



POSSIBILITIES FOR THE USE OF CHEMICALS MATERIALS ALTERNATIVE TO CHLORIDES FOR DECREASING ROAD SLIPPERINESS IN WINTER

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Abstract. Having assessed in various aspects the study materials (salts), used for road maintenance in a cold period of the year, and taking a special consideration of the impact of these materials (salts) on the environment as well as their price, it could be stated that the most acceptable alternative for Lithuania is the already used sodium and calcium chloride salts. A large disadvantage of two materials (sodium chloride and calcium chloride) is that chloride ions strongly increase the speed of corrosion reactions of metals. Larger concentrations of chlorides aggravate vegetation processes and, thus, cause damage to roadside plants. Having assessed all the materials (salts) according to their chemical and physical properties and also according to their price and availability from technological point of view in the production, at present the following compounds could be distinguished: carbamide and calcium magnesium nitrates. When using calcium nitrate fewer chlorides get into the environment and the environment is less corrosive in regard to metals, however, here another problem occurs. If too large concentrations get into the environment, nitrates can cause pollution of ground water and soil. In future, having expanded the production of calcium and magnesium nitrates, it will be possible to start producing certain mixtures, e.g. carbamide with those nitrates or the mixture of carbamide, calcium, magnesium nitrates and calcium chloride, and, thus, to reduce a direct use of chlorides.

Keywords: winter road maintenance, decrease of slipperiness, calcium nitrate.

1. Introduction

Traditionally, winter road maintenance (decrease of slipperiness) requires the use of chemical materials on a base of chlorides. Sodium chloride is effective only until approximately 21 °C, calcium chloride – until 49 °C. However, calcium chloride is substantially more expensive than sodium chloride. A large disadvantage of those two materials is that chloride ions strongly increase the speed of corrosion reactions of metals. Larger concentrations of chlorides aggravate vegetation processes and, thus, cause damage to roadside plants. A molar mass of the study material, i.e. calcium nitrate, is about 1.5 times higher than that of calcium chloride. To achieve the same melting ef-

fect of ice (snow) the needed amount is 1.5 times larger. A good thing is that when using calcium nitrate fewer chlorides get into the environment and the environment is less corrosive in regard to metals, however, here another problem occurs. Nitrogen is the main biogenic element and the increase in its concentration at roadsides and roadside water bodies in a warm period of the year could initiate a more intensive increase in the green biomass. On the other hand, the solely increased nitrogen concentration will give no larger effect if there is no sufficient amount of other biogenic elements – phosphorus and potassium. Unlike chlorides, nitrate nitrogen would be assimilated by both various microorganisms and vegetation in early spring.

2. Alternative materials for decreasing road slipperiness in winter

With the rapidly increasing demand for developing and improving materials used in a cold period of the year to decrease ice melting temperature, the specialists seek for the ways to as cheap and environmental-friendly as possible produce synthetic products alternative to the rock salt (NaCl) used already for so long in winter road maintenance. This salt could be characterized by strong corrosive properties as well as the increase of salt content in underground waters. Sodium chloride is not recommended also because of its negative effect on vegetative processes of plants. The study materials include:

- ethane-1.2-diol (ethylene glycol);
- 1.2-propanediol (propylene glycol);
- 2-propanol (isopropyl alcohol);
- carbamide;
- sodium acetate;
- potassium acetate;
- sodium formate;
- chloride salts;
- calcium and magnesium nitrates;
- mixture of calcium magnesium acetates.

Ethane-1.2-diol (ethylene glycol). This is a colourless, highly water-soluble material having a high biochemical oxygen demand. Ethane-1.2-diol is a hazardous liquid for aquatic world and practically for all mammals, with a characteristic sweet taste. This is a volatile organic material which due to its volatility has a property to very quickly volatilize from the surface, it is harmful if swallowed (R-phrases: 22). Even small amount of ethylene glycol is hazardous to human life. Depending on its concentration, ethane-1.2-diol lowers water freezing temperature even up to $-50\text{ }^{\circ}\text{C}$. Due to its high volatility this material is able to self-remove from the environment (i.e. volatilize) very quickly but due to high pollution can be removed with the use of inert absorbing materials (e. g. sand, silica gel, wood-cement, universal binder).

1.2-propanediol (propylene glycol). By biochemical oxygen demand this material has stronger properties than ethylene glycol and remains in the environment for a longer time (up to 90% breaks down in 5 days). 1.2-propanediol is less toxic to flora and fauna than ethylene glycol. This is an especially highly water-soluble compound, also well soluble in most organic solvents. 1.2-propanediol is an odourless, colourless liquid. It lowers water freezing temperature up to $-29.5\text{ }^{\circ}\text{C}$, without doubt, depending on the amount of propylene glycol. This material is attributed to the risk phrases R10-flammable and R23-toxic by inhalation.

