EFFECTIVENESS OF USING ORGANIC BY-PRODUCTS IN DECREASING THE FREEZING POINT OF CHEMICAL SOLUTIONS

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1. ABSTRACT

Finding an effective and environmentally friendly de-icer has been a major objective for many agencies in the field of winter maintenance. Although there are many snow and ice control chemicals such as calcium chloride, sodium chloride, potassium chloride, urea, etc. Each has its own advantages and disadvantages. Some are highly corrosive, others are not effective at low temperatures, and others may negatively effect the environment.

In the later half of the 1990's, a new type of de-icer was developed and was marketed under the brand name "Magic". Magic is a mix of organic by-products from agriculture industries blended with liquid magnesium chloride. The product is marketed as a material for use in snow and ice control operations.

The product has been claimed to be effective as lower temperatures as a pre-wetting agent, can be used as an anti-icing liquid. It has been tried in different areas with varying results. Also, it is being promoted as an environmentally friendly product since most of it is natural substance.

In 1998 the Regional Municipality of Ottawa-Carleton conducted field trails with the product premixed with road salt as a pre-wetting agent. Subsequently in year 2000, the municipality started testing the product in the lab to determine its freezing point and assess its value as a de-icing material and as a pre-wetting agent at lower temperatures.

The purposes of this study were to determine the freezing point and a working temperature for the product, as well, to study its effect, at different ratios, on lowering the freezing point of sodium chloride brine solution. Finally, conduct a comparison between the effect of the product on a sodium chloride brine solution and the effect of a magnesium chloride solution on lowering the freezing point of the sodium chloride brine solution.

2. INTRODUCTION

Ottawa is one of the most snowed capital cities in the world. According to Environment Canada records the temperatures reach their lower limits during the months of January and February. Over the past thirty years the average minimum temperatures during the months of January and February were –15.5 ºC and –14.0 ºC respectively. On the other hand the minimum extremes temperatures along the same period (thirty years) were –35.6 ºC and –36.1 ºC for the months of January and February respectively. Regarding the snowfall, the average amount over the last thirty years was 221.5 cm with the maximum amount of 444 cm, which happened during winter 1970-1971. In order to maintain safe and passable roads during winter months, a significant amount of chemicals are used to in de-icing operations.

Although there are many snow and ice control chemicals such as calcium chloride, sodium chloride, potassium chloride, urea, etc. Each has its own advantages and disadvantages. Some are highly corrosive, others are not effective at low temperatures, and others may negatively effect the environment. A long stream of research and studies has been conducted with the main objective of finding an effective and environmentally friendly de-icer and an anti-icer.

In the later half of the 1990's, a new type of de-icer was developed and was marketed under the brand name "Magic". Magic is a mix of organic by-products from agriculture industries blended with liquid magnesium chloride. The product is marketed as a material for use in snow and ice control operations. The product has been claimed to be effective as lower temperatures as a pre-wetting agent, can be used as an anti-icing liquid. It has been tried in different areas with varying results. Also, it is being promoted as an environmentally friendly product since most of it is natural substance.

In 1998, the above-mentioned product was introduced to the Regional Municipality of Ottawa-Carleton in the form of a stockpile treatment for salt to have the effect of pre-wetted material. Further to the field trails, in the year 2000, an extensive laboratory study was conducted in order to evaluate the effectiveness of using this new product within Ottawa local weather conditions.

The objective of this paper is to present the methodology and the results of the experimental study conducted in the winter material laboratory at the new City of Ottawa (Former Region of Ottawa-Carleton) in order to evaluate the effectiveness of the product, "Magic", used within winter maintenance operations.

3. BACKGROUND

A number of factors affect the performance of a de-icing or an anti-icing chemical. Such factors may include temperature, application rates, and road surface type. This paper is focused on the three factors that control the science of a de-icing chemical; they are temperature, time and concentration. While keeping in mind that the real objective behind using chemicals to control snow and ice, is that the chemical is used to lower the freezing point of the solution of snow (water) and the used chemical.

3.1. Concentration

Concentration of the chemical solution is one impacting the effectiveness of any chemical de-icer. In general, as the concentration increases the performance of a given de-icer increases. However, after a certain limit of concentration such performance begins to have the adverse effect. It should be noted that this limit is not fixed for all types of chemicals, where each chemical has its own limit. A phase diagram is the best tool to show the behaviour of the chemical given its concentration levels at the various temperatures.

