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Contribution of Applied Chemistry to Maintaining Russian Highway Infrastructure in Winter

A. N. Glushko, E. A. Loseva, L. S. Kislyakova, A. M. Bessarabov, O. A. Zhdanovich, and R. A. Sandu

State Research Institute of Chemical Reagents and Special Purity Chemical Substances (IREA), ul. Bogorodskii val 3, Moscow, 107076 Russia
e-mail: tetrazoli@yandex.ru

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Abstract—The road maintenance key objective is to increase the wheel–road adhesion factor in the autumn and winter periods and, at the same time, preserve the quality of the bituminous concrete surface. With this aim in mind, chemical research institutions created anti-icing chemicals (AICs) that are used by highway services. The key physicochemical index of AIC quality is its melting salts content. The melting salts used are calcium chloride, sodium chloride, potassium chloride, or sodium formate. When the same pellet comprises all the required components in needed proportions, an anti-icing pelleted compound is best suited to serve the purpose of road maintenance in winter. Due to exothermal dilution of $CaCl_2$, the freezing point goes down to –20°C, and NaCl dissolution rate and ice-melting rate rise. The pellets penetrate deeply into ice right to the road surface and the solution breaks the ice-to-pavement bond, making it much easier to remove ice and snow.

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Given the geographical vastness of Russia, its highways play a most important strategic role. Binding together territories by means of mass transfer of cargo and passenger transportation, and providing access to various recourses, highway infrastructure decisively facilitates the development of constituent territories of the Russian Federation. By contrast, any unsettled problem seriously hinders economic advancement of both the country and its regions.

Due to their prominence among RF transportation sub-branches (see Fig. 1), highways are crucial in solving some of the most pressing political and economic issues facing the country today, such as:

– upgrading linkage between territorial entities of the RF and overcoming territorial disunity;

– streamlining the transport–infrastructure share in the gross domestic product;

– exploiting the advantage of transit capabilities and increasing exports of transportation services [1].

Highway transportation exceeds manyfold all other transportation systems (airborne, water-borne, and railroad) in terms of their key indicators (freightage, passenger carriage, length of communication lines, etc.). However, today's quality of the RF highway infrastructure is relatively low when compared with that in other countries.

Highway performance index is *quality of roads* [2]. The index is derived from opinion polls among companies' executives and experts based on a scale from 1 to 7, where 1 is the lowest score (roads are very bad) and 7 is the highest score referring to a ramified and effective system of roads according to international standards. Alternatively, quality of roads can be measured using EUROSTAT's or World Bank's quantitative data: length of the road network (including length of local, long-distance and interstate roads), types of road pavements and the amount of asphalt-covered roads, and road density (ratio of the length of the country's total road network to the country's land area).

Quality analysis using quantitative data gives a better understanding of the country's road network condition.

Road quality rating should be updated annually so that all the changes are taken into account.