2-propanol (isopropyl alcohol, level B). This material, though having good stability and good both chemical and physical properties when using it in a cold period of the year, as a de-icing (i.e. temperature reducing) measure, is highly volatile, in the result of what if this compound gets in the form of vapour into various hot airplane parts at the airport it causes a sudden danger for a hardly-extinguishable fire. Due to this reason the use of 2-propanol in

the systems reducing water freezing temperature is strictly limited. This material can cause drowsiness and dizziness (this is shown by R-phases: R1 – highly flammable, R36 – irritating to eyes, R67 – vapours).

Carbamide. This is odourless, colourless crystals of tetragonal family. It is highly soluble in water, ethyl alcohol, liquid ammonia. When heated in $150\text{--}160\text{ }^{\circ}\text{C}$ temperature the split away ammonia and carbamide turn to prussic acid; the latter is partly polymerized and forms a biuret. When heated in a higher than $30\text{ }^{\circ}\text{C}$ temperature a water solution educes NH_3 and CO_2 during a carbamide hydrolysis. This material has a large biochemical oxygen demand (BOD) value. Carbamide breaks down into nitrogen-containing compounds, mainly into ammonia which is highly hazardous to aquatic flora and fauna, and speeds up algae formation. Based on UN Orange Paper, international transportation codes RID, ADR (EU agreement on transportation of dangerous goods), IMDG (transportation of dangerous goods by water) and international regulation on transportation of dangerous goods by rail transport) carbamide has not been classified as a dangerous material. The eutectic point of carbamide and water mixture is $-13\text{ }^{\circ}\text{C}$, when increasing or decreasing concentration of carbamide in the mixture with water the mixture freezing temperature raises. Carbamide is most effective at the ambient temperature up to $-7\text{ }^{\circ}\text{C}$. Impact on humans: when breathing for a long time larger than permissible carbamide concentration dust this can cause a chronic inflammation of bronchi and trachea mucous, a lesion of liver and kidney functions. The limit value of long-term effect is equal to 10 mg/m^3 .

Sodium acetate. This compound is sold as a granular solid material the purity of which reaches 97%. First of all, sodium acetate is less toxic to fish and mammals than carbamide and its biochemical oxygen demand is lower than that of carbamide in the result of what it remains in the environment for a shorter time and its possibilities to be used for the decrease of ice melting temperature are lower. Sodium acetate breaks down in the environment up to carbon dioxide and water making no significant toxic impact on the environment. The eutectic point of sodium acetate and water mixture is up to $-22\text{ }^{\circ}\text{C}$. This material is attractive in its cheap prices (20 t cost only 500–800 US dollars), therefore, it is produced in large industrial amounts. Sodium acetate is delivered in granular form and its consumption amount for the same operation as carbamide – to de-ice – is even 40% less than that of carbamide.

Potassium acetate. The eutectic point of potassium acetate is $-29\text{ }^{\circ}\text{C}$, however, the best efficiency is achieved up to $-9\text{ }^{\circ}\text{C}$. A very important property is that potassium acetate can act better than other salts as a conductor to electricity. It can be used as a moist solution before the use of sodium formate. Potassium acetate is used in lubricant up to 50%. It is not dangerous and low toxic material for flora and fauna, though, due to its conductivity to electricity it can cause large troubles in engineering. Potassium acetate is not a corrosive material and its biochemical oxygen demand indicator is close to that of sodium acetate and is lower than

that of carbamide or other measures. It is not dangerous for the environment since it breaks down only up to carbon dioxide and water.

Sodium formate. This material in its properties is very similar to potassium acetate and is composed of strong base and weak acid residual. The eutectic point of sodium formate and ice mixture reaches $-13\text{ }^{\circ}\text{C}$. It should be mentioned that the biochemical oxygen demand indicator of sodium formate is very low and this is, without doubt, favourable for the environment, however, its remaining effect for de-icing is lower. It is not dangerous for flora and fauna mainly because of the fact that its pH is about 7, and this is very important for solving problems related to the properties of corrosive non-freezing materials. Sodium formate is a hygroscopic material capable of absorbing moisture from the environment. Its consumption is almost twice less than that of carbamide. According to its composition and properties this material has not been classified as dangerous. It irritates eyes, airways and skin (the risk phases are R36/37/38).

