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Deicers Based on Magnesium and Calcium Nitrates

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Abstract—Based on a study of the phase equilibria in cuts of a $Mg(NO_3)_2$–$Ca(NO_3)_2$–H_2O system at temperatures of 0 to –50°C, new deicers have been developed, including a liquid solution of magnesium and calcium nitrates and a solid composition of dehydrated nitrates. The ice-melting capacity of the agents under equilibrium conditions was determined. It was established that agents made of dehydrated magnesium and calcium nitrates interact with ice via heat release, which accelerates ice melting. The corrosion activity of liquid of a nitrate agent toward metals (in the collaboration with the All-Russian Institute of Aviation Materials) was determined. It was established that it can be significantly decreased at the introduction of a corrosion inhibitor. The possibility of synthesizing agents from natural mineral raw materials (dolomite, magnesite, and calcite) has been considered.

Keywords: phase equilibria, magnesium and calcium nitrates, deicers, ice melting capacity, corrosion activity, dehydrated nitrates

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INTRODUCTION

The development of new efficient and environmentally safe deicers and their methods their synthesis from natural and technogenic raw materials currently remains a topical chemical and technological problem.

The aim of this work is to find salt compositions forming low-temperature eutectics with ice in a $Mg(NO_3)_2$–$Ca(NO_3)_2$–H_2O system, to develop deicers on their basis and to determine the possibilities of synthesizing them from natural mineral raw materials. It is noteworthy that the solubility polytherm of this system was studied earlier [1]. In this work, the goals were different; thus, it is considered reasonable to perform a special study to find the low-temperature eutectics in this system.

EXPERIMENTAL

To find an optimal salt composition based on magnesium and calcium nitrates, the phase equilibria in the system with different component ratios (3 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 3) at temperatures of 0 to –50°C were studied. The studies were performed by visual polythermal analysis [2] (liquid nitrogen was used as a refrigerating medium. The diagrams of the phase equilibria in $Mg(NO_3)_2$–H_2O, $Ca(NO_3)_2$–H_2O systems and in the cut of a $Mg(NO_3)_2$–$Ca(NO_3)_2$–H_2O system with a 1 : 1 ratio between the nitrates at temperatures lower than 0°C are shown in the figure.

The ice melting capacity of the composition at preset temperatures was determined by the ice crystallization polytherms according to the formula $A = (100-C_t)/C_t$, where A is the ice-melting capacity of the composition (in kilograms of ice per 1 kg of agent) and C_t is the concentration of salts in the solution at the temperature t (°C). The results are summarized in Table 1.

It is noteworthy that the data characterize the ice-melting capacity of salts under equilibrium conditions. The real ice-melting capacity depends on the specific conditions, e.g., on the direction and power of the wind or the thickness and density of the ice. Dehydrated nitrates were synthesized at temperatures of 150 and 200°C in a drying chamber.

RESULTS AND DISCUSSION

In Table 1, the data on the deicing properties of magnesium and calcium nitrates and nitrate compositions are shown.

As follows from Table 1, a $Mg(NO_3)_2 + Ca(NO_3)_2$ composition (1 : 1) forms the lowest-temperature eutectic with ice at a temperature of –41°C and is characterized by a high ice-melting capacity.

The next step of the work was to synthesize dehydrated nitrates and to study the character of their interaction with water.

Table 1. Data on the deicing properties of salts and salt compositions

No.	Salts and salt compositions	Parameters of eutectics with ice		Ice melting capacity, g/g at temperature, °C	
		temperature, °C	concentration of solution, %	minus 5	minus 10
1	$Mg(NO_3)_2$	–31.5	32.8	7.7	4.5
2	$Mg(NO_3)_2 + Ca(NO_3)_2$ (3 : 1)	–33.0	35.5	6.8	4.3
3	$Mg(NO_3)_2 + Ca(NO_3)_2$ (2 : 1)	–34.5	36.5	6.8	4.0
4	$Mg(NO_3)_2 + Ca(NO_3)_2$ (1 : 1)	–1.0	40.0	6.8	4.0
5	$Mg(NO_3)_2 + Ca(NO_3)_2$ (1 : 2)	–31.5	38.5	5.7	3.5
6	$Mg(NO_3)_2 + Ca(NO_3)_2$ (1 : 3)	–31.0	40.0	5.7	3.4
7	$Ca(NO_3)_2$	–29.0	42.0	5.7	3.2

Data on the eutectic temperature in $Mg(NO_3)_2$–H_2O and $Ca(NO_3)_2$–H_2O systems (Nos. 1 and 7) correspond to the literature [3].

