay-water mixtures' vitability is a relevant task.

Purpose. Work purpose was to establish regularities of influence of water preparation conditions, clay component nature and its preparation conditions on sand and water, as well as sand, water and clay frozen mixtures vitability.

To achieve the purpose, the following tasks have been solved in the work:

1. To investigate the influence of impurities and water preparation conditions on the quality of its ice.
2. To investigate the influence of ice quality on frozen sand-water and sand-clay-water mixtures' vitability and to establish samples of frozen mixtures in air destruction kinetics under their own weight influence.
3. To establish relationship between frozen mixtures' indicators of viability adopted in the work.
4. To optimize main technological parameters of sand-water mixture water preparations according to vitability indicators.
5. To elaborate recommendations concerning sand-water and sand-clay-water mixtures use for manufacturing frozen products.

Methods. In the present research we used: quartz sand with an average particle diameter of 0.2 mm and clay content of up to 0.1 % (by mass); distilled water and distilled water solution with 3 % (by mass) H_2O_2, fresh artesian ("raw", boiled) water; fresh artesian water saturated with CO_2, sea water (solution of 1.5 and chemical purity 5.0 % NaCl in distilled water). Boiled fresh artesian water is prepared by heating it to 100 °C in enameled container followed by holding it in boiling state for a given time (from 1 to 30 min). Water is heated and boiled in free surface open to environment conditions. According to the research schedule, upon finishing to boil the water, it is used in hot (at 99 ± 1 °C) or quickly cooled (cooling in test tube for 1 min to 24 ± 1 °C) state.

Influence of water condition and its preparation for crystallization method on ice quality is estimated visually (qualitatively) after hardening water in glass tubes with an internal diameter of 8 mm (Fig. 2, *a**) at ice in tubes cross sections level according to the diagram in Fig. 2, *b**.

According to visual assessment of ice in test tubes, using schemes in Figs. 2, *b** and *c**, its quality is indicated by appropriate index. That is, if in cross-section A (Fig. 2, *b**) in test tube (Fig. 2, *a**) the ice looked similar to scheme "*a*" in Fig. 2, *c*, in section B – similar to scheme "*d*" in Fig. 2, *c*, and in section C – similar to scheme "l" in Fig. 2, then such ice quality is characterized as *Aa-Bd-Cl*.

According to the obtained data on ice quality, water preparing method for freezing is selected and technology parameters for manufacturing frozen sand-water mixtures from it are optimized.

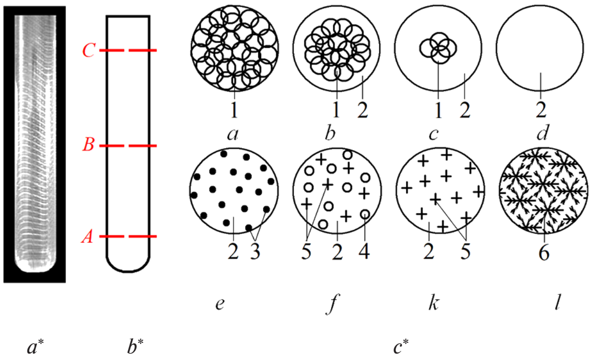


Fig. 2. Appearance of a test tube with distilled water at background of corrugated surface (*a**), *scheme of control cross-sections location in ice samples* (*b**), *scheme of gas and salt inclusions distribution in ice cross-sections structure* (*c**):

1 – gas bubbles; 2 – ice without inclusions (*dense ice*)*; 3 – crystal hydrate of hydrogen peroxide particles* ($H_2O_2 \cdot 2H_2O$)*; 4 – big individual gas bubbles; 5 – sodium chloride crystal hydrate particles* ($NaClO_2 \cdot 3H_2O$)*; 6 – snow*

In order to identify ice quality influence on frozen sand-water and sand-clay-water mixtures' vitability, beam-type samples from mixtures (Tables 1–3) are studied that were cooled to –15 °C followed by holding them in air at +24 ± 1 °C up to their destruction.

