Deicing Salts: An Overview

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Abstract

The world production of salt (NaCl) was over two hundred million tons in 2015. The US is the second larger producer of salt after China, produced over four million tons of which 43% were consumed in highway deicing. While NaCl is the most commonly used salt, other salts are added to it to improve its performance, such as $CaCl_2$, $MgCl_2$. To reduce the use of the deteriorating NaCl, other salts are also used, such as magnesium acetate, calcium magnesium acetate or potassium and magnesium formate. The addition of sand and other inorganic insoluble compounds to aid in making surfaces less slippery is discussed, as well as the recent use of organic deicers and the problems that these can induce.

The paper aims to present an overview of deicing salts, and the differences with anti-icing or antifreeze solutions. It also discusses the problems they induce to vehicles, buildings and constructions, while also considering the negative aspect they have for the environment as well as their contribution to air pollution. Some examples are presented to illustrate the problem and less aggressive alternatives are discussed, especially with regard to the conservation of valuable architectural heritage.

Keywords: deicing salts, building deterioration, environmental pollution

1. Introduction

The world production of salt (NaCl) was over two hundred million tons in 2015. The US, the second largest producer of salt after China, generated over four million tons of which 43% were consumed in highway deicing. While NaCl is the most commonly used salt, other salts are added to it to improve its performance, such as $CaCl_2$, $MgCl_2$. To reduce the use of the metal corrosive NaCl, other salts are also used, such as magnesium acetate, calcium magnesium acetate or potassium and magnesium formate, urea, and even sugar containing solutions from either sugar processing or equivalent procedures.[1]

While the use of deicing salts is necessary, they do have a negative impact on the environment, such as: soil contamination, negative effect on plants and trees near the highways/streets, contamination of water courses and eventual drinking water, air contamination by powdered salts, corrosion of reinforced concrete in bridges and structures, as well as of cars and trucks. For example, in Austria it has been estimated that half the induced vehicle corrosion could be attributed to de-icing salt.[2] As deicing salts are distributed, the finer particles (<10 µm, usually referred to as PM10) can remain suspended in the air, thus contaminating it.

Differentiation between deicing and anti-icing or antifreeze should be made. Deicing salts are applied after snow events, their effectiveness being based on lowering the freezing point of water. Antifreeze solutions of glycerol or various glycols are applied prior to the event to prevent a strong bond between the pavement surface and frost by applying a freezing point depressant. These are mainly used on aircraft, machinery and vehicles as they are non-corrosive, however, most of them are toxic.[3] Other solutions have been developed based on special coatings.[4]

2. Deicing salt varieties

Deicing salts can be roughly divided into inorganic salts, such as sodium chloride (NaCl), organic salts, such as magnesium calcium acetate ($CaMg(CH_3COO)_4$) and organic compounds such as urea ($CO(NH_2)_2$). Salts can be used in various mixtures, and other substances added, such as anticaking agents, e.g., potassium ferrocyanide[5] or anticorrosion agents such as ammonium phosphate or sodium hypochlorite.[6] Also, they can be spread directly in granulated form, or as a solution, i.e., brine. With the former, the mixture with sand (e.g., 75% sand-25% NaCl), or other equivalent materials such as fine gravel or expanded clay pellets contributes to decrease the slippery surface of compacted snow[2]; however, they do increase small particulates in air by about 45%.[7] Recently, potassium carbonate (K_2CO_3) has been studied in comparison to NaCl, and it was found that while it was more adsorbed to soil colloids, the pH was elevated more than for NaCl, and the species composition of the area where it had been applied changed significantly.[8]

2.1. Chloride based deicers

Chloride ions from deicing salts will mobilize and increase soil salinity near the roadways where they are applied. While magnesium and calcium ions increase the stability and permeability of the soil, sodium ions will decrease them. Furthermore, sodium, magnesium and calcium chlorides may contribute to the mobilization of trace metals from the soil to surface and groundwater. The solid chloride deicers, i. e., NaCl, may contribute to air pollution through particulates released into the air.[2,7]

2.2. Acetate based deicers and others

Soil microorganisms will break down acetate ions resulting in oxygen depletion of the soil, which can impact vegetation. A similar oxygen depletion is most likely to occur in slow flowing streams and small ponds into which these ions migrate.[7] While the toxicity of calcium magnesium acetate (CMA) to fish and invertebrates is low, when also containing potassium, CMAK (50% CMA-50% KA), they have higher toxicity. Acetate deicers will result in the decrease of air pollution as sand use can be reduced; however, the solid deicers, CMA and sodium acetate, NAAC, may contribute fine particulates to the air increasing its pollution. These deicers are mainly approved for use at airfields and aircraft, as they are less corrosive, as is the case for potassium formate, in either liquid or solid form.

