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Phase Equilibria in Water–Salt Systems from Sodium, Magnesium, and Calcium Nitrates and Deicing Properties of Nitrate Compositions

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Abstract—Phase equilibria have been studied in the sections of $Mg(NO_3)_2$–$NaNO_3$–H_2O and $Ca(NO_3)_2$–$NaNO_3$–H_2O systems at the ratio of salt components from 3 : 1 to 1 : 3 at temperatures of 0 to –35°C. A series of nitrate compositions has been determined, which are promising as deicing agents. Their theoretical (under equilibrium conditions) fusion ability with respect to ice at –5 to –10°C has been calculated. The corrosion activity of the composition of calcium and magnesium nitrates (1 : 1) with respect to cement concrete (in collaboration with the test laboratory of OOO RSTs Opytnoe) has been measured. It has been found that the reagent meets criteria according to the action on cement concrete and can be used in aerodromes. This composition has been chosen as original for the development of a solid granular deicing agent on its basis for aerodromes.

Keywords: phase equilibria, deicing properties, water–salt systems, nitrate compositions

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INTRODUCTION

At present, there is an acute demand for the design of new low-temperature solid granular deicing agent for airfield pavements. Many years of experience in the application of deicing agents on the aerodromes of Russia shows that only solid granular agent provides the complete destruction of the sheet of glazed frost on the runway (R). Liquid reagents are employed for preventive treatment of R because they are hardly suitable for the destruction of the formed glazed frost.

The granular deicing agent NKMM, which was designed at the Institute of General and Inorganic Chemistry of the Russian Academy of Sciences [1], is intrinsic for relatively low fusion ability with respect to ice (3.0–4.0 g/g at –5°C) because it interacts with ice without evolution of heat. It is only effective up to temperatures of –12 to –15°C. This work follows investigations aimed at developing new effective low-temperature solid granular deicing agent for airfields.

EXPERIMENTAL

During the study of phase equilibria in water–salt systems, sodium, magnesium, and calcium nitrates of analytical grade were used as starting substances. To determine low-temperature eutectics, we studied the phase equilibria in the sections of $Mg(NO_3)_2$–$NaNO_3$–H_2O and $Ca(NO_3)_2$–$NaNO_3$–H_2O systems at the ratio of salt components from 3 : 1 to 1 : 3 at temperatures of 0 to –35°C. Studies were performed using the visual polythermal analysis [2]; liquid nitrogen was used as a refrigerant. The fusion ability of salt compositions of various contents with respect to ice was calculated according to polytherms of fusion (crystallization) of ice using the following equation: $A = (100 - C_1)/C_1$, where A is the fusion ability of the salt composition at the specified temperature and C_1 is the concentration of salts in the solution at the given temperature.

RESULTS AND DISCUSSION

Phase Equilibria in $Mg(NO_3)_2$–$NaNO_3$–H_2O and $Ca(NO_3)_2$–$NaNO_3$–H_2O Systems

The results of an investigation of phase equilibria in the indicated systems are given in Table 1 and Figs. 1 and 2. As follows from Table 1, a series of salt compositions is characterized by high deicing properties and they can be employed for the development of deicing agents. The highest fusion ability with respect to ice (7.3 g/g) is intrinsic for magnesium nitrate and the composition from magnesium and sodium nitrates (3 : 1 and 2 : 1). However, they only form eutectics with ice at temperatures of –27 to –31.5°C, which is only slightly lower than the temperature of the eutectics formed by the NKMM reagent. The lowest temperature of eutectics with ice among the metal nitrates