Table 1

Compositions of sand-water mixtures

Sample	Quartz sand and water mixtures' compositions , % (by mass)					
	Water					Quartz sand
	Artesian				Sea water (5 % NaCl) at 24 ± 1 °C	
	Boiled during 30 min		"Raw" (basic) at 24 ± 1 °C	Saturated at 24 ± 1 °C		
	Hot at 99 ± 1 °C	Cooled to 24±1 °C				
S1	5	–	–	–	–	95
S2	–	5	–	–	–	95
S3	–	–	5	–	–	95
S4	–	–	–	5	–	95
S5	–	–	–	–	5	95
S6	10	–	–	–	–	90
S7	–	10	–	–	–	90
S8	–	–	10	–	–	90
S9	–	–	–	10	–	90
S10	–	–	–	–	10	90

Table 2

Compositions of sand-clay-water mixtures with bentonite clay

Sample	Quartz sand, bentonite clay and water mixtures' compositions, % (by mass)						
	Water				Quartz sand at 24 ± 1 °C	Bentonite clay	
	Artesian					Clay swelling time in water, hours	
	Boiled during 30 min		" Raw" (basic) at 24 ± 1 °C	Saturated at 24 ± 1 °C			
	Hot at 99 ± 1 °C	Cooled to 24 ± 1 °C				0	24
B1	5	–	–	–	90	5	–
B2	–	5	–	–	90	5	–
B3	–	–	5	–	90	5	–
B4	–	–	–	5	90	5	–
B5	5	–	–	–	90	–	5
B6	–	5	–	–	90	–	5
B7	–	–	5	–	90	–	5
B8	–	–	–	5	90	–	5
B9	10	–	–	–	85	5	–
B10	–	10	–	–	85	5	–
B11	–	–	10	–	85	5	–
B12	–	–	–	10	85	5	–
B13	10	–	–	–	85	–	5
B14	–	10	–	–	85	–	5
B15	–	–	10	–	85	–	5
B16	–	–	–	10	85	–	5

Table 3

Compositions of sand-clay-water mixtures with kaolin clay

Sample	Quartz sand, kaolin clay and water mixtures compositions, % (by mass)						
	Water				Quartz sand at 24 ± 1 °C	Kaolin clay	
	Artesian					Clay swelling time in water, hours	
	Boiled during 30 min		"Raw" (basic) at 24 ± 1 °C	Saturated at 24 ± 1 °C			
	Hot at 99 ± 1 °C	Cooled to 24±1 °C				0	24
K1	5	–	–	–	90	5	–
K2	–	5	–	–	90	5	–
K3	–	–	5	–	90	5	–
K4	–	–	–	5	90	5	–
K5	5	–	–	–	90	–	5
K6	–	5	–	–	90	–	5
K7	–	–	5	–	90	–	5
K8	–	–	–	5	90	–	5
K9	10	–	–	–	85	5	–
K10	–	10	–	–	85	5	–
K11	–	–	10	–	85	5	–
K12	–	–	–	10	85	5	–
K13	10	–	–	–	85	–	5
K14	–	10	–	–	85	–	5
K15	–	–	10	–	85	–	5
K16	–	–	–	10	85	–	5

For manufacturing beam-type samples (18×18×155 mm) from tested mixtures, weights of corresponding components are prepared mixing them with each other. Mixture is poured into wooden equipment and manually is compacted in equipment working space. This process is schematically presented in Fig. 3.

After mixture compaction in its equipment, it is placed in a refrigerating chamber with temperature of –15 ± 1 °C for 24 hours. At the end of the process, the equipment is removed from the refrigerating chamber and within 10 s a frozen mixture sample is installed in horizontal position on supports that had a distance of 135 mm between them.

The investigation is conducted at the relative humidity of the environment of 60–75 %, air temperature of 24 ± 1 °C, and its movement velocity up to 0.5 m/s.

After the sample being installed on supports, on its central part cross-support a bar is placed and movable rod of a clock-

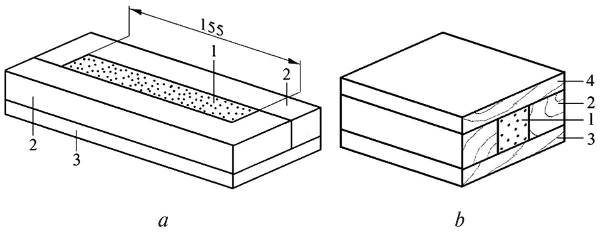


Fig. 3. Scheme of equipment for manufacturing beam-type sample, which is filled with compacted mixture (a), cross-section of equipment with compacted mixture during its freezing and transportation to test site (b):

1 – tested mixture (sample); 2 – side wall; 3 – basement; 4 – cover plate type indicator is positioned on it. This procedure is schematically presented in Fig. 4.

Time registration (a stopwatch switched on simultaneously with sample video recording) in the experiments is carried out from the moment of removing the sample from equipment. At the same time, the following are accepted as indicators of mixtures vitability:

- time (τ_1) from the moment of sample removal from the equipment to the moment of its deflection on supports by $f = 1$ mm;

- time (τ_2) from the moment of sample removal from the equipment to the moment of its destruction on supports (Fig. 4, *c*).

