Deicers and anti-icers comparative study

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ABSTRACT

Chloride sodium is the most commonly used deicer (more than 99% of the total consumption) on the French road network. Different substitution products to NaCl appear on the market: de-icers and anti-icers used on airports, industrial formulations, or mixture of abrasive and de-icers.
These considerations led the Center for Technical Studies of Equipment in East of France (CETE de l'Est), with the French Civil Aviation Technical Centre (STAC) and the Technical Department for Transport, Roads and Bridges Engineering and Road Safety (Setra) to characterize and compare these products.
This paper shows a comparison of their physico-chemical characteristics through criteria such as the percentage of active compounds, pH or electrical conductivity. Environmental impacts were evaluated by determining the biochemical and chemical oxygen demand, the biodegradation time, and the toxicity. The third part deals with perfomential properties with the freezing curves, and the capacity of ice melting. This article draws some recommendations of use depending on the products characteristics, on managers objectives and on weather phenomena.

1. INTRODUCTION

The French recent winters were particularly rigorous and snowy, and sodium chloride consumption have achieved levels rarely reached before. Some road managers have also searched alternative products with higher performance and increased availability than sodium chloride. Specific deicers are used on airport sector for the treatment of runways and taxiways. They appear now as alternative products on the road network, as well as new off-the-shelf formulations. As part of its missions, the Equipment Technical Study Center of eastern of France (CETE Est), in partnership with the French Civil Aviation Technical Center (STAC) and the Technical Department for Transport, Roads and Bridges Engineering and Road Safety (Setra), characterized and compared product families. This article present physical, chemical, environmental and functional properties by product's typologies.

2. PRODUCTS STUDIED

CETE de l'Est, commissioned by Setra, has developped an almost exhaustive list of all new products commerically avaible to describe them. It is also based on STAC's studies to characterize runway deicers. These investigations are regarding solid deicers [1] as

sodium acetate (2 products), sodium formate (2 products), ionic products (sodium chloride NaCl and calcium choride $CaCl_2$). Several studies have been conducted on liquid products as potassium acetate (4 products), potassium formate (4 products), based on glycerol (2 products), an additive to NaCl and a mixture of abrasive and deicer.

3. PHYSICAL AND CHEMICAL PROPERTIES OF DIECERS

Deicers are different in their appearance. (solid, liquid or mixture). Also, their fonctionnalities differ from each other. Deicers are meant to avoid ice formation and/or to melt it [1]. Deicers are soluble, by definition, in contrast abrasives which are used to increase the adhesion of snowy road. They are also a complementary solution on high level network in specific cases (lorry traffic, ramp). Abrasive spreading requires, in France, a sweeping operation, product collection, cleaning and its disposal as waste road material [2].

The objective of deicers in abrasive product consists in assisting particule penetration in ice or snow or to prevent freezing of the stock. Salt additives are used to maintain salt particules on the pavement, inparticular for road with high service level and preventive strategy. The grip on pavement is obtain by particules coating with liquid product. The same principle is applied with the pre-wetted salt, with a solution of NaCl at 23% w/w.

Proportions of active compounds range between 23%w/w to 50%w/w for liquid deicers and represent approximately 90%w/w for solid products (Figure 1). However, all deicers have to be in solution to be efficient. Thus, liquid deicers are used preferably to a speed action, because they already are in solution. On the othjer hand, solid deicer are meant to last. Roughly 3% of deicers are incorporated in abrasive to formulate mixt product.