Chloride salts. The very long ago used sodium chloride or rock salt (NaCl) is widely used for road spreading operations, though, in aerodromes it is completely prohibited due to its very strong corrosive effect. Sodium chloride, like calcium chloride, is a corrosive material strongly affecting and polluting underground waters and, thus, causing their high salinity. These materials make a large effect on various natural vegetative processes (Hill, McCreary 2008). Calcium chloride has been acknowledged as being more advantaged than sodium chloride since calcium chloride solutes in water and emits heat (an exothermic process takes place), in the result of which the adjacent materials are heated in a contact with soluting sodium chloride. Calcium chloride in a solution, depending on the concentration, reduces the melting temperature of a mixture with ice up to $-52\text{ }^{\circ}\text{C}$. Magnesium chloride is also widely used in a cold period of the year in spreading both the roads and the sidewalks. However, magnesium chloride has a harmful property to damage insulators and this in electrical engineering causes power-cut and a large danger of fire. Besides, like in case of sodium and calcium chloride, magnesium chloride is corrosive to steel and aluminium and this is dangerous in aviation. Anhydrous magnesium and calcium chlorides have a property to absorb moisture, therefore, they can be used to prevent fog on roads. The eutectic point of magnesium chloride and ice mixture is $-33\text{ }^{\circ}\text{C}$, though, the best efficiency of magnesium chloride is achieved up to $-15\text{ }^{\circ}\text{C}$. This compound is more hazardous for various vegetative processes than calcium chloride. But this is only for a comparison, since neither calcium chloride nor magnesium chloride are terrible destroyers of nature. Besides, magnesium chloride is more corrosive than calcium chloride. The salts containing chloride anions should be avoided as chlorides are hazardous for various species of aquatic world if their concentrations are close to 1000 mg/l (Kunkel et al. 2010).

Calcium and magnesium nitrates. These materials are well known and have been thoroughly studied when see-

king for their use in a cold period. However, they are still nitrates which affect both flora and fauna and stimulate vegetative processes, therefore, a wide use of these materials is still restrained. It is important to note that these materials have a characteristic lower corrosiveness than chlorides. Without doubt, nitrogen is one of the elements necessary for the animate nature but calcium and magnesium are also microelements structurally important for the vegetation. When using calcium nitrate as a measure to decrease the ice melting temperature, the melting temperature of ice and calcium nitrate mixture falls down even to $-49\text{ }^{\circ}\text{C}$ when concentration of calcium nitrate in initial solution amounts to about 50%. To achieve the mentioned temperature the amount of magnesium nitrate in initial solution shall make about 40% (Hill, McCreary 2008). Calcium and magnesium nitrates irritate eyes and skin (their risk phases are R36/38). Based on EU requirements the amount of nitrates in above-ground water shall not exceed 50 mg/l or 50 ppm (in parts per million) (Baltrėnas, Kazlauskienė 2009; Baltrėnas et al. 2006; Kamaitis 2008; Laurinavičius et al. 2010; Sivilevičius 2011).

Mixture of calcium magnesium acetates. To decrease the consequences of corrosion caused by chlorides when spreading roads with these mixtures, already in the 1970's the Federal Highway Administration (FHWA) of USA identified the mixture of calcium magnesium acetates as the low-corrosion chemical, compared to chlorides, alternative to rock salts and calcium chloride salts in a cold period of the year (Holleman, Wiberg 2001). The mixture of calcium magnesium acetates makes no effect on vegetative processes, however, the ions of magnesium and calcium make an effect on the environment (i.e. they harden water). One of the most important good properties of the mixture is that it is low corrosive to concrete, aluminium and steel, and that was proved by a series of tests. The mixture does not initiate algae formation processes and breaks up in approximately 5 days at $20\text{ }^{\circ}\text{C}$, in 10 days – at $10\text{ }^{\circ}\text{C}$, in 100 days – at $2\text{ }^{\circ}\text{C}$. Since calcium and magnesium are microelements necessary for the vegetation they may slightly affect growing of plants. The mixture of calcium magnesium acetates is not harmful for the environment as it breaks up to final decomposition products – carbon dioxide and water. The freezing temperature of the mixture of calcium magnesium acetates and water is about $-36\text{ }^{\circ}\text{C}$ when the concentration of acetate mixture amounts to approx 32.5% in water solution. In the mixture a molar ratio of calcium and magnesium is 3:7, respectively. In practice, the acetates are delivered in granular form, up to 91% of purity (Predyot et al. 2002).

Having studied de-icing materials that can be used and are effective for decrease of road slipperiness in winter, as well as other alternative materials (Petkuvienė, Paliulis 2009), calcium nitrate was selected for further investigation. One of the main reasons for this selection – this material is produced in Lithuania. Various possibilities to lower the freezing temperature of solutions have been studied, analyzed and assessed, a corrosive effect on metals in the environ-

ment was determined, also the impact on the environment and human health (Chollar *et al.* 1991; Locke, Kennelley 1998).

3. Ability of calcium nitrate to lower the freezing temperature of solutions

Rock salt has been used for road spreading already since 1930 when practical properties of rock salt were noticed to improve road condition in a cold period of the year. During long decades the other materials were also investigated those that are able to lower the freezing temperature of solutions (Leonovich *et al.* 2007). The most widely used materials for this purpose are given in Tables 1 and 2.