The procedure of optimization of technology parameters for manufacturing frozen sand-water mixtures is carried out based on simplex planning experiments results by constructing simplex triangles and superimposing their formatted images on each other with painted fields between isolines that corresponded to frozen sand-water mixtures' highest vitability.

For isolines constructing on simplex lattices have been used mathematical model, developed according to results of simplex-lattice plan realization for incomplete cube in ternary system H. Scheffe, and diagram in Fig. 5.

The mathematical model of an incomplete cube in ternary system according to H. Scheffe plan has the following form

$$Y = \beta_1 \cdot x_1 + \beta_2 \cdot x_2 + \beta_3 \cdot x_3 + \beta_{12} \cdot x_1 \cdot x_2 + \beta_{13} \cdot x_1 \cdot x_3 + \beta_{23} \cdot x_2 \cdot x_3 + \beta_{123} \cdot x_1 \cdot x_2 \cdot x_3, \qquad (1)$$

where Y is mixture property; β – regression coefficient; x – material in mixture amount (by mass) or parameter.

Regression coefficients for mathematical model (1) are calculated according to formulas

$$\beta_1 = \xi_1; \quad \beta_{ij} = 4 \cdot \xi_{ij} - 2 \cdot \xi_I - 2 \cdot \xi_j;$$

$$\beta_{123} = 27 \cdot \xi_{123} - 12 \cdot (\xi_{12} + \xi_{13} + \xi_{23}) + 3 \cdot (\xi_1 + \xi_2 + \xi_3),$$

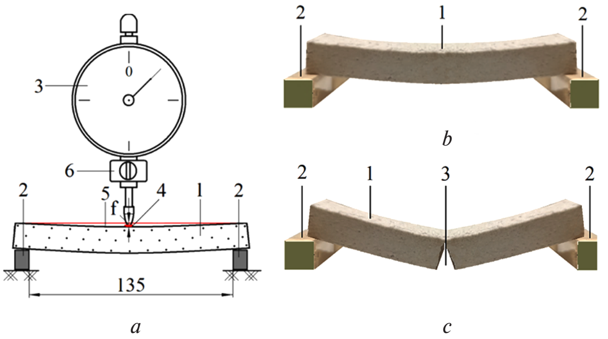


Fig. 4. Scheme for determining samples' (a) deflection beam radius (f), appearance of a sample with bending (b) and sample destruction (c):

1 – sample; 2 – sample supports; 3 – clock-type linear movement indicator; 4 – wooden cross-support bar (18 × 1 × 3 mm); 5 – upper sample surface after the testing time – τ_1; 6 – clock-type linear movement indicator fastener

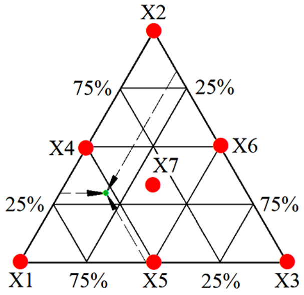


Fig. 5. Simplex triangle and its "keys"

where ξ_i, ξ_j, ξ_{123} are experimental results at simplex lattices' points (Fig. 5).

Results. To evaluate ice quality, water presented in Table 4 is frozen in glass tubes with initial temperature of 24 ± 1 °C.

Appearance of the ice from investigated water is presented in Fig. 6, and its quality index by visual assessment is given in Table 5.

From the analysis of images in Fig. 6 and data in Table 5 it follows that any influence on water (change in water chemical composition, water thermal treatment and thermal treatment duration, etc.) inevitably leads to its ice quality changing (Table 5).

In particular, hydrogen peroxide presence in water composition (s1* in Fig. 6) leads to its turbidity. It is well-known that, unlike fresh water, during crystallization hydrogen peroxide is compressed forming crystal hydrate $H_2O_2 \cdot 2H_2O$ white crystals. Obviously, exactly these crystal hydrates give water ice 1* uniform white color reducing its "living" cross-section by their presence.

Table 4

Water types frozen for the research

Water No.	Water type
1*	distilled water with 3 % H_2O_2
2*	sea water (artesian "raw" water + 5.0 % NaCl)
3*	sea water (artesian "raw" water + 1.5 % NaCl)
4*	"raw" artesian water
5*	artesian water cooled after boiling during 1 min
6*	artesian water cooled after boiling during 30 min
7*	saturated artesian water with exposure to air for 3 minutes before use
8*	saturated artesian water with exposure to air for 60 minutes before use
9*	"raw" artesian water after F\D cycle during 1min and exposure to air for 3 min
10*	"raw" artesian water after F\D cycle during 1min and exposure to air for 60 min
11*	artesian water boiled during 3 min water after F\D cycle during 1min and exposure to air for 3 min
12*	artesian water boiled during 3 min water after F\D cycle during 1min and exposure to air for 60 min
13*	artesian water boiled during 30 min and placed on freezing with initial temperature of 99 °C
14*	artesian water boiled during 30 min, cooled and exposed to air before freezing for 3 min
15*	artesian water boiled during 30 min, cooled and exposed to air before freezing for 60 min
16*	artesian water cooled after boiling during 5 min
17*	artesian water cooled after boiling during 10 min
18*	artesian water cooled after boiling during 20 min