Table 2. Data on the composition of dehydrated nitrates

Composition of starting nitrates	Composition of nitrates dehydrated at temperature, °C	
	150	200
$Mg(NO_3)_2 \cdot 6H_2O$	$Mg(NO_3)_2 \cdot 1.7H_2O$	$Mg(NO_3)_2 \cdot 1.1H_2O$
$Ca(NO_3)_2 \cdot 4H_2O$	$Ca(NO_3)_2 \cdot 0.4H_2O$	$Ca(NO_3)_2$

Determination of the Conditions of the Dehydration of Magnesium and Calcium Nitrates and the Study of the Character of a Solution of Dehydrated Salts in Water

The samples of magnesium and calcium nitrates were dehydrated in a drying chamber at 150 and 200°C. The data on the composition of dehydrated nitrates are shown in Table 2. The samples of dehydrated magnesium and calcium nitrates and their mixture of the composition of 1 : 1 with a weight of 3 g were placed in 5 g of distilled water with a temperature of 19°C. After mixing and solving the precipitates, the solution temperature was measured. The data are shown in Table 3.

As follows from Table 3, the samples of dehydrated nitrates are soluble in water with heat release. With the use of the dehydrated salts as deicers, the melting rate of ice must increase. It is noteworthy that, in a solution a magnesium nitrate sample dehydrated at 200°C in in water, a low quantity of a flocculent precipitate is formed, which apparently indicates the formation of some quantity of insoluble hydroxonitrate as a result of the hydrolysis. Thus, to avoid hydrolysis, the starting nitrate should be dehydrated at a lower temperature (150°C). The next step of the work was corrosion testing for a 1 : 1 composition.

Table 3. Data on the change in temperature in a solution of dehydrated nitrates in water

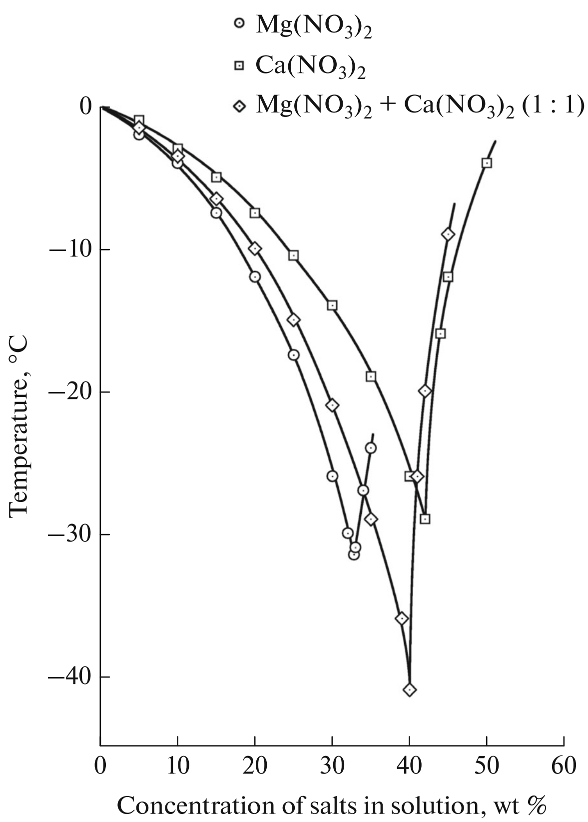
Composition of dehydrated sample	Maximum temperature of solution, °C
$Mg(NO_3)_2 \cdot 1.7H_2O$	37
$Mg(NO_3)_2 \cdot 1.1H_2O$	37
$Ca(NO_3)_2$	30
Mixture $Mg(NO_3)_2 \cdot 1.1H_2O$ + $Ca(NO_3)_2 \cdot$ (1 : 1)	34

Study of the Corrosion Activity of the Deicing Compositions Toward Metals and Alloys and Selection of a Corrosion Inhibitor

This part of the work was performed together with the All-Russian Institute of Aviation Materials. The studies for determining corrosion activity of the most promising deicing composition (a solution of magnesium and calcium nitrates in a ratio of 1 : 1) toward the common aviation materials were performed in accordance with the requirements of the OST 54-0-830.74-99 Civil airfields. Anti-icing chemicals for artificial surfaces. The technique of the corrosion tests is detailed in [2].