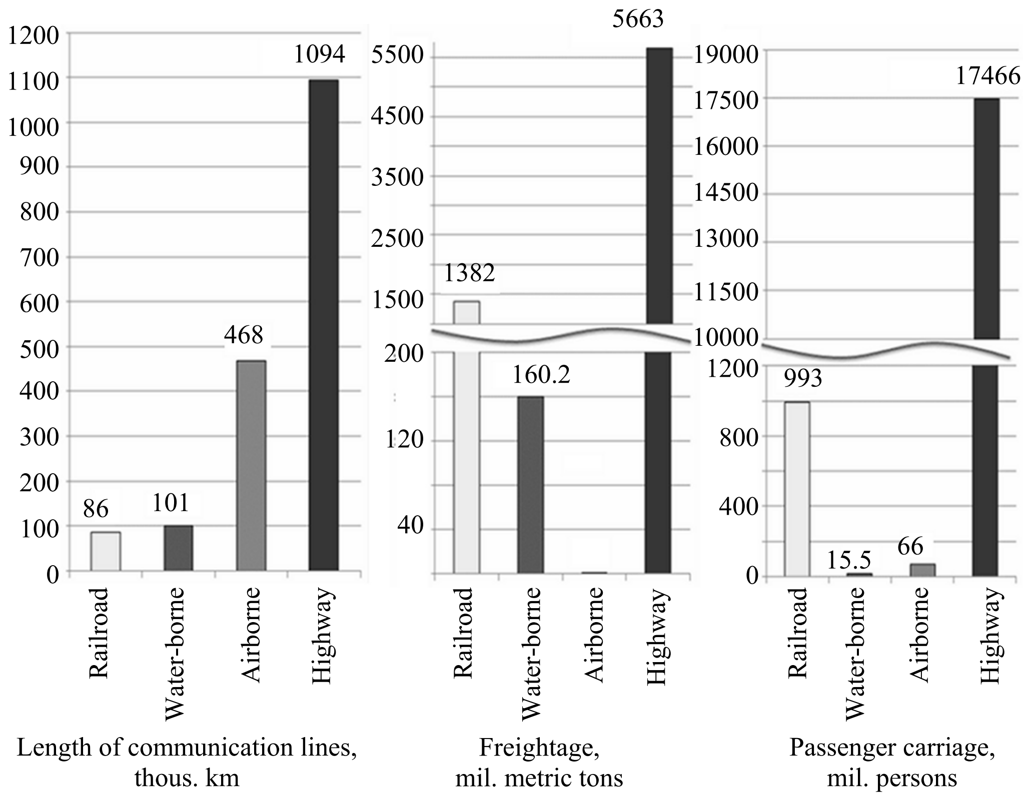


Fig. 1. Comparative properties of RF transportation sub-branches.

Roads are complex engineering structures, and their state is a direct function of how they are maintained and what technologies are used.

When applying international practices of road maintenance, we must remember that in terms of climatic, technological and other conditions the largest part of Russia's territory differs from any other country (Table 1) [3].

Therefore, international practices can be used only partially, and Russia's conditions require a particular approach to road-maintenance technologies.

The following four factors affect the selection of road-maintenance technology and, ultimately, the state of roads:

– Climatic and natural conditions;

– level of technological culture;

– state of roads;

– level of traffic load [1].

Ambient temperature, air humidity and the amount and type of precipitations affect the condition of the

Table 1. Comparative data on factors affecting road-maintenance technologies in the RF and foreign countries

Country	Climatic and natural conditions	Level of technological culture	Condition of highways	Level of traffic load
USA	–	–	–	+
Great Britain	–	–	–	+
China	–	–	+	+
Germany	–	–	–	+
Canada	+	–	–	–
Finland	+	+	+	–

Fig. 2. Roadway networks in (a) the USA and (b) China.

road asphalt-concrete surfacing, whether it is dry, wet or covered with snow and/or ice. The amount of sunshine (UV rays) is also part of the overall climatic environment, and it specifically influences the rate of decay of the asphalt surface course.

Therefore, climatic and natural conditions can be sufficiently described in terms of maximum and minimum air temperatures, amount of precipitations and amount of incoming solar energy.

In Moscow, during the autumn-winter season of 2013–2013, there were up to 70 cycles of ambient temperature passing 0°C, while in Canada, by contrast, there are usually no more than 14 such instances in a season.

The state of automobile roads depends on climatic and natural environment, overall technological culture including human factor, traffic load and, most importantly, on the traffic capacity of highway network determined by its pattern.

There are two types of highway network patterns in the world: grid and radial patterns. In the USA, the Interstate Highway System built in 1950s–1970s is a grid; China's National Trunk Highway System built in 1996–2010 is also a grid. In the Russian Federation, the highway network pattern is radial (see Fig. 2 and 3) [5].