Note: F\D – Freezing\Defrosting

Table 5

Quality index of ice from investigated water

Water No.	Ice quality index	Water No.	Ice quality index	Water No.	Ice quality index
1*	A_e–B_e–C_e	7*	A_l–B_l–C_l	13*	A_a–B_a–C_a
2*	A_k–B_k–C_k	8*	A_l–B_l–C_l	14*	A_b–B_b–C_b
3*	A_f–B_f–C_f	9*	A_b–B_C–C_C	15*	A_b–B_b–C_b
4*	A_b–B_c–C_b	10*	A_b–B_b–C_b	16*	A_a–B_C–C_C
5*	A_b–B_c–C_b	11*	A_b–B_C–C_b	17*	A_a–B_a–C_a
6*	A_d–B_d–C_d	12*	A_C–B_C–C_C	18*	A_a–B_b–C_a

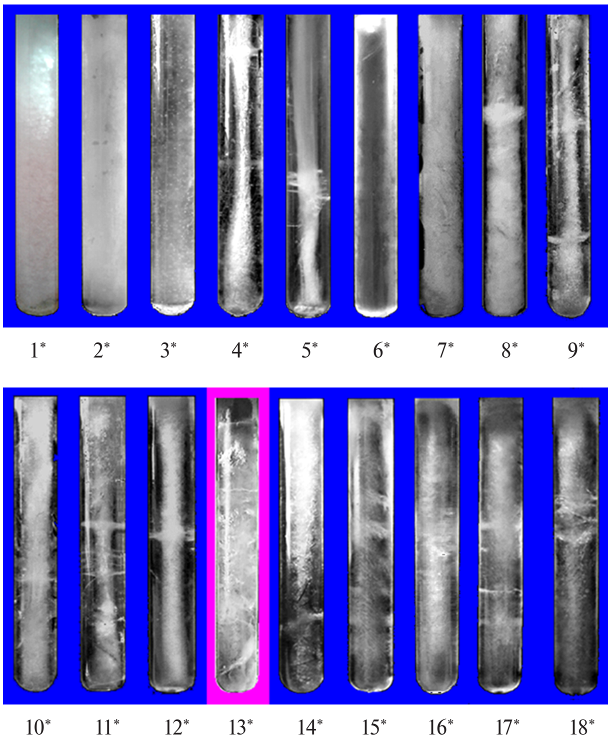


Fig. 6. Water ice appearance in test tubes Nos. 1^*–18^*

Similar situation is observed in seawater ice, where sodium chloride crystal hydrates are formed (2^* in Fig. 6). At the same time, at NaCl concentration in water decreasing (3^* in Fig. 6), not only sodium chloride crystal hydrates but also local gas bubbles appear in its ice.

In ice from "raw" artesian water (4^* in Fig. 6) and cooled artesian water after boiling for 1 min (5^* in Fig. 6), dense transparent ice regions are observed. Inside these regions gas bubbles' "frozen vortices" are located, respectively, of larger and smaller sizes. Reason for such "frozen vortices" appearance in ice structure is gases releasing into independent phase during water crystallization.

At the same time, there are no gas bubbles in ice from artesian water cooled after boiling for 30 minutes (6^* in Fig. 6). That is ice is dense in test tube any position. This indicates that boiled water cooling in test tube for 1 min to room temperature is not enough to re-saturate water with gases to their equilibrium state at room temperature.

Ice from saturated artesian water turns into snow – crumbly ice mass (7^* and 8^* in Fig. 6) regardless of exposure time under atmospheric pressure in air. Reason for this is excessive content of residual CO_2 (8^* in Fig. 6) dissolved in water. Its amount, even when kept at atmospheric pressure for 60 minutes, probably did not decrease in test tube to equilibrium concentration at room temperature.

F\D cycle realization also did not give positive result in terms of obtaining dense ice. In particular, ice from "raw" artesian water after F\D cycle for 1 min and exposure to air for 3 min is peripheral layer of dense ice with clearly defined "frozen vortex" inside (9^* in Fig. 6).