Table 1. Data on deicing properties of metal nitrates and nitrate compositions

No.	Systems	Characteristics of water–salt eutectics		Fusion ability at (–5°C), g/g	Fusion ability at (–10°C), g/g
		concentration, wt %	temperature of eutectics, °C		
1	$Mg(NO_3)_2–H_2O$	32.8	–31.5	7.3	4.5
2	$Ca(NO_3)_2–H_2O$	42.0	–29.0	5.6	3.2
3	$NaNO_3–H_2O$	38.0	–17.5	6.7	3.0
4	$Mg(NO_3)_2 + NaNO_3$ (3 : 1)–H_2O	35.0	–30.0	7.3	4.3
5	$Mg(NO_3)_2 + NaNO_3$ (2 : 1)–H_2O	34.0	–27.0	7.3	4.0
6	$Mg(NO_3)_2 + NaNO_3$ (1 : 1)–H_2O	34.0	–23.0	6.7	3.8
7	$Mg(NO_3)_2 + NaNO_3$ (1 : 2)–H_2O	35.0	–21	6.7	3.5
8	$Mg(NO_3)_2 + NaNO_3$ (1 : 3)–H_2O	36.0	–20.0	6.7	3.5
9	$Ca(NO_3)_2 + NaNO_3$ (3 : 1)–H_2O	46.0	–31.0	5.6	3.0
10	$Ca(NO_3)_2 + NaNO_3$ (2 : 1)–H_2O	45.0	–28.0	5.6	3.0
11	$Ca(NO_3)_2 + NaNO_3$ (1 : 1)–H_2O	42.0	–23.0	5.6	3.2
12	$Ca(NO_3)_2 + NaNO_3$ (1 : 2)–H_2O	45.0	–21.0	5.6	3.0
13	$Ca(NO_3)_2 + NaNO_3$ (1 : 3)–H_2O	40.0	–19.0	5.6	3.0
14	$Mg(NO_3)_2–Ca(NO_3)_2$ (1 : 1)–H_2O	40.0	–41.0	6.8	4.0
15	NKMM–H_2O	60.0	–26	4.3	2.0

under study, namely, –41°C, has been indicated [3] for the composition of magnesium and calcium nitrates (1 : 1). Consequently, it can be used as a deicing reagent at low temperatures of up to –30 to –35°C. Its fusion ability with respect to ice is significantly higher than that for the NKMM reagent (Table 1). This composition was chosen as the standard, based on which the development of solid granular deicing agent for airfield cement concrete pavements is planned. The investigation of the corrosion activity of the composition with respect to metals and alloys and the choice of the corrosion inhibitor were performed earlier in [1]. In this paper, the results of an investigation of this composition with respect to cement concrete are given.

Study of the Effect of the Composition of Magnesium and Calcium Nitrates (1 : 1) on Concrete

The aim of tests was to determine the corrosion activity of the composition of magnesium and calcium nitrates at a 1 : 1 ratio with respect to cement concrete in accordance with the OST 54-0-830-74–99 procedure "Civil Aerodromes. Chemical Reagents for the Fight Against Icing on Artificial Pavement. Technical Requirements." Tests were conducted compared with carbamide.

In order to provide the necessary degree of the validity of experimental results, three identical speci-

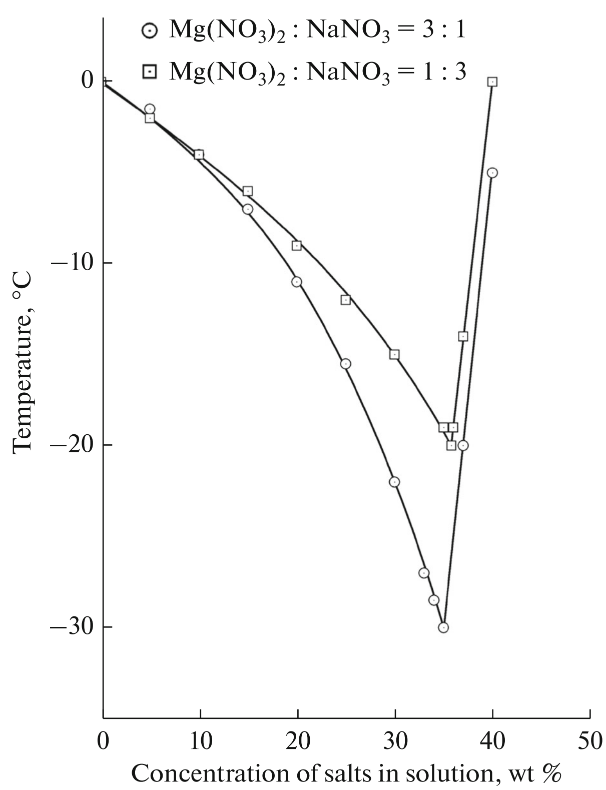

Fig. 1. Phase equilibria in the section of $Mg(NO_3)_2$–$NaNO_3$–H_2O system.

