

Experimental Study on the Characteristics of Eco-Friendly Deicers Utilizing Calcium-based Industrial By-products

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Abstract— Due to the report of incidences of damage caused by chloride deicers in recent years, the need for eco-friendly deicers has increased. However, it is necessary to enhance the quality and economic feasibility. The present study derived the optimal mix of eco-friendly deicers utilizing industrial by-products and compared their performance with those of existing chloride deicers. The test results showed that the eco-friendly deicer had better performance in terms of freezing point and in ice melting tests than calcium chloride-based deicers. The eco-friendly deicer displayed little corrosion in the steel corrosion test. In the snow melting performance evaluation, liquid eco-friendly deicers demonstrated a better performance in initial snow melting than powder calcium chloride-based deicers, verifying their applicability to real sites.

Keywords— Snowmelt, Calcium chloride, By-product

I. Introduction

Chloride-based ice-melting agents such as calcium chloride and salt have been widely used to facilitate road traffic conditions on roads during snowfall in winter. Chloride deicers have the advantages of melting ice on roads, preventing re-freezing of water over the road surface, and facilitating snow melting work by separating compacted snow from road surfaces. Other methods such as mixing with sands and spraying can be done to improve the sliding friction resistance coefficient. However, the above snow removal methods can be problematic in that they cause damage to surrounding environments and degrade road facilities. They can also cause problems such as inhibiting plant growth leading to etiolation or necrosis of leaves and early deciduous leaves; in addition, the corrosion of reinforced steel and degradation problems on the surfaces of concrete pavement have been reported in relation to road structures.



Figure 1. Damages at road facilities due to chloride-based deicers

As a method to solve the above problems due to deicers, the use of eco-friendly deicers has been investigated. However, although eco-friendly deicers have been developed actively, they have been low economic feasibility, which has prevented their wide application.

On the other hand, as industrial developments have continued a pace, the number of by-product wastes has increased more and more in industrial processes. In particular, organic wastes of by-products from food waste treatment processing and manufacturing processes of electronic products have increased significantly. Furthermore, calcium-based by-products from the cement and steel industries, which produce building materials, have created a recycling issue. Nonetheless, only simple treatments and processes have been used to process them, which have increased the demand on resource re-utilization from a recycling point of view.

As a result, the present study has conducted basic research to reduce the impact on surrounding environments and manufacture eco-friendly deicers, which can recycle industrial by-products.

II. Used material and test method

A. Used materials

In the present study, potassium acetate solution was fabricated using industrial by-products based on an optimum mix ratio derived through reagent grade organic reactions (acetic acid + calcium carbonate) and eco-friendly deicers were fabricated by mixing crude glycerin, which is a performance-enhancing material. The materials used in this test are as follows:

- Waste acetic acid: Acetic acid separated via vacuum evaporation method from mixed acid waste solution, which is a by-product in LCD fabrication process, was used. The quantitative analysis result of inorganic elements in the waste acetic acid is shown in Figure 2.
- Calcium carbonate by-product: Limestone dusts generated in manufacturing processes in the steel industry contain more than 50% of Ca. When calcium ion additive and non-ionic settling agents are added, calcium carbonate is fabricated. In Table 1, the chemical composition of the calcium carbonate by-product is summarized.
- Crude glycerin: Glycerin has been reported to be effective in alleviating freezing injuries and promoting ice melting, which can be applicable to a

source of deicers. The present study used crude glycerin which had undergone no refining process as a raw source of deicers. The characteristics of the used material are shown in Table 2.

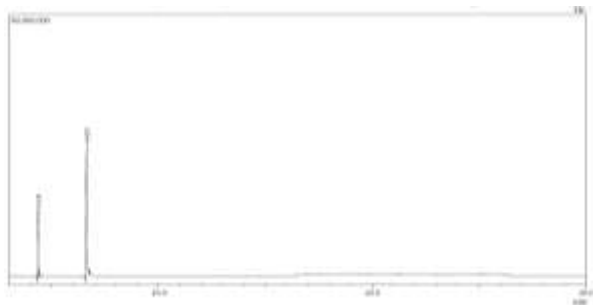


Figure 2 Result of quantitative analysis of inorganic elements in waste acetic acid

Table 1 Chemical properties of calcium carbonate by-product

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO	Lg-Loss
Component ratio (%)	2.1	1.1	2.6	51.7	2.3	1.0	41.8

Table 2 Composition of crude glycerin

	glycerin	Ash	Moisture	MOMG
Component ratio (%)	80~81.5	5.5~9.0	8~14	0.5~1.5

B. Experimental design

For the eco-friendly deicer, calcium acetate was fabricated by using a method in which calcium carbonate by-product, waste acetic acid, and water were put and mixed based on an optimum mix ratio derived through reagent grade organic reactions for a certain period of time and then non-reactants were filtered. For test control group, calcium chloride (powder), which was generally and widely used, was employed. The test conditions are summarized in Table 3.