Carbonated water exposure time increasing in air from 3 to 60 minutes only led to ice dense surface layer thickness decreasing and spreading "frozen vortex" across cross-section (10^* in Fig. 6). It could be that such change in ice quality is result of additional water saturation with oxygen from air during its exposure to air and indirectly indicates the process' of excess CO_2 releasing from water low speed.

Similar to quality of ice from water 4^* and 9^* (with a "frozen vortex") has ice from artesian water boiled during 3 min after F\D cycle for 1 min and exposed to air for 3 min (11^* in Fig. 6), and within 60 minutes (12^* in Fig. 6). This indicates that short-term complex boiling action in combination with subsequent one-time F\D cycle also does not allow obtaining dense ice.

Ice from artesian water 13^* (Fig. 7), which has been boiled for 30 minutes and frozen with an initial temperature of 99 °C, has a large number of small gas bubbles evenly distributed in its structure. This shows that boiling water for 30 minutes allows removing most of gases dissolved in water from it. But, due to high solidification rate (Mpemba effect), even remaining amount of gases dissolved in water turns out to be sufficient to be isolated in an independent phase during rapid water crystallization.

From comparison of ice quality water 6^* (Fig. 6), 14^* and 15^* (Fig. 7), it follows that cooling time of water boiled for 30 min increased from 1 min for 6^* to 3 min for 14^* and 60 min for 15^* leads to water saturation with gases from air and does not allow obtaining dense ice.

Influence of artesian water boiling time from 1 to 30 min with its subsequent cooling for 1 min on ice quality can be seen by comparing the changes in ice structure from water 5^*, 6^*, 16^*–18^*, given in Fig. 6, where water 5^* has been boiled for 1 min, water 16^* – 5 min, water 17^* – 10 min, water 18^* – 20 min, water 6^* – 30 min. From specified water ice appearance analysis, it follows that with increasing boiling time, ice density increases. At the same time, completely dense ice is given by water 6^*, which has been boiled for 30 minutes. From this it also follows that water degassing by boiling is not fully realizing immediately after water reaches 100 °C, but requires certain boiling time.

As for Mpemba effect, based on data obtained about ice quality (4^* and 13^* in Fig. 6), this paper authors believe that hot water's faster, compared to cold water, crystallization is the reason of difference in their ice quality (density). That is, high initial temperature of freezing water causes a smaller amount of gases dissolved in it. This leads, during water crystallization, to formation of ice with greater density and, accordingly, greater thermal conductivity. In cold water are dissolved more gases (Fig. 1), and therefore its crystallization is accompanied by relatively large gas bubbles in ice formation. These bubbles reduce not only ice density and thermal conductivity, but also increase due to this cold water's crystallization time.

From the results of ice quality analysis, it follows that among the studied varieties of water and its preparation for freezing methods, there are only two methods that allow obtaining ice with uniform structure – with same quality throughout its volume:

- fresh artesian water freezing after boiling it for 30 min and cooling it quickly (within 1 min) to room temperature, which allows getting dense ice;

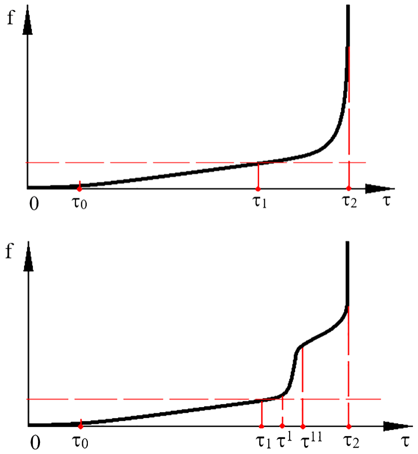


Fig. 7. Scheme for kinetics type "A" (a) and "B" (b) of frozen mixture samples' deformation, where: period 0–τ_0 is incubation period:

τ_0–τ_1 – period when deflection beam reaches bending value of $f =$ $= 1$ mm; τ_1–τ_2 – period of transition to sample failure, time τ^I and τ^{II} – limits of changes in sample deformation rate under its own weight

- fresh water previously saturated under pressure with CO_2 (carbonated water) freezing, which allows you to obtain snow (ice with crumbly structure).

In order to determine the effect of ice quality on frozen sand-water mixtures' vitability (τ_1, τ_2), deformation kinetics type and failure places of samples from frozen sand-water mixtures, appropriate preliminary studies are conducted. These results serve as classification features for a scheme of samples' deformation kinetics types. The adopted schemes are presented in Fig. 7.