Table 1. The list of chemical materials most widely used for winter maintenance

Chemical material	The form of use	
	Bulk	Solution, %
Common salt (NaCl)	+	23
Calcium chloride (CaCl ₂)	+	~32
Magnesium chloride (MgCl ₂)	+	26–29
Calcium magnesium acetates*	+	25
Sodium formate (CHOONa)	+	–
Potassium formate (CHOOK)	+	–
Sodium acetate (CH ₃ COONa)	+	60
Potassium acetate (CH ₃ COOK)	+	49
Carbamide	+	30–35
Potassium chloride (KCl)	+	–

* – a mixture is obtained by treating dolomite with acetic acid

Table 2. Chemical materials able to lower the freezing temperature of water solutions if eutectic points are compared

Chemical material	Concentration, %	The lowest temperature, °C
Ethane-1,2-diol	66	–46
1,2-propanediol	50	–24
2-propanol	–	–
Carbamide	30–35	(–13)–(–7)
Sodium acetate	63	–29
Potassium acetate	–	–94
Sodium formate	–	–13
Magnesium chloride	26	–46
Sodium chloride	23	(–22)*–(–9)
Calcium chloride	29	(–43)–(–32)
Calcium nitrate	~50	–49
Magnesium nitrate	40	–45
Mixture of calcium magnesium acetates	32,5	–36**

* – eutectic point of sodium chloride (NaCl);

** – eutectic point depending on a ratio of calcium and magnesium acetates of the mixture

(given for the mixture where a molar ratio of Ca and Mg is 3:7, respectively)

Table 1 shows that potassium nitrate is not the most widely used material for winter road maintenance. For this purpose the other materials are most often used in a form of solutions, i. e. common salt, calcium chloride, magnesium chloride, etc. However, if their eutectic points are compared, calcium nitrate is attributed to the chemical materials that are able to strongly (even up to –49 °C) lower the freezing temperature of water solutions (Table 2). Whereas, sodium chloride, which is most often used for winter road maintenance, can lower the freezing temperature of water solutions only up to –9 °C–(–22) °C. Due to these and the earlier discussed reasons, calcium and magnesium nitrates are well known materials used for winter road maintenance in a cold period of the year.

4. Corrosive impact of calcium nitrate on metals

Only since the 1990's the inhibitors (corrosion reducing agents, mostly of organic origin) were started to be added to rock salt and various acetates: calcium, magnesium, potassium, sodium. To decrease the consequences of corrosion caused by chlorides when spreading roads with these mixtures, already in the 1970's the Federal Highway Administration (FHWA) of USA identified the mixture of calcium magnesium acetates as the low-corrosion chemical, compared to chlorides, alternative to rock salts and calcium chloride salts in a cold period of the year. Based on these arguments the same technologies were started to be used also in the West European countries.

In the laboratory the tests were carried out to determine the speed of corrosion of sodium chloride solutions with calcium chloride, calcium nitrate and carbamide agents. Solutions of the following concentrations were used:

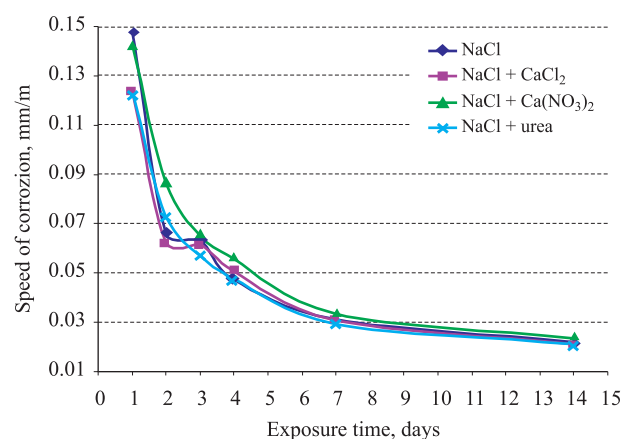
- 23% sodium chloride solution (where pH = 6.75);
- 23% sodium chloride solution and 30% calcium chloride solution in a ratio of (9:1) (where pH = 8.3);
- 23% sodium chloride solution and 30% calcium nitrate solution in a ratio of (9:1) (where pH = 4.3);
- 23% sodium chloride solution and 30% carbamide solution in a ratio of (9:1) (where pH = 8.5).

For the determination of corrosivity of solutions the steel plates (12×7×100 mm) of type 09Г2С were used. The speed of corrosion was determined by weighing method. The selected exposure time in the study solutions were 1, 2, 3, 4, 7 and 14 days. The exposure temperature (22.0 ± 1.0) °C.