Table 3 Test conditions

No.	Item	Type
P	Calcium chloride	Product (powder)
D1	Eco-friendly De-icing (1)	Calcium acetate (liquid)
D2	Eco-friendly De-icing (2)	Calcium acetate + glycerin (liquid)

The performance evaluation on the eco-friendly deicer was verified through freezing point measurement, ice melting test, corrosion performance test, and snow melting performance evaluation.

- Freezing point: The freezing point measurement of deicer was done in accordance with ASTM D1493 “Test Method for Solidification Point of Industrial Organic Chemicals” and the measurement scene is shown in Figure 3.
- Ice melting: In the ice melting test, the mass of melted liquid was measured at certain intervals (10, 20, 30, 45, and 60 min) after putting the ice melting agent over the frozen ice inside a container.

- Corrosion performance: This test was conducted in accordance with the “Performance Evaluation on Deicers - Testing Method of the Corrosion Effect on Steel” in EM502-1 among EL-610 certification standards.
- Snow melting performance: To evaluate the snow melting performance of deicers at real sites, a region of 2x2 m² was set up and a snow melting area was compared over time. Figure 4 shows a photograph of the test.



Figure 3 Photograph of freezing point measurement



Figure 4 Photograph of snow melting performance test

III. Experimental Results

A. Freezing point

The results of the freezing point measurements according to mixing conditions are shown in Figure 5. A previous study reported that for calcium chloride, which was a control group, the eutectic point was found to be -51.1°C at 29.8% of concentration and our test result showed that a freezing point of -30.4°C was measured at 30% of concentration. The test result was quite significantly different compared to the eutectic point in the previous study. This was due to the fact that calcium chloride, which was a commercial product, was di-hydrate.

For the eco-friendly deicer, a freezing point of 16.2–40.2°C was measured at D1 and D2 mix conditions and a superior freezing point was found at a mix which had a high proportion of solid within a range recommended in the present test conditions. This result was consistent with a previous study result in which the highest freezing point was

found around 30% of concentration as proposed in existing studies on eco-friendly deicers.

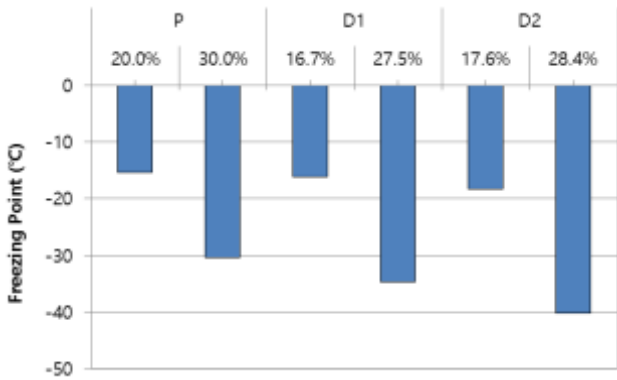


Figure 5. Freezing point measurement results by mix conditions

B. Ice melting

Figure 6 shows the ice melting test result performed at -7°C, in which the cumulative ice melting amount over time is shown.

For calcium chloride as a control group, the ice melting effect was low initially. This was due to a relatively lower specific surface area than the liquid deicer that was reacted between power deicer and ice.

For the eco-friendly deicer, ice melting performance was superior initially and after 60 min, a more than 22% better ice melting effect was achieved compared to that of calcium chloride. Furthermore, the test result revealed that ice the melting performance was improved when mixed with crude glycerin.

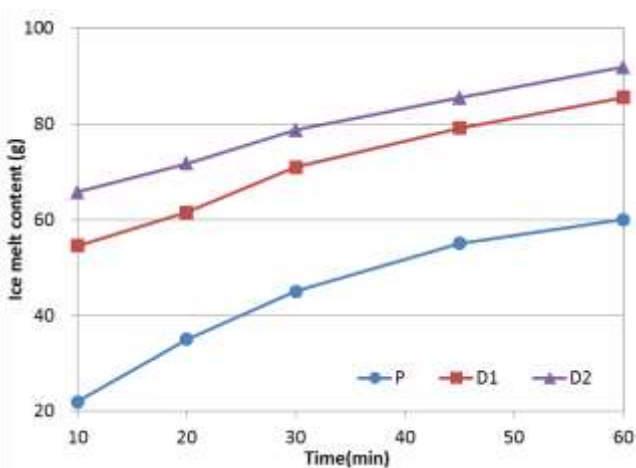


Figure 6. Measurement result on ice melting amount by mix condition

C. Corrosion on steel

A deicer liquid of mass ratio 3% concentration was fabricated for each piece and 70 x 150 mm and 1mm-thick steel was fabricated without plating or coating process, which was then immersed in the deicer for three weeks to measure corrosion. Prior to the measurement, steel was degreased and cleansed with acetone to prevent rust