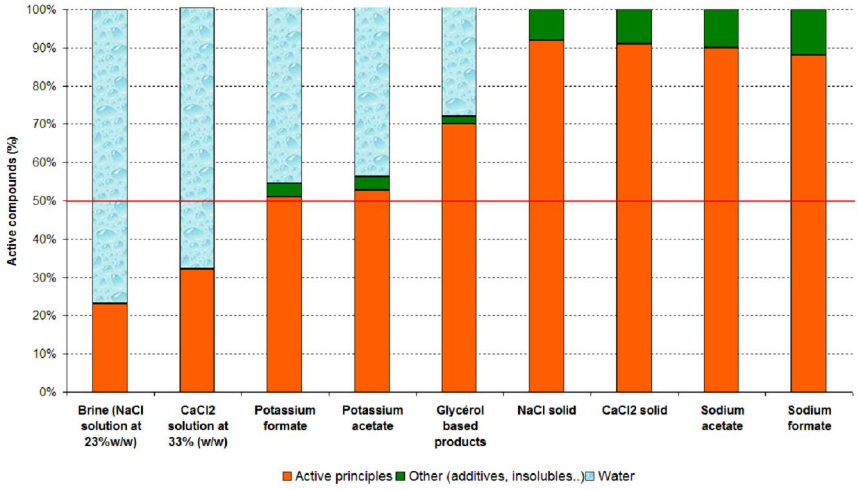

Figure 1 - Percentage active compounds of liquid and solid off-the-shelf formulations (%)

Chemical salts in water increase the conductivity of water by dilution of deicers in ice or snow. This property contributes to the corrosion of road infrastructure metals. So, diecers with high conductivity may affect metals such as steel, zincé (Figure 2). Because they are organic, glycerol-based products are less conductive than mineral de-icers. Formate and acetate products, used on airport sector, generally contain corrosion inhibitors in small amounts, which significantly reduce metal corrosion.

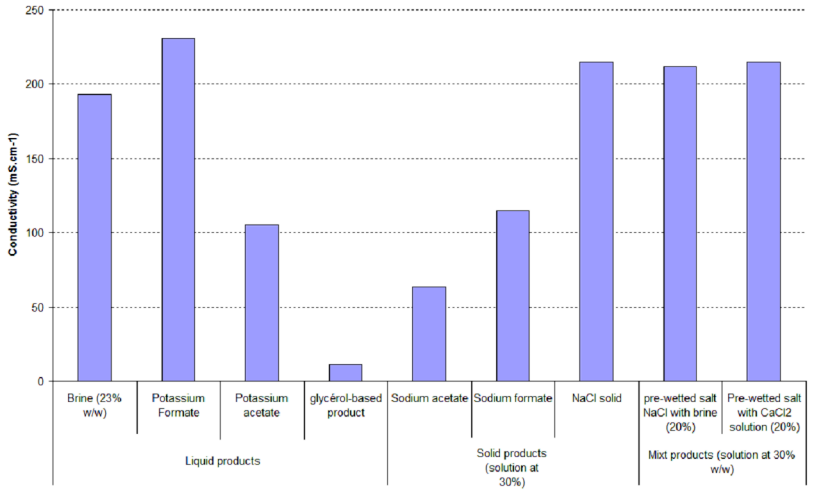

Figure 2 - Conductivity of deicers for winter maintenance

Kinematic viscosity was studied on liquid deicers at maximum concentration and on solid deicers in solution at 30%w/w. For all products, viscosity increases as temperature drops (Figure 3). Some of them may induce a grip decrease on pavement, when they are spread in preventive treatment at negative surface temperature. The variation in viscosity induced by the temperatures to which the products are exposed could lead us to recommend the use of products with stable viscosity in geographical zones where winter conditions are rarely severe (low ranges of temperature). Given the viscosity of glycerol-based products, they must be tested on pavement before use, especially for specific pavement (cobblestones, wooden surface, etc.)