Among important factors affecting highway network performance are also the following: its total mileage (which is, for instance, 11 times less in the RF than in the USA [6]); freeway mileage; road density (ratio of the network's mileage to the country's land area – in the RF it is 20 time less as compared with the USA [6]); average travelling speed (in Moscow, New York, London and Seoul figures are 21.8, 38.0, 29.6, and 38 km/h accordingly) [5]; rate of the highway network growth: ratio of the growth of the number of registered vehicles to the rate of highway network expansion (in the RF, over the period of 2000–2011, the number of vehicles had grown 1.8 times, while the increase in the highway mileage was only 12%, namely, from 898 to 1094 thousand kilometers [7]; quality of roads (for instance, there were 8% of hard-surface roads in the RF, while in France all roads were hard-surface [8]; time span after which road pavement loses its standard properties and requires repair (in the

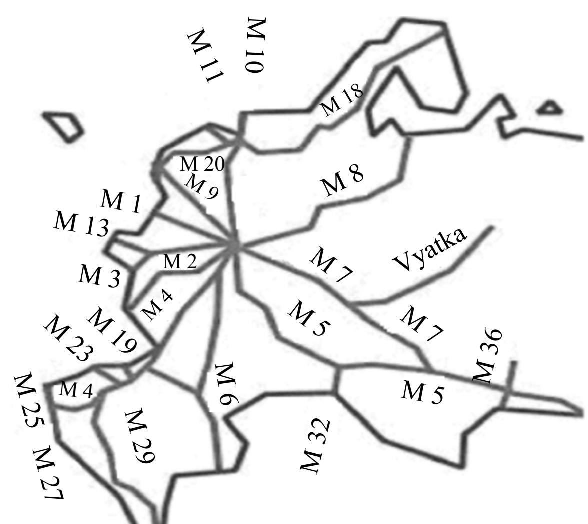


Fig. 3. Network of Federal roadways.

RF it is about 3 to 4 years, while in the U.K. it is about 18 to 20 years [6]); provision of proper road facilities (length of roads with illumination, communication means, road marking, safety fences and car-service stations).

Type of road maintenance needed directly depends on the character of traffic load. For instance, in a megalopolis it is best to have dry roads all year round. By contrast, in northern lands, where there is actually no traffic in winter, roads can be kept under packed snow [1]. Also, it is not infrequent that in some places a sudden heavy snowfall may break out that will leave the road services overwhelmed, and enormous traffic jams may form, as it happened on M1 highway near Tver, Russia, in the autumn-winter period of 2012–2013.

Traffic load is a function of the volume of freight and passenger traffic, of the number of motor vehicles per capita (for instance, figures for Moscow, New York, London and Seoul are 350, 900, 550, and 600 vehicles per 1000 residents, accordingly), and of the number of vehicles passing a reference point per unit of time. To compare flows of road traffic in different countries it is helpful to use:

– "humanitarian index," that is, ratio of total annual passenger performance (in passenger-kilometers) to total annual freight performance (in ton-kilometers) (figures for the EU, the USA and the USSR (1990) are 3 plus, 1.4 and 0.44, accordingly [9];

– and population mobility index (in the RF the mean value is 5,000 passenger-kilometers per capita, while in the USA it is 27.000 passenger-kilometers per capita) [5].

Technological culture is closely connected with social relations and economic capabilities. The quality of road-maintenance equipment, professional training of the staff and the necessity of taking into account the environmental effects of road maintenance measures: all this is determined by the level of technological culture.

The effectiveness of technological operations depends on two factors: performance standards for the maintenance of vehicle roads [10], and the resources used (materials, road-maintenance machinery and crews engaged). Under RF legislation [11], performance standards for road maintenance are governed by federal norms [12–15, 22] and some local norms, for instance, Moscow City norms [16–19, 23] and norms of the Moscow Oblast [20] regulating the order of road maintenance (it should be mentioned that winter and summer road-maintenance protocols differ considerably).

The condition of road infrastructure is of strategic importance in terms of reviving and furthering macroeconomic ties between Russia's regions and between Russia and neighboring countries. On the other hand, the development of road infrastructure speeds up the growth of national economy, living standards, workforce productivity and it also enhances the competitive ability of Russian goods and services.

Road density and quality of roads reflect the scientific and technological progress of a country and its economic advancement with the road-building sector ensuring the effectiveness of road infrastructure.

The road-maintenance key objective is to increase the wheel-road adhesion factor in autumn and winter periods and, at the same time, preserve the quality of the bituminous concrete surface. With this aim in mind, chemical research institutions created anti-icing chemicals (AICs) that are used by highway services.