According to Fig. 7, common to both schemes is initial stage ($0–\tau_0$) – incubation period in which samples deformation does not occur – and stage of samples deformation beginning at constant speed ($\tau_0–\tau_1$). Differences in frozen samples' deformation kinetics begin at reaching time τ_1. In this period ($\tau_1–\tau_2$) some samples are characterized by continuous deformation rate increasing (Fig. 7, *a*), others – deformation with variable rate, which, apparently, dealt with ice quality and processes of heat and mass transfer in capillary-porous media, which investigated mixtures are. Based on this, deformation kinetics of frozen mixtures samples with continuously increasing speed is designated as type "A" (Fig. 7, *a*), deformation kinetics of samples with variable speed – as type "B" (Fig. 7, *b*).

The results of τ_1, τ_2 determination and samples from frozen sand-water mixtures of deformation kinetics type are given in Table 6.

From the data in Table 6 analysis, it follows that in terms of frozen sand-water mixtures' vitability, it is advisable to use boiled fresh artesian water with subsequent cooling (S6) or carbonated water (S9). That is, mixtures with uniform ice quality throughout the entire volume of a test tube have the highest vitability. At the same time, ice should be either as dense as possible or maximum crumbly.

Based on this, S6 water and frozen sand-water mixtures' preparation parameters have been optimized to achieve vitability indicators highest values – τ_1 and τ_2.

In this investigation the following is optimized: water mass content in mixture (m, %); water boiling time until its filling into the mixture (τ_B); prepared mixture' exposure time in air before its installation in rigging into refrigerating chamber (τ_E). The implemented optimization-based experimental plan-matrix is presented in Table 7.

The calculated values of regression coefficients are given in Table 8.

Based on the Table 8 data, simplex triangles with frozen mixtures viability indicators' isolines have been constructed. Simplex triangles are presented in Fig. 8.

Based on the results of simplex triangles' scaled image superimposing, it was established that in quartz sand fresh artesian water the optimal content should be 7–8 % (by mass), water boiling time is τ_B = 28–29 min, prepared mixture's standing time at air in rigging before its cooling start – τ_E – 5–7 min. That is, frozen mixture preparation according to these parameters ensures its vitability in time τ_1 at least 250 s (~4 min) and in time τ_2 – at least 332 s (~5.5 min).

Table 6

Values τ_1 and τ_2, deformation kinetics type and frozen sand-water mixture's failure position

Water (according to Table 1)	Time, s		Deformation kinetics type (Fig. 7)
	τ_1	τ_2	
S1	200	253	B
S2	222	272	A
S3	180	242	B
S4	150	197	B
S5	0	0	B
S6	367	493	B
S7	260	333	A
S8	327	426	B
S9	373	485	B
S10	242	315	B

Table 7

Experimentally realized plan-matrix

Mixture code	Optimization parameters			Time, s	
	m, % (by mass)	τ_B, min	τ_E, min	τ_1	τ_2
X_1	8	29	2	210	302
X_2	8	29	10	202	290
X_3	4	1	10	143	198
X_4	8	29	6	261	360
X_5	6	15	6	204	280
X_6	6	15	10	170	234
X_7	6.67	19.6	7.3	194	275

Note: τ_B – water boiling time before its filling into mixture; τ_E – prepared mixture's exposure time in air before its installation in rigging into refrigerating chamber; τ_1 – sample deflection by 1 mm time; τ_2 – time to sample failure

Table 8

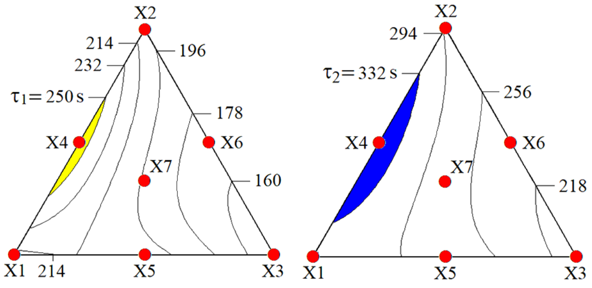
Regression coefficients

Parameter	Regression coefficients						
	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{123}
τ_1	210	202	143	261	204	170	294
τ_2	308	290	198	256	12	-40	-693

From technological point of view about using prepared water for manufacturing frozen products from sand-water mixtures, carbonated water is more technological. This is due to the fact that saturated water retains its foaming ability during crystallization for a long time (at least 1 hour) in air, has no thermal-time limitations during using and storing. Also, its preparation is faster and less energy-intensive compared to boiled water.

At the same time, frozen sand-water mixtures' time τ_1 and τ_2 values depend only on mass content of carbonated water in it, as evidenced by the data in Table 9 and dependences in Fig. 9.