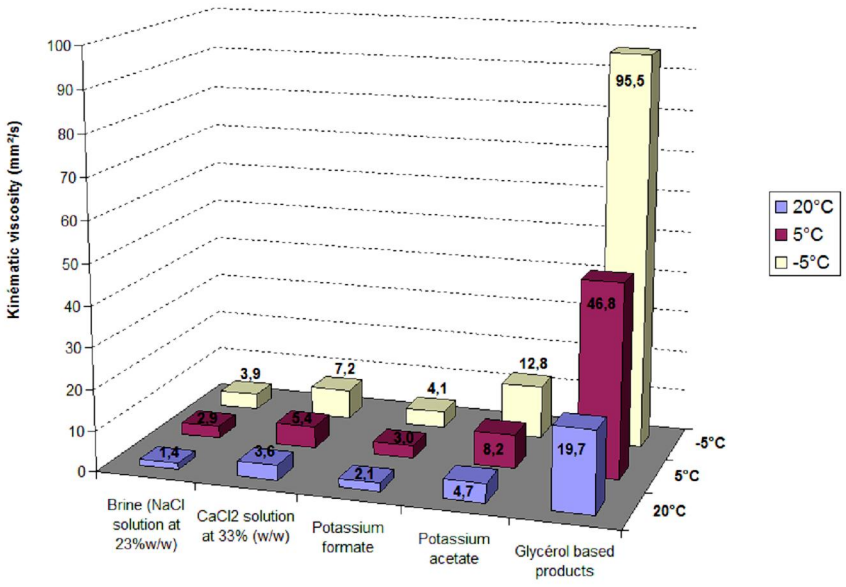

Figure 3 - Average kinematic viscosity of liquid deicers at different temperatures

The studies of solid deicers were focused on the analysis of size particle, to assess their compatibility / consistency with conventional deicer's spreaders (Figure 4). The analysis refers to French standard NF P 98-180 [3] of sodium chlorid wich must be within three grading ranges: fine, medium or coarse. The particule-size ranges of solid deicers (acetate or formate formulations) have a high proportion of coarse components with a diameter between 2 and 5 mm. Abrasive products have commonly a grain size between 3 and 6 mm. One product was very specific, with spherical particles. This characteristic induces spreading issues with particules bouncing on pavement. The grain size variability,

along with hygroscopic properties of solid deicers, must engage road manager to ensure quality controle of spreaders (regular contrôle, calibration with used deicer)

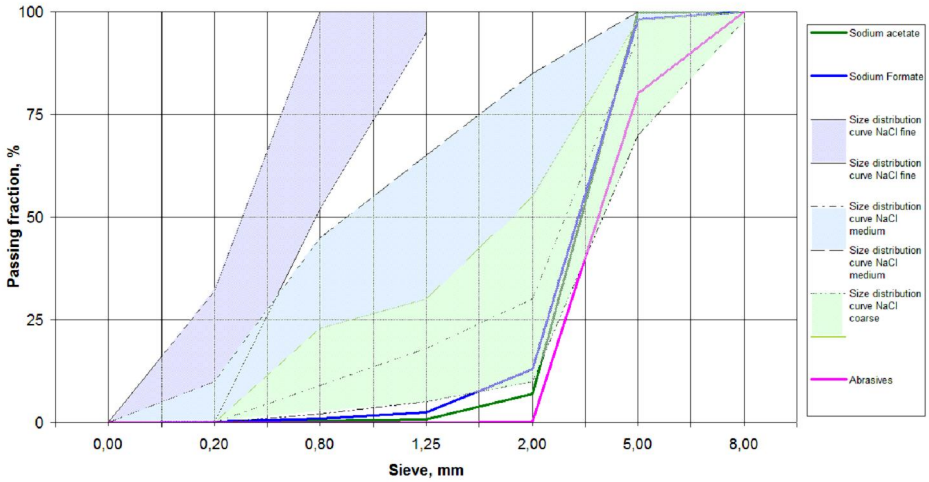

Figure 4 - Size distribution curves for solid deicers ï Comparison with the particule size bracket of standard NF P 98-180

Despite the size of the pellets, some products remain particulary friable and powdery. A special care must be taken for their use.

4. ENVIRONMENTAL CHARACTERISTICS

The question of the impact of deicers on the environment lies in their organic load and in their biodegradability. The Chemical Oxygen Demand (COD) is the oxygen O_2 consumption to oxidise the product by strong chemical oxidants. It represents the total organic material wich can be degraded. The amounts of biodegradability material in 5 days by biochemical oxydation (oxidation by aerobic bacteria) is defined by the Biochemical Oxygen Demand parameter (BOD). These tests had not been made on chloride products because of its incompatibility with respect to the tests. It is essential for the environment that the substances spread are biodegradable to avoid them accumulation in the ecosystem, but the amount of oxygen needed for their degradation must not be too high, to avoid asphyxiation into environment [4-5]. Formate products (solid or liquid) seem less problematic than acetate or glycerol-based products, the latter being particularly harmful for the environment lœenvironnement (Figure 5).