Moscow City Department for Housing and Utilities Infrastructure (HUI) is in charge of taking care of the street and road network and of all the amenities. The HUI Department is also in charge of accepting, storing and supplying anti-icing chemicals and 2–5 mm crushed rock. It also checks consumption rates of anti-icing chemicals and 2–5 mm crushed rock at road facilities it services. Pursuant to the Government Decree of the City of Moscow no. 242–PP of April 10, 2007, the order of using anti-icing chemicals is regulated by the Inter-agency Task Force involving representatives from four Government Departments and three state unitary enterprises [21]. AICs turnover control (testing, bidding, delivery, and environmental impact assessment) is carried out by two other Moscow Government Departments. Laboratory studies and large-scale tests of AICs offered by manufacturers (suppliers) to be used in Moscow are carried out by chemical research institutions under the direction of the HUI Department.

There is a variety of norms regulating the use of AICs in Russia. The RF Ministry of Transportation has developed Requirements Applicable to Anti-icing Agents [14, 22] and Anti-icing Agents Testing Technique [15] used by Federal road-maintenance agencies in some RF regions. The Moscow City HUI Department has developed two documents: Guidelines on Clearance of the Traffic Areas of Roads, Streets,

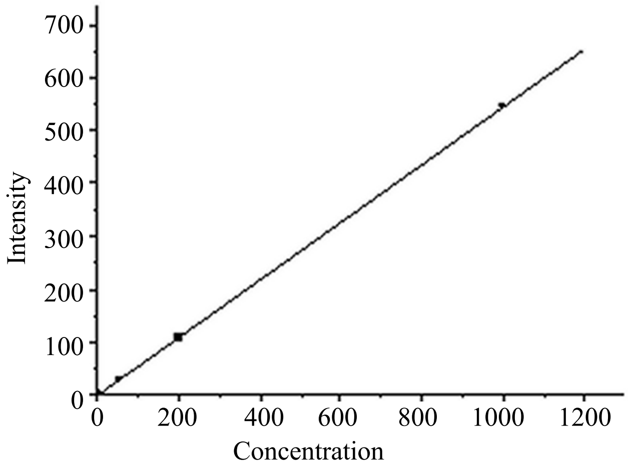


Fig. 4. Calibration for quantitative determination of potassium in AIC.

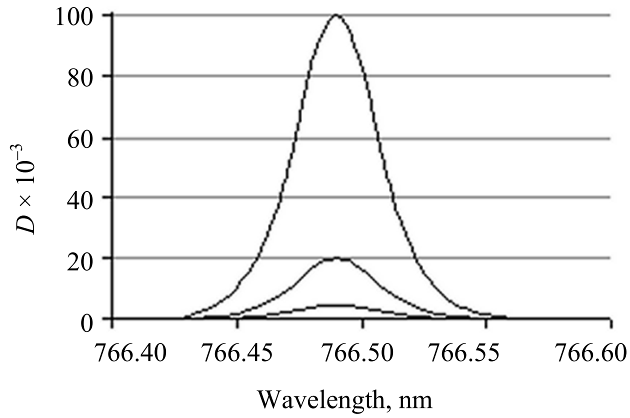


Fig. 5. Potassium analytical emission line.

Driveways, and Squares (Public Road Facilities of the City of Moscow) with the Aid of Anti-Icing Compounds, and Schedules and Process Lists on Complex Maintenance of Public Road Facilities in the Winter and Sommer Periods [16–19, 23].

There are also various practices of using AICs. Much experience in using AICs has been gained in the city of Moscow which is the biggest transport hub of the RF with all its subsequent problems exacerbated by complex natural climatic conditions. Moscow is the only city in the RF where a range of various AICs is used in winter [22]. To streamline methods of winter road maintenance based of the use of chemicals, the Moscow City government has been involving IREA's researchers.