Regarding sand-water mixtures vitality, effectiveness of using hot boiled and cold saturated water is explained in the following way. From the Table 6 data it follows that ice acquires uniform structure only in a case of boiled water's rapid cooling before freezing or in a case of using saturated water. During sand-water mixture preparation, hot boiled water is mixed with relatively cold quartz sand, which makes it possible to cool water quickly exactly before freezing in mixture. As a result, probably, dense ice cuffs, which have appeared between frozen mixture particles, provide it with gas permeability and vitability increasing. In a case of using saturated water in mixture, ice takes the form of snow which has high porosity. At the same time, ice with such structure expands significantly during its formation and fills entire space between sand grains in mixture. As a result, contact points number between sand grains and porous ice in the mixture increases, and its vitabil-



a *b*

Fig. 8. Simplex triangles for τ_1 *(a) and* τ_2 *(b)*

Table 9

Saturated water content in sand-water mixtures and their vitability

Saturated water mass content, %	0	3	5	8	10
τ_1, s	0	90	150	275	337
τ_2, s	0	116	197	352	485

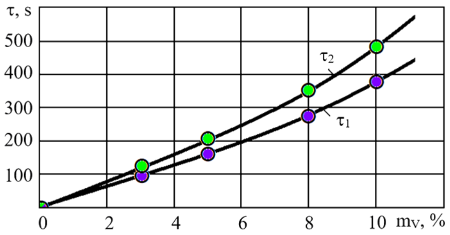


Fig. 9. Frozen sand-water mixtures time τ_1 and τ_2 dependences from carbonated water mass content

ity increases, with, probably, its gas permeability and thermal conductivity decreasing significantly.

The research results of sand-clay-water mixtures' vitability are given in Table 10.

From Tables 10 and 4 data analysis it follows that bentonite or kaolin clay addition in sand-water mixture increases its vitability. At the same time, according to the indicators adopted in this work, vitability of mixtures with kaolin clay is greater than with bentonite clay.

To achieve the greatest vitability, swollen or non-swollen bentonite clay can be added to boiled hot or cold water, as well as to "raw" water. In contrast to bentonite clay, greatest vitability is observed in sand-water mixtures with swollen or non-swollen kaolin clay when using "raw" water or with swollen clay in combination with hot boiled water.

In terms of manufacturability for using such mixtures in technological processes, in particular, for frozen foundry molds or rods manufacturing, sand-water mixture (K11) with non-swollen kaolin clay and "raw" water is more suitable provided the following composition (by mass): 85 % – quartz sand, 10 % – "raw" artesian water, 5 % – unswollen kaolin clay. Its samples' vitability in frozen at –15 °C condition is at least 8.5 minutes.

Table 10

Time τ_1, τ_2 and frozen sand-clay-water samples deformation kinetics schemes

Water (according to Table 2)	Time, s		Deformation kinetics type (Fig. 7)	Water (according to Table 1)	Time, s		Deformation kinetics type (Fig. 7)
	τ_1	τ_2			τ_1	τ_2	
Mixtures with bentonite clay				Mixtures with kaolin clay			
B1	262	334	B	K1	334	440	B
B2	251	331	A	K2	319	419	B
B3	269	328	A	K3	365	483	A
B4	305	370	A	K4	315	417	B
B5	306	382	A	K5	328	430	A
B6	302	381	A	K6	321	427	A
B7	329	424	B	K7	322	425	B
B8	233	311	A	K8	301	387	A
B9	384	548	B	K9	437	600	B
B10	379	511	A	K10	420	567	A
B11	427	551	B	K11	512	635	B
B12	434	557	B	K12	432	557	B
B13	382	513	B	K13	486	661	B
B14	419	545	B	K14	433	556	B
B15	370	499	B	K15	491	663	B
B16	366	488	B	K16	482	601	B

The Tables 6, 7, 9, 10 data being used, dependence between the indicators of mixtures' vitability adopted in this work has been plotted and is presented in Fig. 10.

From the dependence course analysis, Fig. 10, it follows that, within the scope of the research carried out in this paper, there exists direct proportional relationship between time τ_2 and τ_1, which can be calculated using a formula

$$\tau_2 = 1.28 \cdot \tau_1. \quad (2)$$

Therefore, dependence (1) is inherent for sand-water and sand-clay-water frozen mixtures regardless of water (among the water types studied in this research) used in these mixtures.

Conclusions.

1. Among studied water varieties and its preparation methods for freezing, only two methods by which it is possible to obtain ice with uniform structure have been discovered, they are:

- freezing fresh artesian water after boiling it for 30 minutes and cooling it quickly (within 1 minute) to room temperature, which allows you to get dense ice;

- freezing fresh carbonated water, which makes it possible to obtain snow – ice with crumbly structure.