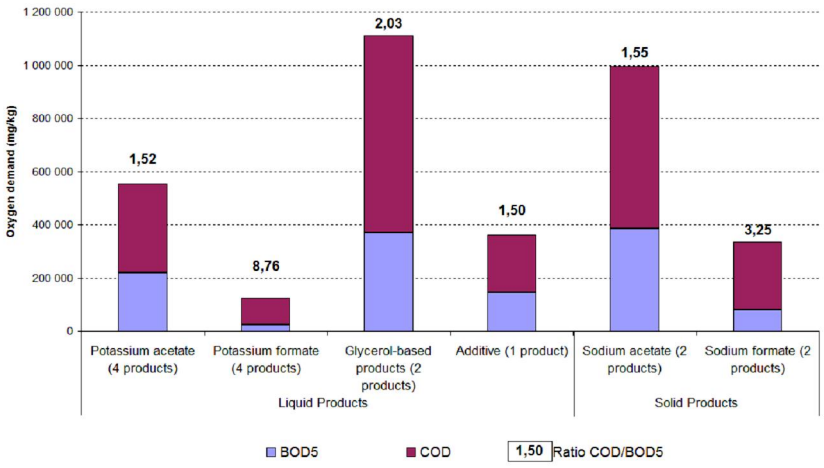

Figure 5 - Biochemical Oxygen Demand in 5 days BOD_5 (NF EN 1899-1) and Chemical Oxygen Demand COD (NF T 90-101) of deicers, ratio COD/BOD_5

Biodegradabily is considered by two parameters: COD/BOD_5 ratio and the biodegradation time. This last parameter is the expression of the percentage of biodegraded product in a given time. Taking into consideration the DOB_5 and the COD, the environnemental impact of formates is significantly lower than glycerol and acetates. This initial appreciation should be put in into perspective, given the biodegradabily and the time it takes for them to be biodegraded. The biodegradability (ratio COD/BOD_5) shows that formate are more difficult to biodegrade than other products. The biodegradation time results confirm the previous point: formates degrade at a slower rate than acetate and glycerol (Figure 6).

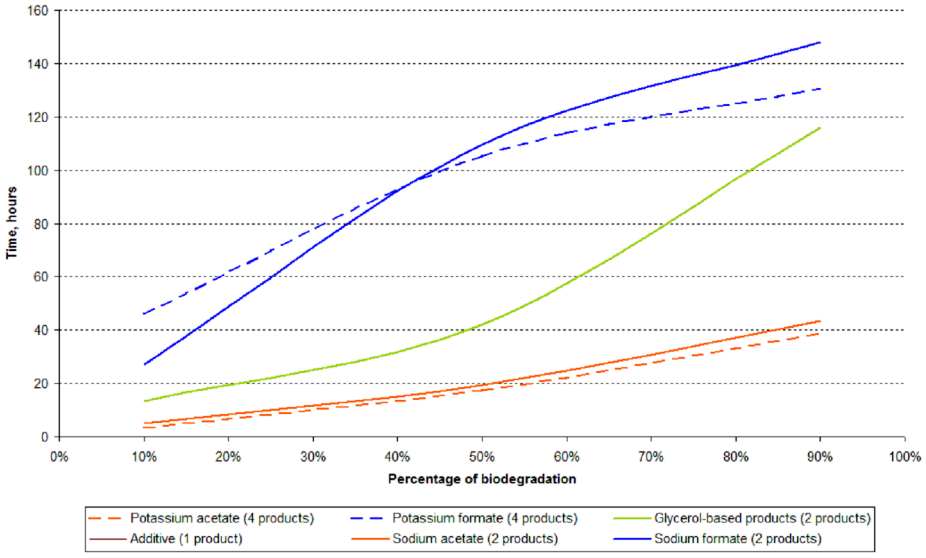

Figure 6 - Biodegradation time at 20°C of deicers for winter maintenance.