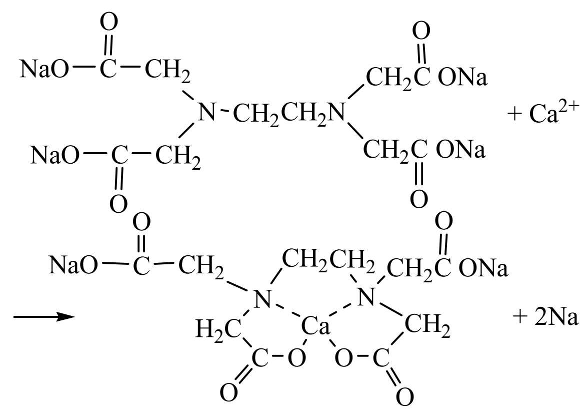
All the chemicals authorized for use [23] undergo incoming control, by certified laboratories, of their physical-chemical and environmental properties.

Key Performance and Qualitative Indicators of AICs

Total Melting Salts Content

One of the key physical-chemical indices of AIC quality is its melting salts content. The melting salts used are calcium chloride, sodium chloride, potassium chloride or sodium formate. In most cases, determination of these salts is carried out through titration.

Calcium chloride is determined by the complexometry method based on the formation of disodium dihydrogen ethylenediaminetetraacetate (Trilon B) [24]. The complexometric indicator used for determining the end point of titration is calcion:



Quantification of sodium chloride is performed by mercurimetry. Chloride ions are titrated in the presence of a diphenylcarbazone indicator.

Potassium chloride is determined by inductively coupled plasma atomic emission spectrometry. The calibration plot for determining potassium in AICs is shown in Fig. 4.

Presented in Fig. 5 is potassium analytical emission line at 766.490 Nm.

As seen from Figs. 4 and 5, the method features a high signal-to-noise ratio, and the correlation factor for the calibration curve is close to one. These data indicate high precision, reliability, and low detection limit of the method.

Tests of AICs samples showed that the weight fractions of calcium chloride and sodium chloride used as active material comply with the terms of supply to the city of Moscow. As to calcium chloride, some quality deviations were evidenced.

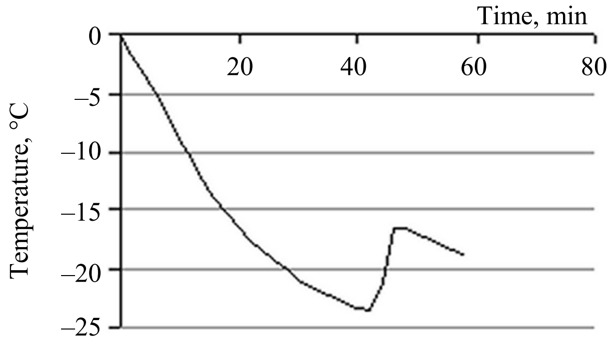


Fig. 6. Freezing curve for a 20% solution of MACsol.

Sodium formate is a new active material used in the AIC formula. It has a number of advantages as compared with calcium chloride and sodium chloride, namely:

– much lower corrosion rate;

– chemical stability

– resistance to aging at low temperatures of up to –20.

Its environmental impact is minimal, because when dissolved in water it undergoes complete biological degradation without causing any oxygen deficit in water environment.

A titrimetric method for quantitative determination of alkali formates in anti-icing compounds has been developed. It involves:

– processing aqueous solution of the sample with 0.1 mole/dm³ alkaline bromine solution and adding glacial acetic acid adjusting to pH 1;

– conditioning the sample at room temperature;

– adding potassium iodide hydrochloride solution and titrating with 0.1 mole/dm³ pentahydrate solution of sodium thiosulfate to light-yellow color;

– adding 0.5% starch solution in water and titrating to discoloring.

At the first processing stage, the redox reaction of formate with sodium hypobromite in an acetate media takes place. It is this reaction with the formation of alkalis bromide and carbon dioxide that eliminates the harmful influence of calcium chlorides in determining formates in the anti-icing compound [25].

AICs quality management showed that the anti-icing effect of sodium formate is identical to that of sodium chloride.