The test was performed in the following way. The weighted metal plates were activated by immersing them into 30% hydrochloric acid solution, after that they were washed with water and immersed into the prepared appropriate solutions (volume of solution – 400 cm³). Having passed the selected exposure time in the study solution the plates were taken out, washed with water, immersed into 10% hydrochloric acid solution with urotropine, once

Table 3. The obtained results of corrosivity of the study solutions

Composition of the study solution	Exposure time in a solution, days					
	1	2	3	4	7	14
NaCl	0.147404	0.066390	0.063758	0.047380	0.031085	0.022033
NaCl+CaCl ₂	0.123421	0.062588	0.061743	0.050889	0.030918	0.021113
NaCl+Ca(NO ₃) ₂	0.142139	0.086571	0.064993	0.055764	0.033508	0.023342
NaCl+carbamide	0.123226	0.072922	0.057194	0.047672	0.029163	0.021183

**Fig. 1.** Comparison results of corrosivity of the study solutions

again washed with water, placed into a vessel with acetone, taken out, air-dried and weighted. The obtained results of corrosivity of the study solutions are given in Table 3 and Fig. 1.

The values of corrosion speed, given in Table 3, show that the largest corrosive activity in all solutions are in the first 24 hours. The largest speed is represented by sodium chloride solution (0.147404 mm/m) which is followed by sodium chloride solution with calcium nitrate agent (0.142139 mm/m). Corrosive activity of sodium chloride solutions with calcium chloride and carbamide agents is less and equals to 0.123421 and 0.123226 mm/m, respectively.

Having compared data on corrosivity of solutions, obtained after a longer exposure time in the study solutions, it is obvious that corrosivity of sodium chloride solution with calcium chloride agent is higher compared to corrosivity of sodium chloride solution (Fig. 1).

The especially large difference was obtained having compared the results of the speed of corrosion after 2 days of exposure time: the speed of corrosion of sodium chloride is 0.06639 mm/m, and the speed of corrosion of sodium chloride with calcium nitrate agent – 0.086571 mm/m. A lower corrosivity of sodium chloride solutions (after 4, 7 and 14 days of exposure) was obtained in the solutions with calcium chloride and carbamide agents. But the difference in the speed of corrosion in those solutions makes only several thousandth of mm/m (Table 3, Fig. 1).

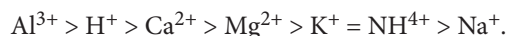
5. Migration of calcium ions in roadside soil

Calcium nitrate (Ca(NO₃)₂), chemical material used in winter road maintenance (to decrease road slipperiness), is highly water-soluble, thus, its ions (Ca²⁺ and NO₃⁻) are easily transferred by roadside soil into surface water bodies and ground waters. Mineral calcium (Ca²⁺), well soluble in soil water, is transferred by infiltration and filtration flows (precipitation) of atmospheric moisture through the surface of roadside soil and through its layers (depending on soil origin) into surface water bodies and ground waters. Calcium cations (Ca²⁺) in the ionic composition of calcium nitrate salts are considered the element of geographical landscape since their migration depends on the type and properties of soil. In dry, glacial-formed derno-podzole roadside soils, distinguished for their good infiltration properties, that are composed of about 90% of sand, 0.5–1 % of humus and the remaining part of light sandy loam, calcium cations (Ca²⁺) are transported by the surface of soil and washed out through its deeper layers into ground waters very effectively (even up to 95%). Thus, the flow of water on the surface of soil is increased, as well as surface destruction, and the soil erosion is induced. The amount of calcium cations (Ca²⁺) in soil is even more reduced due to the fallen acid needles of coniferous trees (especially pines) growing in wooded roadsides and due to good infiltration properties of soils of such roadsides (mostly sands).

Due to the fallen needles of coniferous trees the acid organic compounds are formed which acidify soil and through its layers wash out into ground waters up to 90–95% of calcium cations (Ca²⁺). Consequently, precipitation and water accumulated in roadsides easily wash out calcium cations (Ca²⁺) from acid soils (where pH is less than 7) into surface water bodies and ground waters.

Birches, black alders and oaks growing in fertile carbonaceous, loamy and clayey roadside soils of large-leaved vegetation landscape, where humus makes 3% and more, by their capillaries are able to feed on calcium originated from calcium nitrate used to decrease road slipperiness. Thus, every year the large-leaved vegetation of this species brings back into roadside soil up to 5–6 t/ha of calcium which together with other elements forms a floor of organic materials. Biological mass of organic falls under the effect of atmospheric phenomena and disintegration gives back to the soil many calcium cations (Ca²⁺) which

chemically neutralizes organic acids. For example, in the soils of such roadside landscapes the calcium (Ca^{2+}) and hydrogen (H^+) cations are continuously interacting which extrude from the absorbed biological mass the cations of magnesium (Mg^{2+}), potassium (K^+), ammonium (NH_4^+), sodium (Na^+) in the following way (Fig. 2):



Whereas, aluminium (Al^{3+}) cations are more resistant to wash-out than those of calcium (Ca^{2+}). Most often the composition of roadside soils of large-leaved vegetation landscape contains clays (i.e. aqueous rock with the diameter of particles less than $2\ \mu\text{m}$), therefore, humus and colloidal particles contained in soil create absorptive barriers of heavy metals.