The choice of deicer can be driven by reglementary and environmental constraints / requirements : products with slow biodegradation time, low COD and BOD_5, also with a low risk of environment asphyxiation can be used preferably in sewerage system wich are able to manage effluents for long periods [6]. Typical example are ditches on roadside. On the orther hand, deicers with high COD and BOD_5 and fast biodegradation speed should be preferred when surface water is treated in wastewater facilities with oxygenation (wastewater collection systems, public water collection network, etc.)

This approach of environmental impact of deicer may be too restrictive and may require a larger scope study throughwidening of analyse with product life cycle. Previous investigations have shown that fossil energy consumption to manufacture this products is larger than sodium choride [9]. Other parameters are taken into account such as the location of production, transportation modes used, the packaging and application instructions which affect the spreader consumption.

5. PERFORMANCES OF WINTER MAINTENANCE DIECERS

The freezing point at maximum concentration appears to be the principal criteria for deicerõs performance. This approach should be put in perspective knowing that these products are efficient only when they are in solution, and that the surface temperatures in France could sometimes be as low as -20°C. These freezing curves have been drawn with a protocol of CETE de lõEst [7]. The off-the-shelf liquid formulations (potassium acetate, potassium formate and glycerol-based product) are in solid phase around –65°C. Only the calcium chloride has a specific behavior with an eutectic temperature of approximately -

50°C. The freezing-curves of solid formulations are similar for a concentration up to 25% (Figure 7).
To protect a pavement from ice within a temperature range of -20°C to 0°C and a given water amount, the quantities of the product to be applied are globaly doubled for liquid deicers with respect to solids.

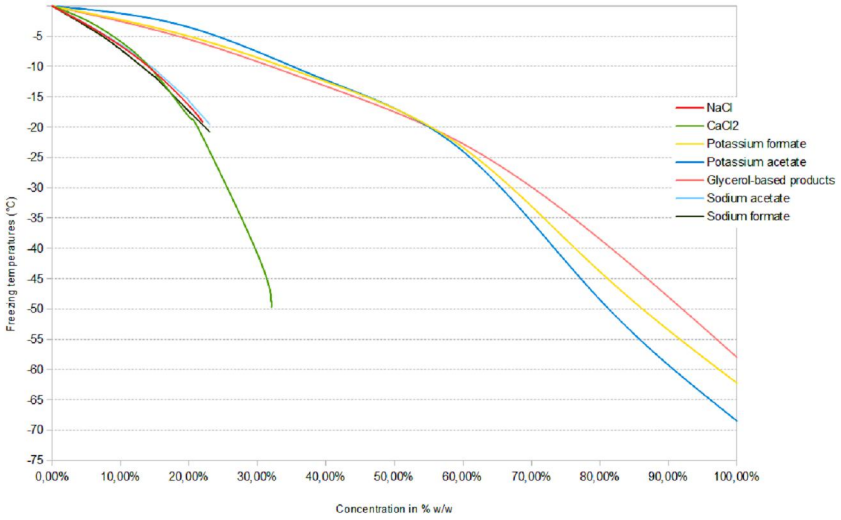

Figure 7 - Freezing curves for off-the-shelf deicers for winter maintenance

The dynamic aspect was approached by the ice melting test, according to a protocol built for aiports contexts [8]. These results highlighted the melting speed of liquid products and the duration of solid deicers (Figure 8).