Evidence for the equality of anti-icing effects of the chemicals was obtained general physicochemical analysis of the freezing point depression of the solutions. Thermodynamic analysis showed that the freezing point depression can be represented by the ratio [26]:

$$T_0 - T = vm(RT_0^2/hW)\varphi,$$

where v is the stoichiometric factor; m, molality; RT_0^2/hW, cryoscopic constant (h is the latent molar heat of melting and W, molecular weight of water); and φ, osmotic coefficient. Therefore, it is obvious that the freezing point depression in case of one solvent totally depends on the value of the osmotic coefficient. The osmotic coefficients for sodium formate and sodium chloride at solution freezing points were calculated basing on literature data. It was demonstrated that for molar solutions the coefficients are φ(HCOONa) = 0.769 and φ(NaCl) = 0.776, accordingly, evidencing that anti-icing effects of both chemicals are virtually the same [1]. The advantage of sodium formate is that it does not have an adverse effect on top soil and vegetation. The less sodium chloride is used the better it is for the top soil and vegetation.

On the basis thereof, IREA Chemical Enterprise in cooperation with EuroChem Group has developed new liquid and solid AICs containing sodium formate. New AICs had been subjected to laboratory tests that confirmed their effectiveness. Launching them into manufacture at the Novomoskovsk CHLORINE factory has been planned.

Chilling Points of AICs

The chilling point and freezing range of ice and the chilling point of salt are important indicators of compound's quality.

The chilling points of AIC solutions are determined according to State Standard 18995.5-73 [27].

The chilling point of a solution of the multiagent anti-icing solid composition of calcium chloride, sodium chloride, potassium chloride and sodium formate (MACsol) as determined from the curve in Fig. 6 is –16.8.

Melting Ability

The most important technology parameter of AIC is its cost-effective melting ability which predicts the usage rate of AIC. Therefore, the determination of the actual value of the melting ability of AIC is an essential task when assessing the properties of a compound.

In comparing the effectiveness of anti-icing compounds it is useful to take into account the so-called equilibrium melting ability which can be computed basing on the dependence of solution chilling point on solute concentration [28].

The equilibrium melting ability is the maximum possible amount of ice (snow) that can be melted with 1 g of AIC at the given temperature conditions to achieve thermodynamic equilibrium of the solution–ice (or snow) system.

To determine the equilibrium melting ability, the AIC weight fraction–chilling point freezing curves are plotted. Curves are plotted for 1% to 25% aqueous solutions of AIC at varied temperature within the range of –1 to –20°C. The freezing curves are recorded automatically by means of a computerized apparatus for the determination of the chilling points of dilute solutions at ambient pressure (84.0–106.7 kPa) and temperature (20–30°C).

The chilling points of dilute solutions of the sample within the concentration range of 1% to the concentration (weight fraction) of the original solution or the eutectic concentration of a solid reagent are determined to plot the freezing curves of AIC solutions (Fig. 7).

The measurement results are processed using MS Excel. The experimental chilling points of dilute AIC solutions are used to obtain an AIC weight fraction–chilling point freezing curve which is drawn through the origin of coordinates (0; 0).

The equilibrium melting ability equation is a fourth-order polynomial, where y is the AIC equilibrium melting ability and x, AIC solution freezing point.

Studies showed that all the types of AICs used in the city of Moscow affect snow-and-ice bodies at temperatures not lower than –23°C.

Dynamic Viscosity of AICs

Viscosity of AICs solutions is the most important quality factor in terms of road-traffic safety. It is important both in liquid and solid compounds, because it affects the slipperiness of the surface processed, in other words, tire-to-surface friction factor [29].

Dynamic viscosity is measured by the time (in seconds) it takes for a given volume of AIC solution to leak under gravity out of a calibrated glass viscosity gage at constant temperature [15].