Figure (1) illustrates the phase diagram for Sodium Chloride (salt), a commonly used roadway de-icer. As illustrated in the figure, the phase diagram is a graph representing the relationship of the freezing point of the materials versus concentration. The given example indicates that the performance of the sodium chloride increases as its concentration increases.

Then after a certain point, which is known as the eutectic point, the effect starts to reverse and higher concentration means diminished capacity to lower the freezing point of the solution.

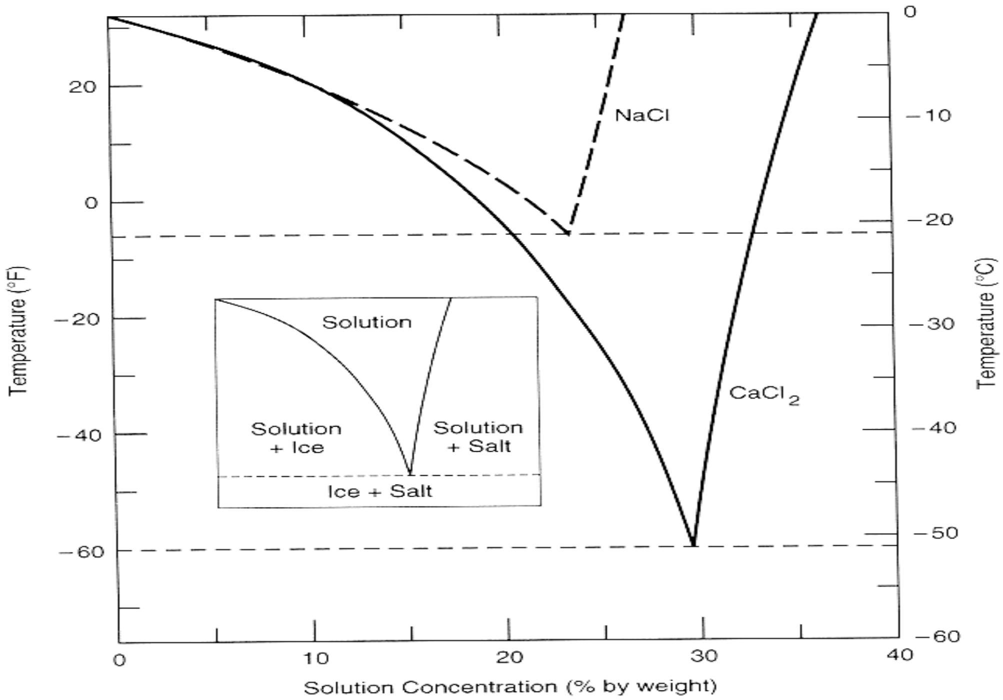

Figure (1): Phase Diagram For NaCl and $CaCl_2$

(From: FHWA Manual of Practice for an Effective Anti-icing Program)

3.2. Temperature

Temperature is another critical factor concerning the effectiveness of de-icing chemicals. The chemical bonds that exist between the ions in a solution are greatly affected by the flow of heat into, and out of, the system. As temperatures drops, the amount of de-icer needed to melt a given quantity of ice increases. For example salt can melt five times as much ice at -1°C than at -6°C. Therefore, two temperature points have to be identified for each de-icer chemical:

- Working Temperature: is the temperature at which the chemical exhibits obvious melting capacity within 20-30 minutes of application.
- Eutectic Temperature: is the lowest temperature at which the chemical is able to suppress the freezing point of water at its optimum concentration level.

Temperatures mentioned above are referring to pavement temperature not air temperature. Past research work showed that there is a significant difference between pavement and air temperatures within the same environment. Consequently using air temperature to evaluate the performance of a de-icing chemical may not entirely accurate. And if used in the winter operation decision process may lead to errors in timing of application, or application rates.

3.3. Time

A de-icing chemical should work reasonably fast under cold temperature conditions. Some chemicals require more time to react when the temperatures are lower than their working temperature. The effectiveness of various chemicals in temperatures above -6°C may not vary significantly, however, at lower temperatures the variation in reaction is clear. For example, Sodium Chloride takes longer to act than Magnesium Chloride or Calcium chloride.