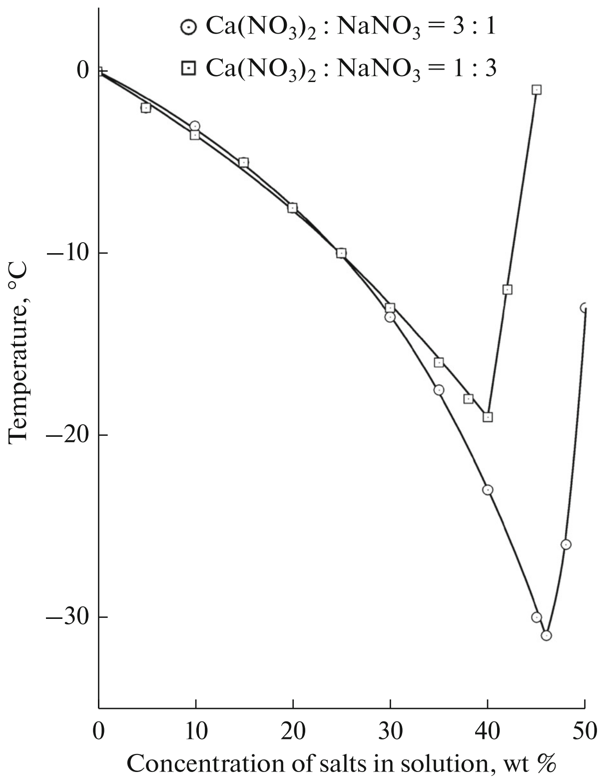

Fig. 2. Phase equilibria in section of $Ca(NO_3)_2$–$NaNO_3$–H_2O system.

mens with sizes of 100 × 100 × 100 mm in each series were tested. Freeze-thaw resistance of the surface layer of concrete was determined on an automated setup, which provides a decrease in and the maintenance of the temperature of the air medium in the working volume of the chamber, which corresponds to –30°C.

The specimens were prepared for tests according to GOST 10060–95. After saturation with water and the measurement of the volume by hydrostatic weighing according to GOST 12730.1–78, specimens were mounted by the test side down on the stand of the setup. After 1.5 h of achieving an air temperature of –30°C in the chamber; then, every 1 h, 5% aqueous solution of the specimen of nitrate composition and 10% carbamide solution were spilled along the tray.

The state of specimens during tests was controlled according to the change of their volume after particular number of cycles after their preliminary water thawing at 20 ± 2°C. The freeze–thaw resistance of concrete was considered, and the volume of the destruction of the surface layer of specimens reduced to the area of the test side, corresponding to 0.04 cm^3/cm^2, which coincides with the standard criteria on weight loss on one side (GOST 10060–95).

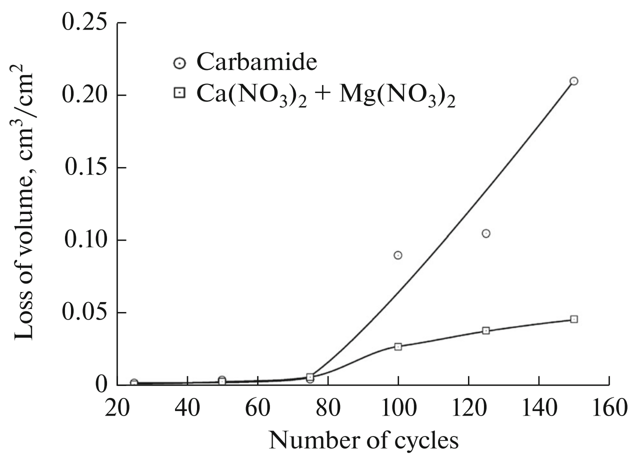

Fig. 3. Dependence of specific loss of volume of cement concrete specimens on the number of freeze–thaw cycles.