2.3. Urea

Urea [$CO(NH_2)_2$] is used as a deicing agent for airport runways[9] though it has been mostly discontinued in larger US airports.[10] The main reason is that as a fertilizer (46% by weight nitrogen content) it contributes to environmental pollution, e.g., acute toxicity to aquatic invertebrates and plants, as well as some fish.[11] Several soil bacteria contain the urease enzyme that catalyzes the decomposition of urea into NH_4^+ and HCO_3^-. Furthermore, NH_4^+ (or NH_3) is oxidized by nitrifying bacteria, Nitrosomonas and subsequently by Nitrobacter, in a two-step process to NO_3^-, an ion that is regularly found on building façades.

Urea forms an eutectic mixture with water (at ~33% by weight) with the eutectic point at 11.5°C. Solubility is about 1Kg/L at 20°C, the dissolution being endothermic, and the equilibrium RH is 76.5% at 25°C. In dilute solutions (not specified but probably below 5%), urea decomposes to NH_3 and CO_2 (the formation of isocyanic acid occurs upon heating, temperature not specified). The most common impurity in synthetic urea results from the condensation of two molecules to form biuret ($C_2H_5N_3O_2$) or carbamylurea, a compound that interferes with plant growth. As a deicer, urea proves practically useful, i. e., deicing within 15-20 minutes, at temperatures below -9.4°C taking into account that its dissolution is endothermic.[12] Many studies have addressed the decomposition of urea in aqueous solutions[13], while others address its use to decrease vehicular emissions of NOx which contribute to the formation of nitrates or nitrites in buildings along the streets.[14]

2.4. Glycols and other alcohols

Methanol was used as antifreeze in windshield fluids, but because of health concerns the amount added is restricted. Ethylene glycol, commonly referred to as "glycol" is used as engine cooling antifreeze. The freezing point of ethylene glycol is about −12°C, however, mixed with water, this is depressed, e.g., a mixture of 60% EG-40% water freezes at −45°C. Propylene glycol has replaced ethylene glycol in many uses because of its lower toxicity. These products are used for aircraft deicing fluids (heated aqueous solution of ethylene glycol), and as antifreeze, as undiluted, thickened propylene glycol.

2.5. Other organic deicers

In the USA, the Minnesota Department of Transportation claims to have pioneered the use of sugar beet juice based on the huge sugar beet industry in the Red River Valley of Minnesota/North Dakota, and the massive need for re-use of sugar beet waste helped create a market for it, and the fact that these states get a lot of snow and ice contributed to the testing.[15] The sugar beet syrup is mixed in with traditional salt, sand or chloride brines to improve performance and reduce the impact on the environment.[16] Not only sugar beet syrup is used, but other residues of distilled or fermented agricultural products[7] such as corn, barley and even pickle brines. The addition of syrup from sugar processing to brines has been shown to improve their effectiveness and has been approved in Switzerland since 2015.[17]

3. Impact of deicing salts on buildings

When considering the effect of deicing salts on buildings and constructions the immediate image that comes to mind is the damage at the foot of walls, resulting from the rising damp from the solution of the melted snow and salts, as shown in *Figure 1*.

Experience has shown that to this deterioration mechanism two other direct contamination processes have to be added. The first one occurs in damp winter conditions and affects buildings located along high traffic roads, where topography contributes to accumulate the salt containing melted snow and that vehicular traffic and snow clearance vehicles splash on to the building walls or disperse into the air so that they enter directly at a certain height (*Figure 2* left). The second process occurs during dryer winter periods when the excess deicing salts applied recrystallize and accumulate at the base of buildings (*Figure 2* right).

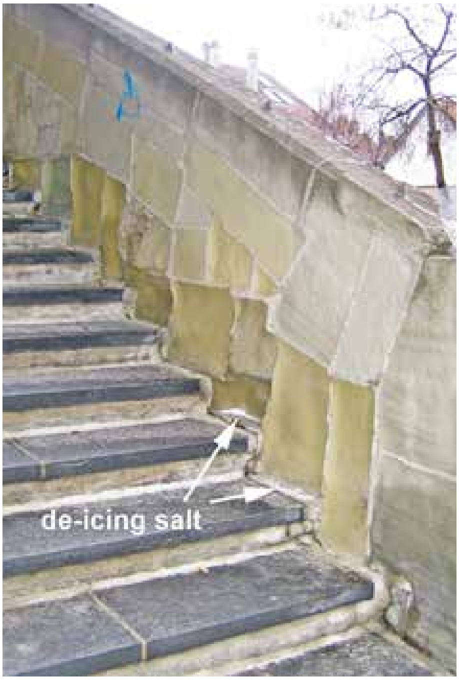

Figure 1: Lausanne (canton de Vaud, CH), Pierre Viret stairs (20.01.2010). Deicing salts are spread lavishly on the practically non-porous gneiss, and the salt and melted snow mixture accumulates at the base of the porous molasse-sandstone bridge wall that promptly powders and disaggregates.