Those colloidal particles of soil retain all elements contained in water solutions. For example, 1 g of colloidal clay particles, depending on their swelling degree, makes a $10\text{--}100\ \text{m}^2$ area surface and forms a large sorption capacity of soil surface.

Clay minerals and humus, contained in roadside soils of large-leaved vegetation landscape, always have a negative electric charge and absorb from solutions the cations of heavy metals (and also of calcium (Ca^{2+})). Colloidal particles of clay, contained in such roadside soils, create conditions for the accumulation of moisture of low initial capacity. Moisture capacity of soil decreases due to the swelling of colloidal clay particles. In this way a water runoff is formed on the surface of roadside soil. Increase in the density of clay particles adhesion in soil at a depth of up to 30 cm stabilizes infiltration and surface runoff processes in it.

Consequently, in roadside soils of heavy mechanical composition calcium cations (Ca^{2+}) are transported into surface water bodies more by its surface (up to 70–80%) but not through deep soil layers (up to 30 cm) having the largest accumulation capacity (Löfgren 2006; Marsalek *et al.* 2003; Ramakrishna, Viraraghavan 2005).

6. Migration of nitrate ions in roadside soil

With a dissolving calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) in the environment of roadside soils due to atmospheric precipitation, not only calcium cations (Ca^{2+}) are formed, migrating by the soil surface and through soil layers, but also the most harmful to the environment form of nitrogen – nitrate anions (NO_3^-). Due to a negative charge nitrates are very mobile in soil. They are more poorly assimilated by roadside plants, therefore, intensively migrate by soil, depending on its origin, into adjacent surface water bodies and ground waters. Nitrate anions (NO_3^-), having additionally appeared in soil, acidify the vibes (from 7.5 to 5.5 pH) and change the absorptive barriers of heavy metals. At that time hydrogen (H^+) cations extrude from the absorbed biological mass the (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) cations (Fig. 3).

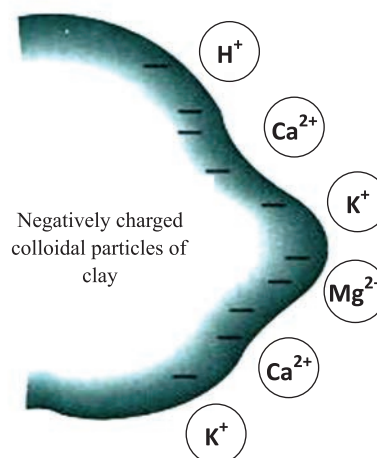


Fig. 2. Absorptive barrier of heavy metals in roadside soil

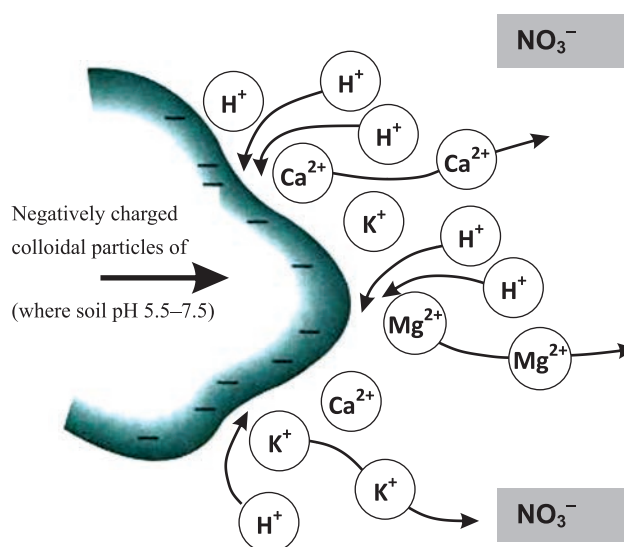


Fig. 3. Effect of nitrates on the absorptive barrier of heavy metals in roadside soil

Excess of nitrates in soil can negatively affect environmental quality. Large amounts of nitrates in soil (exceeding $130\ \text{mg/kg}$) can influence their rather large concentrations in ground water (more than $50\ \text{mg/l}$). Max permissible concentration (MPC) of nitrates in ground water shall not exceed the value of $50\ \text{mg/l}$. Based on requirements of EU directives, environmental measures shall be taken when concentration of nitrates in water is continuously increasing and reaches 75% of MPC (i.e. $37\ \text{mg/l}$). It is also important that soluble nitrogen compounds, having got from soil into water ecosystems, can disturb their balance by causing their eutrophication, decrease in the amount of oxygen in water and distinction of aquatic plants. Having got into human organism nitrates turn into nitrites that are capable to cause cancer, to turn haemoglobin into methemoglobin and to disorder oxygen delivery to tissues.