2. Frozen sand-water and sand-clay-water mixtures' vitability (τ_1, τ_2) depends exclusively on water content mass in them and quality of ice formed during freezing.

3. The greatest vitability is inherent in frozen mixtures in which ice is exceptionally dense or crumbly.

4. Depending on ice quality mixtures' composition, their deformation kinetics under their own mass action can proceed according to schemes with continuously increasing or variable speed at the stage of sample transition to destruction.

5. Within realized research limits, directly proportional dependence existence between viability's indicators (τ_1, τ_2) adopted in this work for frozen sand-water and sand-clay-water mixtures has been established. Based on this, for frozen mixtures' relative vitability control only one indicator – τ_1 or τ_2 – could be recommended for using.

6. For sand-water mixtures, optimal fresh artesian water content in quartz sand is 7–8 % (by mass), time for water boiling is 28–29 min, time for air exposure of the prepared mixture before it starts to cool in equipment (mixture formation time in rigging) – 5–7 min. It ensures vitability for the samples accepted in this work by time τ_1 at least 4 min.

7. In terms of practical using of prepared water for producing frozen products from sand-water mixtures, more technological is carbonated water in amount of 10 % (by mass), which ensures vitability for samples accepted in the work as per time τ_1 at least 6 minutes.

8. Regarding manufacturability of products from sand-clay-water mixture, the most suitable mixture is the one containing (by mass): 85 % – quartz sand, 10 % – "raw" artesian water, 5 % – unswollen kaolin clay, whose samples viability in frozen condition at –15 °C according to time τ_1 is at least 8.5 min.

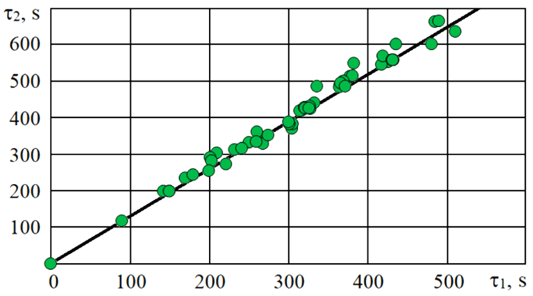


Fig. 10. Indicator τ_2 on time value τ_1 dependence

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Вплив структури льоду на живучість заморожених піщано-водяних і піщано-глинистих сумішей

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Мета. Встановити закономірності впливу умов підготовки піску, води та глини на живучість заморожених сумішей із комбінацій даних компонентів для підвищення якості виливків у ливарному виробництві, а також для вдосконалення технологій штучного заморожування ґрунтів під час підземного будівництва.

Методика. У дослідженнях використовували пісок, глину та воду. Якість льоду оцінювали візуально після заморожування води при –15 °С у скляних пробірках. Живучість заморожених при –15 °С сумішей досліджували на зразках балочного типу. Показниками живучості прийнято час до вигину на 1 мм зразків на опорах та час до їх руйнування. Час фіксували секундоміром, температуру – спиртовим термометром, масу – електронними вагами, стрілу вигину – індикатором годинникового типу.

Результати. Наявність і кількість водорозчинних домішок у вихідній воді суттєво впливають як на характер, розмір і розподіл газових бульбашок у льоді, так і на живучість заморожених піщано-водяних сумішей. Живучість заморожених сумішей зростає з підвищенням у них кількості води, і для сумішей пісок + вода живучість максимальна, якщо лід має однорідну структуру. Для сумішей із глинами найбільшу живучість має суміш із ненабряклою каоліновою глиною. З точки зору живучості розроблені рекомендації щодо виготовлення виробів із заморожених ливарних сумішей.

Наукова новизна. Уперше досліджена кінетика деформаційних змін (стріли вигину) під впливом власної маси зразків балочного типу із заморожених при –15 °С сумішей кварцового піску з водою та кварцового піску, глини й води, що були попередньо підготовані різними способами. Подальший розвиток отримали уявлення щодо впливу різних факторів та якості льоду на живучість заморожених сумішей.

Практична значимість. Отримані результати можуть бути корисними для розширення уявлень щодо поведінки природних мерзлих ґрунтів під час циклічних змін їх температури, штучного заморожування ґрунтів на будівництві метрополітенів під час проходження стовбурів шахт, ескалаторних і перегінних тунелів тощо. У ливарних цехах розроблені рекомендації дозволять скоротити технологічні втрати й підвищити якість виливків, що виготовляють із використанням заморожених ливарних форм і стрижнів із піщано-водяних або піщано-глинисто-водяних сумішей, моделей виливків і їх ливникових систем із піщано-водяних сумішей.

Ключові слова: *вода, пісок, глина, заморожування, живучість, лід, газ, домішки, руйнування*

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