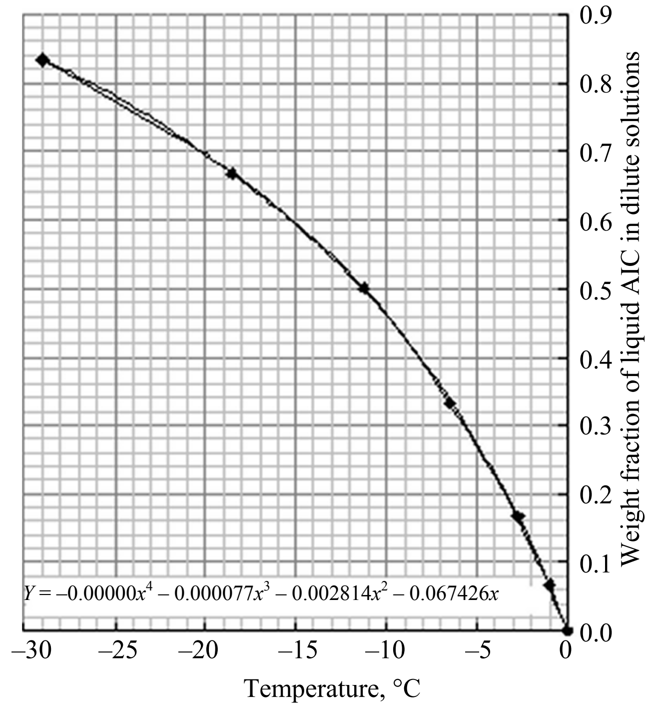


Fig. 7. Freezing curve of a liquid AIC sample.

Corrosiveness of Anti-Icing Materials

One of the reasons limiting the use of anti-icing compounds is that they cause corrosion of steel elements of vehicles and road furniture.

Corrosiveness of an anti-icing compound is tested on St3 steel plates by measuring the rate of weight loss per unit of surface per given time period, according to State Standard R 9.905-2007 [15].

Liquid-phase AICs are more corrosive than solid-phase ones.

pH Value

The pH value should be within the range of 5 to 9, because solutions with pH > 9 have an inhibitory action on vegetation, while solutions with pH < 5 are corrosive and also have an inhibitory action on vegetation.

A narrower pH range is not relevant due to the chemistry of salts contained in the compound.

The pH values are measured with a pH tester determining the electromotive force between a glass electrode and a reference electrode immersed in aqueous AIC solution [15].

Table 2. Requirements to particle size distribution in AICs

Particle size	Allowable weight percent
Above 10 mm	Not allowed
5 mm to 10 mm inclusive	No more than 10
Above 1 mm to 5 mm inclusive	No less than 75
1 mm and below	No more than 15

Specific Effective Activity of Natural Radionuclides

Specific effective activity of natural radionuclides is an important quality parameter of AICs. The activity rate is measured with a radiation meter РКГ-АТ-1320 А.

Natural radioactivity of all AICs is approximately the same: it is 12 times less than the acceptable activity rate of 370 Bq/kg.

Relatively higher levels of radioactivity occur when potassium compounds are present in the AIC.

Permissible Concentration of Hazardous Pollutants

Chemicals used for road maintenance in the winter time inevitably have an adverse effect on the environment, and all possible measures must be undertaken to minimize this effect.

Cd, Hg, Mo, As, Pb, and Se are detected by quadrupole mass spectrometry with inductively coupled plasma and Co, Ni, Cu, Cr, and Zn are detected by atomic emission spectrometry [30] using a multichannel photoelectric system. Fluorine is detected by potentiometric measurements.

Particle Size Distribution of AICs

In most cases, solid AICs are just mechanical mixtures of particles of various chemicals. The physical and mechanical properties of particles depend on their chemistry. For instance, $CaCl_2$ particles are much smaller than the NaCl particles.

The requirements to AIC particle size distribution (in weight percent) are given in Table 2 [15, 23].

However, AICs manufacturers do not always adhere to particle size distribution requirements. According to goal-oriented research, such under-performance will prove impossible when mechanical mixtures are replaced by pelleted AICs, as it is planned in the city of Moscow [31].

When in the same pellet there are all the required components in needed proportions, an anti-icing pelleted compound is best suited to serve the purpose of road maintenance in winter. Due to exothermal dilution of $CaCl_2$, freezing point goes down to –20°C, and NaCl dissolution rate and ice-melting rate rise. Pellets penetrate deeply into ice right to the road surface, and the solution breaks the ice-to-pavement bond making it much easier to remove ice and snow mechanically.

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