The self-wash of nitrates (NO_3^-) occurs in case when water, rotating through soil profile, together carries them out. The largest wash-out occurs (up to 95%) when plants poorly accumulate or do not accumulate nitrates at all and when there is a large amount of precipitation (when the average amount of precipitation exceeds 820 mm per year). In sandy derno-podzole roadside soils the wash-out of nitrates is larger (up to 80–90%) than in clayey roadside soils of heavy mechanical composition (up to 40–50%). In contrast to calcium cations (Ca^{2+}), anions of a negative charge nitrates (NO_3^-) are not absorbed by negatively charged soil colloids which dominate in most of loamy and clayey roadside soils of heavy mechanical composition. Therefore, nitrate anions (NO_3^-) move together with soil water and are easily washed out from soil.

The main transformation process of nitrates (NO_3^-) is denitrification into the other forms of inorganic nitrogen oxides (NO^- and N_2O^-) and gaseous free atmospheric (N_2) nitrogen (Fig. 4).

Denitrification processes are most effectively performed (up to 80–90 %) by bacteria when it is warm (in spring and summer) and when soil is humid (i.e. when more than 60 % of soil pores are filled with water). Denitrification processes in loamy and clayey roadside soils of heavy mechanical composition are more intensive (up to 80–90%) than in sandy derno-podzole soils (up to 40–50%). In a warm period of the year (especially in summer) it is possible to lose nitrates in roadside soils due to denitrification (when soil is waterlogged with plenty of organic materials and poor aeration) in 2–3 days.

Having used calcium nitrate to decrease road slipperiness and during its dissolution a nitrogen mobilization takes place in roadside soils, i.e. fixation of nitrates (NO_3^-) through their assimilation by microorganisms. During mobilization of nitrates, nitrogen accessible for plants (NO_3^-) once again transits into organic form. The activity of microorganisms and the speed of nitrogen mobilization processes increase with the growing ambient temperature

(up to 20–30 °C). The activity of microorganisms is restricted when soil humidity is both too low and too high, and the largest activity is found in humid soils with a relatively good aeration but not in too wet soils (i.e. when 60% of soil pores are filled with water, 40% – with air and pH exceeds 7). Consequently, a nitrogen mobilization process depends on the properties of roadside soils (temperature, humidity, aeration, pH) and on nitrogen amounts necessary for soil microorganisms and plants (Howard, Maier 2007; Chinathamby *et al.* 2006).

7. Impact of calcium nitrate on human health

The active material of molar mass of calcium nitrate (lime saltpetre) is nitrogenous fertilizer used for additional fertilizing of plants. This material is well water-soluble, can make suspension in fat, and is not hazardous under normal conditions. A mobile ion of nitrate (NO_3^-) is the prevailing form of the nutrition of plants. Nitrates are natural compounds which take part in nitrogen cycle and are also approved as a food additive. They play an important role in nutrition and in plant evolution stages. They take part in nitrification and denitrification cycle. Nitrates are important compounds for vegetables which they are apt to accumulate and this can affect biotic and abiotic factors. Larger permissible concentrations of nitrates are apt to be accumulated in leaves, smaller – in the seeds or tubers of plants. Leafy plants, for example, lettuce and spinaches are usually having larger nitrate concentrations. Nitrates get into human organism from the outside through the consumption of vegetables, and slightly less amounts – through the consumption of other food products and water. The Scientific Committee on Food (SCF) announced that the total amount of consumed nitrates is usually much less than the permissible daily dose (PDD) which is 3.7 mg/kg body weight per day, corresponding to 222 mg of nitrate per day for 60 kg weighing adult, however, it recommends to reduce the impact of nitrates consumed with food and water. Since the main source of consumed nitrates is vegetables, the max permissible nitrate concentration in them varies from 2000 to 4500 mg NO_3^- kg, in cereal food products intended for babies and small children and in baby food – up to 200 mg NO_3^- kg (Karraker *et al.* 2008; Koryak *et al.* 2001; Sanzo, Hecnar 2006).

After getting into the environment nitrates can cause pollution of ground water and soil, thus, it is necessary to restrict their spreading. Neutralization possibilities – to water down, to pump into hermetic containers. Ecotoxicity (toxicity to water, soil organisms and other animals and plants) is low, the TLM (Threshold Limited Median) 96 is about 10–1000 ppm. Large amounts of fertilizers are toxic to plants and soil microorganisms (burns off the roots of a plant, destroys soil microfauna).