4. CHEMICALS UNDER STUDY

The paper concentrates on evaluating the effectiveness of the product Magic. Published information on this product is as follows:

<u>Magic Liquid</u>

Concentration of Solution:	50% Ice Ban, 50% solution of 32% $MgCl_2$ (46% magnesium chloride overall)
Practical Working Temperature:	-20°C
Eutectic Temperature:	-30°C plus

<u>Ice Ban</u>

Ice Ban is a natural liquid concentrate residue from the wet milling of corn and the production of alcohol.

Eutectic Temperature:	-40°C when mixed with $MgC\ l_2$

5. EXPERIMENTAL CONSIDERATIONS AND DESIGN

In order to evaluate the effectiveness of the selected product (mentioned above), two experiments were designed to investigate the claim advertised performance of the product. These experiments were designed using temperature, time and concentration as their key elements.

5.1. Experiment I: Thermal Analysis of Magic Liquid vs. Magnesium Chloride

The main purpose of this experiment is to compare the cooling curves of Magnesium Chloride and Magic liquid. A cooling curve demonstrates how a solution freezes with consideration to both temperature and time, allowing for comparison between the two substances.

To achieve the objective of these experiments, two solutions of 6% and 10% $MgCl_2$ by weight were prepared from both the Magic Liquid and the Magnesium Chloride solution. Then the temperature time curves were measured for each solution and graphed. The results of this experiment are presented in detail through the next section.

5.2. Experiment II: Effect of Magic Liquid on the Freezing Point of Salt Brine

This experiment involves three parts:

- To determine the freezing point of magic liquid and water at the following concentrations: 5, 10, 20, and 30 percent volume of magic liquid.
- To determine the freezing point of magic liquid and a 20% salt solution at the following concentrations: 5, 10, 20 and 30 percent volume of magic liquid.

- To determine the time in minutes for each solution to freeze from the previous two parts.

In order to carry out the experiment in the three parts mentioned above, the volume concentrations were prepared by dilution method. Then each sample was inserted into the freezer and the temperatures as well as time, for all samples, were monitored as the solution solidified.

6. RESULTS

6.1. Experiment I

This experiment constructed cooling curves for a 6% and 10% solution (Figures 2 and 3 respectively) by weight of $MgCl_2$ from the MAG and Magic Liquids. For a 6% concentration of $MgCl_2$, the Magic Liquid freezes initially at –1.6°C and the MAG freezes at –3.0°C. Similarly for the 10% solution, the Magic Liquid initially freezes at –4.0°C and the MAG freezes at –5.0°C. This indicates that there is no significant difference between a solution of magnesium and water (MAG) and a solution of magnesium and Ice ban (Magic).

For time considerations, the two chemicals freeze at approximately the same time and cool with relatively the same slope. The magnesium chloride has a very long freezing span, which makes it good for winter application.