As a result of the performed tests, it was established that the studied sample of a deicing composition is corrosion active and, thus, does not meet the requirements of OST 54-0-830.74-99.

To decrease the corrosion activity of the composition, corrosion inhibitors were selected. The following



Phase equilibria in $Mg(NO_3)_2$–H_2O, $Ca(NO_3)_2$– H_2O systems and in cut of $Mg(NO_3)_2$–$Ca(NO_3)_2$–H_2O system with a ratio between the nitrates of 1 : 1 at a temperature lower than 0°C

corrosion inhibitors were tested: methenamine, trisodium phosphate (Na_3PO_4), D-1-Ts, IKB-4AF, IKB-6-2, D-1-Ts, IKB-2-2 (produced by IP NKhP AI RB), and experimental compositions of corrosion inhibitors produced by NPO Tekhnobior.

According to the results of determining the corrosion activity of the composition with corrosion-inhibiting additives, the inhibition of the composition decreases its corrosion activity to values that meet the requirements of OST 54-0-830.74-99. The most efficient inhibitors that decrease the corrosion activity of compositions are the inhibitors produced by NPO Tekhnobior.

Based on the results of the studies, two new deicers have been proposed, i.e., a solution containing 20% magnesium nitrate and 20% calcium nitrate and composition of magnesium and calcium nitrates dehydrated at 150°C with the $Mg(NO_3)_2$: $Ca(NO_3)_2$ ratio of 1 : 1.

In conclusion, it is noteworthy that deicers based on magnesium and calcium nitrates can be prepared from natural mineral raw materials, namely, dolomite, magnesite, brucite, and nitric acid.

As follows from [4], the magnesium and calcium contents in industrially used dolomite is such that, during the synthesis of nitrates from it, on average, the ratio between the quantities of magnesium nitrate and calcium nitrate in the final product is 0.75 : 1. To synthesize the most efficient nitrate composition with a ratio between nitrates of 1 : 1, it is necessary to introduce additional magnesium. For this purpose, magnesite $MgCO_3$ of brucite $Mg(OH)_2$ can be used.

The methods for the industrial production of magnesium and calcium nitrates from magnesite, brucite, dolomite, and calcite, $CaCO_3$, are in described in the chemical literature [5–7]. It is also noteworthy that these products are currently produced in the Russian Federation and are available for purchase.

CONCLUSIONS

The melting polytherms of ice in cuts of a $Ca(NO_3)_2$–$Mg(NO_3)_2$–H_2O system with different component ratios in the temperature interval of 0 to −50°C were studied. Compositions that form eutectics with ice at temperatures of −31 to −41°C and are promising for the development of deicers on their basis were determined.

The ice-melting capacity and corrosiveness to metals and alloys were studied for these compositions. An efficient corrosion inhibitor was selected.

The conditions of the synthesis of dehydrated magnesium and calcium nitrates were selected. Calcium nitrate tetrahydrate is almost fully dehydrated at 150°C, while magnesium hexahydrate loses 4.3 H_2O at this temperature and converts into $Mg(NO_3)_2 \cdot 1.7H_2O$. At 200°C, and magnesium nitrate is partially hydrolyzed with the formation of hydroxonitrate. It was established that dehydrated magnesium and calcium nitrates are soluble in water with a positive heat effect, which must accelerate the process of the dissolution of ice during their interaction with it.

The following substances are proposed as new deicers: a solution containing 20% magnesium nitrate and 20% calcium nitrate and a composition of dehydrated at 150°C magnesium and calcium nitrates with an $Mg(NO_3)_2$: $Ca(NO_3)_2$ ratio of 1 : 1.

The possibility of synthesizing a new nitrate deicer from natural raw materials, namely, dolomite, magnesite, and brucite, was considered.

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