The results of the tests are given in Table 2 and Figs. 3–5.

Using the specific loss of volume, we calculated the aggressiveness of reagents with respect to concrete, (*Pa*), in relative units by the following equation: $(Pa) = M/(Ma)$, where M is the number of freeze–thaw cycles, which lead to a decrease in the volume of the concrete specimen in 10% carbamide solution by 0.04 cm^3/cm^2, and (Ma) is the number of cycles for an identical decrease in the volume of the concrete specimen in 5% solution of the salt composition. The reagent is considered applicable, if the aggressiveness (*Pa*) does not exceed 0.8.

As follows from the results of investigations, the aggressiveness (*Pa*) is $(Pa) = 90/125 = 0.72$ for the test nitrate composition. The nitrate composition can be recommended for practical applications as a deicing agent on cement concrete pavements on airfields.

Table 2. Specific loss of the volume of the surface layer of concrete

No.	Name of reagent	Loss of volume of specimens (mean in a series), cm^3/cm^2, for the number of freeze–thaw cycles					
		25	50	75	100	125	150
1	Carbamide	0.002	0.004	0.045	0.09	0.105	0.21
2	$Ca(NO_3)_2 + Mg(NO_3)_2$	0.001	0.003	0.006	0.027	0.038	0.046

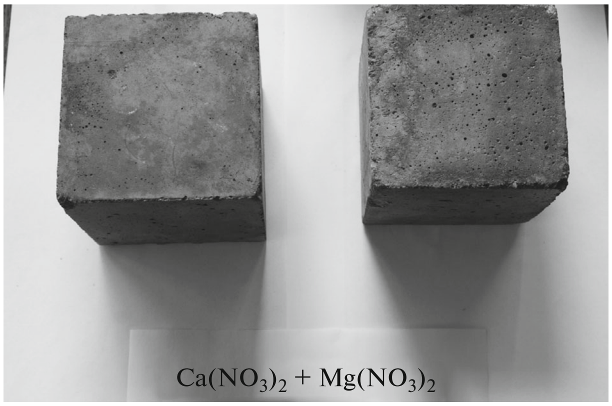

Fig. 4. State of cement concrete specimens prior to test.

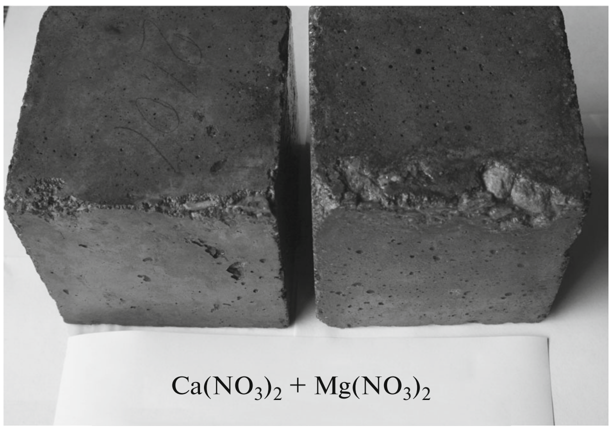

Fig. 5. State of cement concrete specimens after 125 freeze–thaw cycles in 5% $Ca(NO_3)_2 + Mg(NO_3)_2$ solution.

CONCLUSIONS

Phase equilibria have been studied in the sections of $Mg(NO_3)_2$–$NaNO_3$–H_2O and $Ca(NO_3)_2$–$NaNO_3$–H_2O systems at the ratio of salt components from 3 : 1 to 1 : 3 at temperatures of 0 to –35°C. A series of nitrate compositions has been determined, which are promising as deicing agents. Their theoretical (under equilibrium conditions) fusion ability with respect to ice from –5 to –10°C has been calculated.

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