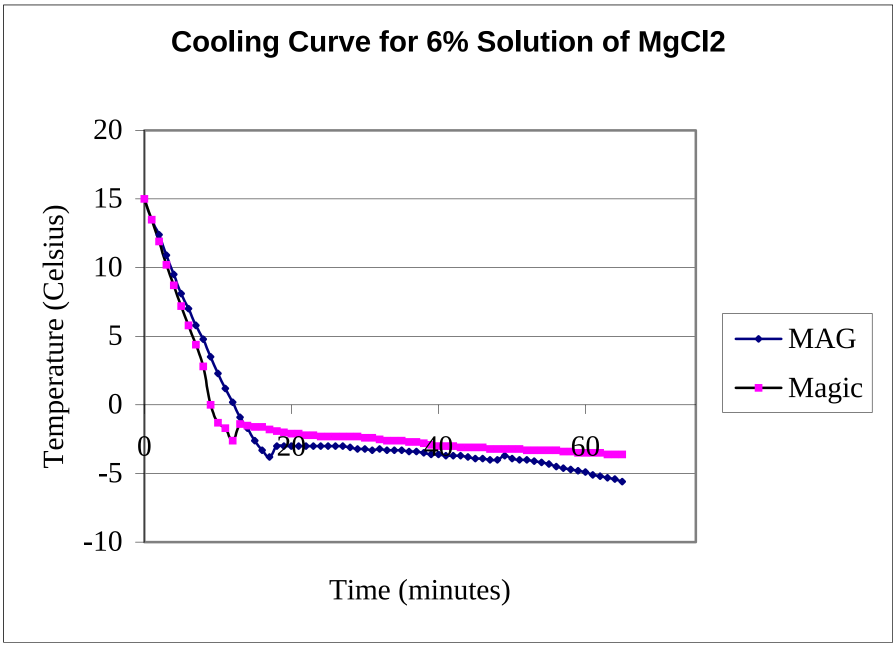

Figure (2): Cooling Curve for 6% $MgCl_2$

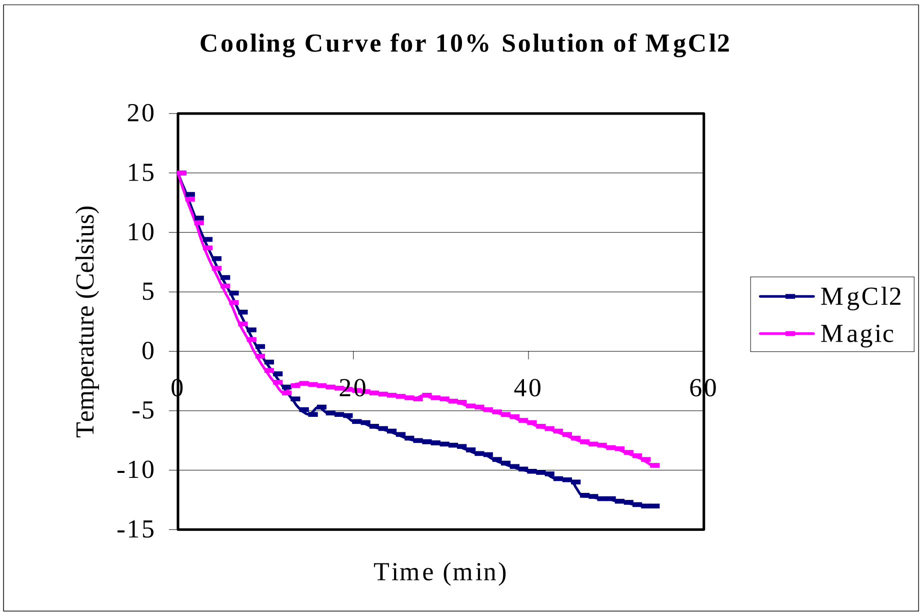

Figure (3): Cooling Curve for 10% $MgCl_2$

6.2. Experiment II

This experiment examined the effect of magic liquid on depressing the freezing point of salt brine. The results from the three parts of this experiment are summarized in Tables 1 and 2. Table 1 shows that magic liquid can alter the freezing point of salt solution by up to six degrees at a 30% ratio. Table 2.0 demonstrates that the time of freezing can be prolonged by almost 50% when using this same ratio.

Table (1): Effect of Magic Liquid on the Freezing Point of Salt Brine

% Magic Liquid & water (by volume)	Freezing Temp Range (°C)	% Magic Liquid & NaCl solution (by volume)	Freezing Temp Range (°C)
0	-0.1to –0.2	0	-16.9 to –18.9
5	-0.9 to –1.1	5	-17.6 to –19.8
10	-1.3 to –1.6	10	-17.4 to –18.6
20	-2.4 to –2.6	20	-18.8 to –21
30	-4.0 to –5.3	30	-19.3 to –23

Table (2): Effect of Magic Liquid on the Freezing Time of Salt Brine

% Magic Liquid & water (by volume)	Time to Initial Freezing	% Magic Liquid & NaCl solution (by volume)	Time to Initial Freezing
0	25.0	0	77.0
5	30.0	5	79.0
10	38.0	10	114.0
20	39.0	20	123.0
30	46.1	30	125.0

Note: The freezing temperature range refers to initial freezing until slush.

7. SOURCES OF ERROR

Laboratory tests may produce results that are different from that of actual field conditions. The tests performed can be used as basis for performance comparison of chemicals in question. As well, the tests can be used to verify concentrations of the material being marketed for use in real life situations. Some of the errors that can alter the results are mentioned below.

7.1. Factors Affecting De-icing Process

As indicated earlier, various factors affect the de-icing action of chemicals. The experiment focused on three main factors: temperature, time, and solution concentration, all specifically relating to the “science” of the de-icing process of used chemicals. The results produced are conservative since in real life situations, other additional factors come into play, some of which are: the effect of the sun on the surface of the pavement, the amount of heat the pavement is able to retain, the level on contaminated in the material used, the amount of traffic on a specific roadway, etc. The results produced here are used as basis for performance comparison between chemicals as well as the relative effectiveness of the chemical and whether it can be integrated into further experimentation.