In certain streets, where regular and intense winds are prevalent, the salt grains on the ground can be mobilized and suspended in the air, as well as thrown against the façades by whirl winds. If the building surfaces are moist or rough, the salts will be “attached” to them and deterioration will eventually occur *(Figure 3)*.

Following the above mentioned processes, it is logical to ask what will be the eventual impact of the presence of these deicing salts in the air on the conservation of buildings and monuments. Recent studies regarding the composition of fine particular matter suspended in urban air have shown the recurrent presence of NaCl.[7,18,19] In sea-side areas, it is obvious that most of the salt present can be attributed to marine spray and fogs, however, this cannot be applicable to inland areas. For example, in Putaud et al. [20] (see figure 3, p. 2584), the measured annual average values of PM10 for NaCl (from January 1998 to March 1999), is referred to as “sea salt”, in both rural areas, such as Chaumont, and urban areas, such as Basel and Zurich, as well as at street level (kerbside)

Figure 2: Left: Belfaux (canton de Fribourg, CH), north façade of the Lanthen-Heid manor (1526).The damages that affect the render and the underlying molasse-sandstone are mainly the result of splashing traffic along this street (3.09.2008). Right: Lausanne (canton de Vaud, CH), rue Saint-Etienne (20.01.2010). During dry winter cycles the residues of recrystallized deicing salts can be seen at the foot of façades that can either be mobilized and suspended in the air or enter the material when dissolved in water via hygroscopicity, rain, or more snow.

Figure 3: Lausanne (canton de Vaud, CH), rue de la Barre, Château Saint-Maire (10.04.2012). The sanding and disaggregation that affects the base of the building and up to 2 m in some areas is mainly due to the presence of NaCl.

in Bern. The PM10 immission of this city is strongly influenced by traffic and showed a value of about 1.5 $\mu g/m^3$ while the other sites range between 0.5 $\mu g/m^3$ for the urban sites to 0.2 $\mu g/m^3$ for the rural site of Chaumont

The chemical composition and the quantity of the coarser fractions in air pollution reflect the contribution of mineral dusts put into suspension by vehicular traffic. These include remaining deicing salts and explain the relatively high concentration of NaCl, as clearly stated by Gianini et al.[21, p. 104]

4. Discussion

There is no question as to the contribution of deicing salts to the deterioration of our architectural heritage as well as to the environment. But it is also clear that deicing salts, as well as antifreezing formulations for airports and aircraft are necessary and have to be used to avoid traffic accidents, disruptions in the economy, and taking into account that the negative impact of closing roads far exceeds the cost of snow and ice removal.[22,23] While airport and aircraft are allowed the use of some formulations that cannot be used freely elsewhere, no such proviso has been considered for our cultural heritage.

Another problem is the introduction of additional hygroscopic salts into salt-containing structures, as the hygroscopic salts will mobilize and activate those present within the structure so that they will migrate and eventually crystallize in other areas. This has been observed on monuments, where salt efflorescence changes places after events introducing moisture and new salts, as described by Rolland et al.[24] who called it the "transporting brine hypothesis". But the problem is now increased with the use of products from the food industry[25] that are added to deicing salts. No one has as yet raised questions regarding their long term effect when retained together with the deicing salts in structures. For example, sugar beet syrup is hygroscopic, with a DRH ~60%[26], so supposing that this, together with NaCl is taken up into the structure, in theory, less salt should crystallize out. Of course, other problems could set in with the introduction of organic materials, such as biocolonization, and deterioration of the stone matrix, should it have some solubility in water. But this is an area that still needs to be studied formally.

Another topic that requires evaluation is whether applying a polymer surface overlay system, such as SafeLane® having an epoxy bonding agent, a special aggregate capable of storing a deicer that automatically releases before frost and ice can adhere to it[4]. The question is how fast is this overlay system worn down by the traffic and how much epoxy is released into the environment.

Conclusions

It is clear that to maintain the economic system that has been developed since the industrial revolution, many changes have been made in the environment and its ecology. But these changes take time to implement, so it is important that, for those of us concerned with the conservation of our architectural heritage, we should point out the problems that threaten it to raise the awareness of the general public so eventually some actions can be taken to protect them. As every building and its situation are different, solutions adapted to the individual case have to be found. Often it is possible to use gravel and no deicing salt at the proximity of the walls of historic buildings, or it is possible to cover the basis of the walls, e.g., with boards to keep salt containing snow away from the walls, similar to the covers used to protect statues during winter. In some instances, a French-drain could be installed by the wall where deicing salts are applied, so that the melted snow and salt will get trapped in it, or as in Switzerland, many staircases are half closed and only a small part kept free of ice or snow. Ingenuity has been the mark of humankind, and it is time for it to come to the rescue should we want to preserve our architectural heritage.

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