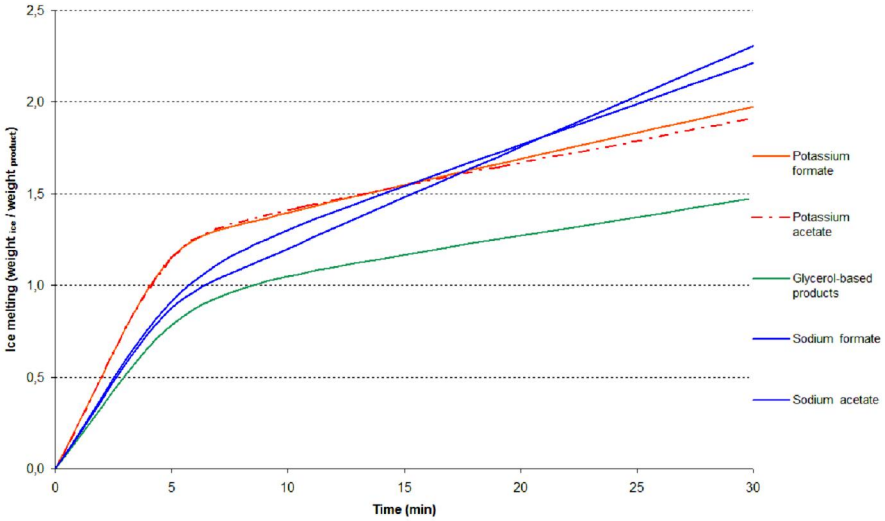

Figure 8 - Ice Melting Test Method for chemicals deicers at -5°C

The choice of a winter maintenance deicer is therefore a compromise between the infrastructure managerôs objectives and the deicer performances (quick return to a normal grip, duration of treatment, etc.)

6. OTHERS ASPECTS OF STUDIED FORMULATIONS

For road managers (urban and interurban networks), the subsistution products to NaCl are usually expensive (Figure 9) with applications recommendations ranging from 20g/m² to 150 g/m². This instructions significantly change the length of circuit or the spreaders

number road manager. Considering these costs, these products are anly appropriated for spot treatment.

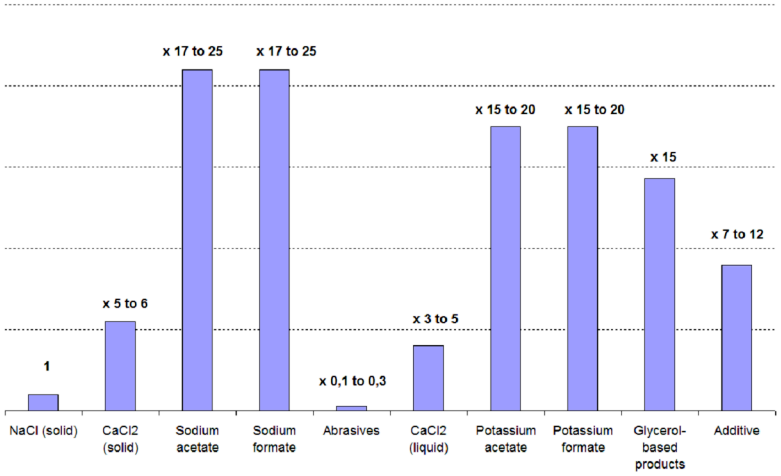

Figure 9 - Estimates of winter maintenance deicers costs on French market

According to providers, formate and acetate have a consumption deadline of 2 years, duration confirmed by a study conducted in parallel. Storage conditions are detailled in safety data sheet. For some liquid products, it should be in containers, which are double walled equipped with a blowhole. Due to their hygroscopic nature, and sometimes packaging in polythen bags, solid products should be stored in cool, dry and ventilated conditions, away from UV light. Large investments may be required in case of a product's change. For chemical product, safety data sheets refer additionally to eye protection, gloves, etc. to safely handle products.

7. CONCLUSION

Deicer other than chloride sodium are on the French market for specific needs : bridge treatment, tunnel entrances and exits, urban environment with specific roads (bike paths, sidewalks). This business can be explained by their lower availability than NaCl.
The result of the continuous search for a ñmiracleò product is the large number of products on this market. Only a representative sampling of products, but restritive has been studied here. Each of these has distinct characteristics suitable for different circumstances. There is no ideal formulation, the choice results of a ñoptimum compromiseò between needs of road manager and charateristics induces and requires of products.
Apart from the performential aspect, any change of product requires an adaptation of the organization: adjustement of spreaders, establishement of adequate storage, change of practices, or modification of treatment strategies. This ñoptimum compromiseò is also the result of the triptic needs / characteristics of products / the constraints of road managers.

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