The material is non-volatile, no poisonous materials are accumulated in the ambient air, therefore, there are no special restrictions, no protective measures for airway are necessary, but the building used for storage must have ventilation. When working for a long time with calcium

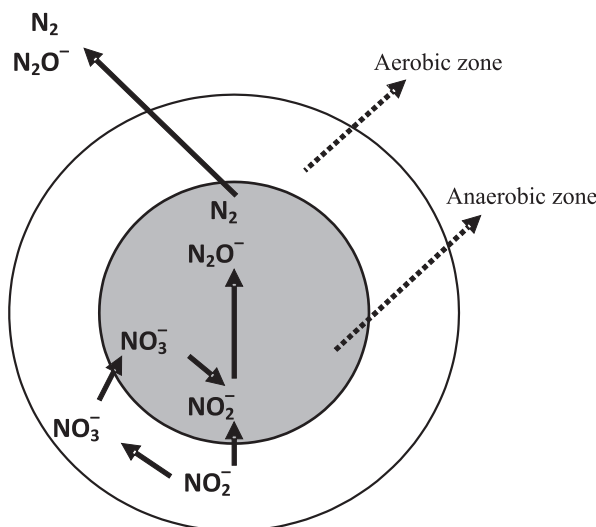


Fig. 4. Denitrification process of nitrates (NO_3^-) in roadside soil

nitrate one shall wear suitable protective clothes, footwear, suitable gloves and use eye protection measures, it is required to wash hands after work, to follow elementary hygienic rules. The material irritates skin. A short-term contact irritates eyes, a long-term irritation can cause eye diseases and danger for eyesight. If it gets on the skin it is recommended to take off polluted clothes, to wash skin with plenty of water, if it gets into eyes – to rinse with clean water and immediately call the doctor. If swallowed, a small amount of solution causes intoxication effect. A large amount causes digestive tract diseases, at the very outside (if swallowed by child) it can result in “the blue disease” or cyanosis (blue spots around lips) (Godwin *et al.* 2003; Forman *et al.* 2003).

8. Conclusions

Having assessed in various aspects the study materials (salts), used for road maintenance in a cold period of the year, and taking a special consideration of the impact of these materials (salts) on the environment as well as their price, it could be stated that the most acceptable alternative for Lithuania is the already used sodium and calcium chloride salts.

Having assessed all the above mentioned materials according to their chemical and physical properties and also according to their price and availability from technological point of view in the production, at present the following compounds could be distinguished: carbamide and calcium magnesium nitrates. For the production of other compounds new technological production equipment are necessary.

The properties of carbamide are rather good compared to other compounds. Therefore, based on all given considerations the most acceptable alternative between the materials (salts) used for decreasing ice melting temperature is carbamide, the production technology of which the company has been already implemented.

Though production of concentrated calcium and magnesium nitrate solutions from quicklime and brucite has been known and not new there is still a question about their efficiency and market possibilities. It is necessary to make laboratory tests and to assess from the marketing point of view the future perspectives of concentrated solutions intended for road maintenance and de-icing.

The largest speed is represented by sodium chloride solution (0.147404 mm/m) which is followed by sodium chloride solution with calcium nitrate agent (0.142139 mm/m). Corrosive activity of sodium chloride solutions with calcium chloride and carbamide agents is less and equals to 0.123421 and 0.123226 mm/m, respectively.

The especially large difference was obtained having compared the results of the speed of corrosion after 2 days of exposure time: the speed of corrosion of sodium chloride is 0.06639 mm/m, and the speed of corrosion of sodium chloride with calcium nitrate agent – 0.086571 mm/m. A lower corrosivity of sodium chloride solutions (after 4,

7 and 14 days of exposure) was obtained in the solutions with calcium chloride and carbamide agents where the difference in the speed of corrosion in those solutions makes only several thousandth of mm/m.

In dry derno-podzole roadside soils, distinguished for their good infiltration properties, that are composed of about 90% of sand, 0.5–1% of humus and the remaining part of light sandy loam, calcium cations (Ca^{2+}) are transported by the surface of soil and washed out through its deeper layers into ground waters very effectively (even up to 95%). However, in roadside soils of heavy mechanical composition calcium cations (Ca^{2+}) are transported into surface water bodies more by its surface (up to 70–80%) but not through deep soil layers (up to 30 cm) having the largest accumulation capacity.

In sandy derno-podzole roadside soils the wash-out of nitrates is larger (up to 80–90%) than in clayey roadside soils of heavy mechanical composition (up to 40–50%). In contrast to calcium cations (Ca^{2+}), anions of a negative charge nitrates (NO_3^-) are not absorbed by negatively charged soil colloids which dominate in most of loamy and clayey roadside soils of heavy mechanical composition. Therefore, nitrate anions (NO_3^-) move together with soil water and are easily washed out from soil.

The active material of molar mass of calcium nitrate (lime saltpetre) is nitrogenous fertilizer used for additional fertilizing of plants. However, if too large concentrations get into the environment, nitrates can cause pollution of ground water and soil.

In future, having expanded the production of calcium and magnesium nitrates, it will be possible to start producing certain mixtures, e.g. carbamide with those nitrates or the mixture of carbamide, calcium, magnesium nitrates and calcium chloride, and, thus, to reduce a direct use of chlorides. Those mixtures in a cold period of the year should have rather good properties and could become a serious alternative to chlorides at present the most frequently used for de-icing of roads.

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