7.2. Re-freezing

Re-freezing occurs when the chemical is no longer able to depress the freezing point of the solution, refreezing can occur under two conditions, on the road, and as ice and snow are melting from the first application of the chemical, it adds more water into the solution, in effect diluting the solution making it less concentrated causing it to freeze (or refreeze) at a higher temperature. On the road, that issue can be addressed by re-application of the snow and ice control chemicals; however, this was not the case in the lab, as the solution concentration is controlled, as well as the dilution rate.

The second condition to have a chemical de-icer loose its effectiveness and refreeze is higher concentration, at a certain temperature, beyond the saturation limit for the solution at that specific temperature. This can be understood by studying the phase diagram of the chemical. It can be seen that a chemical will change behaviour after the solution concentration reaches its optimum level at the eutectic point. After which point, more chemical will mean less effectiveness, and the freezing point will be higher on the curve.

In the lab experiment, the freezing process of the samples could have contributed to the change of concentration of the samples, as the solution become more concentrated as freezing occurred making the time appear longer for freezing.

7.3. Air Moisture

The experiments were conducted in a refrigerator where the air was relatively dry. Evaporation of solution samples used for the tests have been detected, it was evident by the level lines of the chemical on the inner walls of the containers. This would have again contributed to a change the concentration of the substances under observation.

8. FIELD TRAILS WITH MAGIC

The field trails were conducted in the winter of 1997-1998, and they consisted of the purchase of a treatment for approximately 300 tons of salt. The vendor was responsible for providing the Magic Material and for the mixing of the amount of salt designated for this field trail. The material was mixed in a specified area and stored under a covered shed to be used as a premixed, pre-wetted salt for temperatures lower than that used by the on-going operation of pre-wetting with 23% Sodium Chloride solution, which is activated while pavement temperatures are above –10°C. The objective of the field trail is to test the material under low temperature to be used as a pre-wetting agent. It should be noted that the treated material had exhibited a green colour and emitted a smell consistent with organic corn by-product; some operators started refereeing to the treated material as the “green salt”.

Subsequently, several spreader units were designated to load the treated salt when the temperatures dropped to the test propped temperature range. On the first snow storm with pavement temperatures at or below -10°C the treated material was loaded in the spreaders and went to work. The first problem the operators encountered was the inconsistency of the treated material. The material was lumpy and inconsistent. The difficulties continued as the material was being spread through the spreaders, as the material started to stick to the inside of the hoppers as well as stick to the spreader chutes and spinners. At that point the spreaders were ordered back to the patrol yard and gone through a cleaning process to red the unit from the material collected and solidified on the chute and spinners. After more than one unit had the same handling problems the field trials was terminated.

Other separate, limited attempts were conducted under different conditions. Those trails were met with limited success. After evaluating the several trials conducted, it seemed that the treated material will not stick to the equipment when the temperatures are moderate, however, when the temperatures are low the material tend to clot.

The particular field trails that were conducted at the Region of Ottawa-Carleton had not proven the viability of Magic as a pre-wetting agent for extreme low temperatures. Added to that the inability to justify the extra cost for a pre-wetting agent at moderate temperatures, while pre-wetting is being achieved with salt brine at a fraction of the cost.

9. CONCLUSIONS

This paper presented the experimental process carried out in the winter maintenance material laboratory of City of Ottawa to test a product marketed under the brand name “Magic”. And briefly discuss field trail outcome.

Based on the results observed from the experiments conducted, it can be concluded that the addition of magnesium chloride at concentrations ranging from 20% to 25% produces significant results in lowering the temperature of brine or water by at least 5°C. As the concentration is further increased, the freezing temperature is rapidly decreased.

There was no apparent difference between Magnesium Chloride solution at 29% and Magic Liquid. It can also be found the Magnesium Chloride solution has produced more favourable results in some cases.

It can be included that the addition of a magnesium chloride solution will yield similar or more favourable result as the addition of Magic to salt brine solution. Keeping in mind that the Magic liquid consists of 50% $MgCl_2$ solution and 50% Ice Ban. Further, it can be concluded that the addition of Ice Ban did not have any significant advantages to the final mixture properties.

Ice Ban was beneficial in extending the length of penetration through the surface; however, the difference is not significant enough to show significant impact when used in field applications. Further examination to determine the full of effects that Magic have to be conducted for its impact on construction materials and pavement, as well as environmental impacts on local ecological life.