followed by being dried and stored. The corrosion area ratio was calculated by a ratio of the total corrosive area of the specimen to the initial area and the mass reduction was evaluated by measuring the mass of the specimen after removing the corrosion material created after three weeks of immersion. The evaluation results are shown in Figures 7 and 8. Overall, corrosion on steel that was immersed in calcium chloride was worse than others. The mass reduction due to corrosion on the surface of the specimen was 3.92mg/cm². The eco-friendly deicer had little corrosion so its corrosion area ratio was 0% and mass reduction was 0.38-0.29mg/cm², indicating superior anti-corrosion on steel.

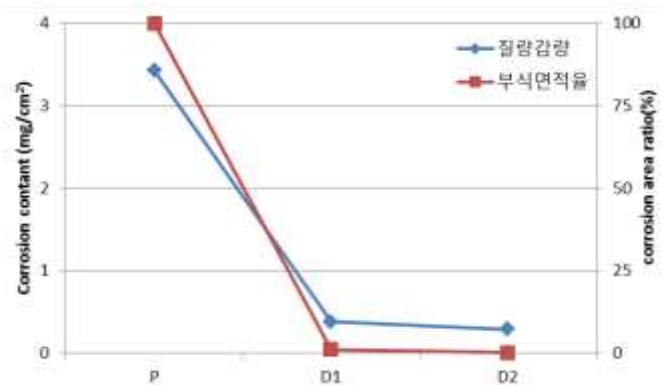


Figure 7. Mass reduction and corrosion area ratio by mix condition



Figure 8. Steel corrosion by mix condition and age

D. Snow melting performance

In order to verify the snow removal performance of the deicer, evaluations on snow removal performance were conducted after real snow fall and the result is shown in Figure 9. The test was done at about 10 mm of snow fall and -0.7°C of mean temperature. Calcium chloride was a powder type and sprayed sporadically at a rate of 100g/m² while the eco-friendly deicer was a liquid type and sprayed with sprayer at a rate of 750g/m².

The test result showed that the eco-friendly deicer had better snow removal performance than calcium chloride. Since calcium chloride was sprayed as powder and a specific surface area where the powder can be reacted during snow and ice melting was smaller than that of the

eco-friendly deicer, the snow removal effect was low. According to time lapse, snow was completely removed after 35 min at the eco-friendly deicer (D2) mix condition whereas calcium chloride did not complete the snow removal completely even after 90 min.

The reason for the different result of snow removal effect of calcium chloride from that of previous study results was because the test was not conducted in real road traffic conditions so that friction due to vehicle wheels was not a factor.

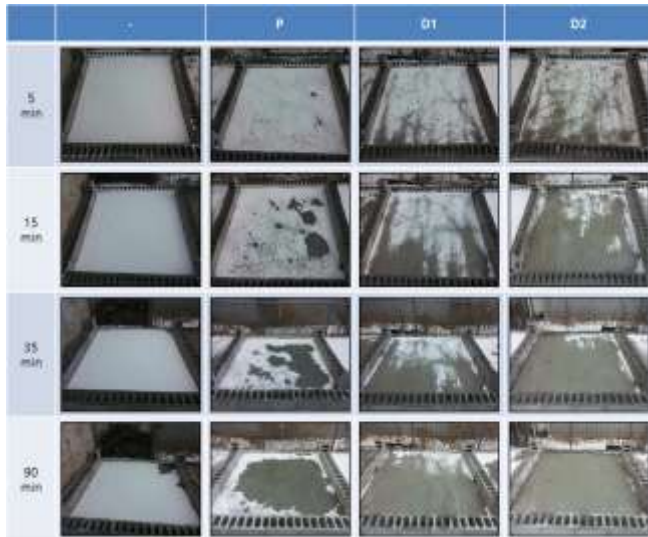


Figure 9. Evaluation result of snow melting performance by mix condition

iv. Conclusion

The present study aimed to derive an eco-friendly deicer mixture and verify the performance in order to reduce damage caused by chlorine-based deicers. The comparison results between calcium chloride and eco-friendly deicer are as follows:

- 1) The freezing point measurement of the eco-friendly deicer showed a lower freezing point than that of calcium chloride (di-hydrate) liquid and the appropriate concentration was approximately 30%.
- 2) The ice melting test result showed that the liquid eco-friendly deicer had better ice melting performance than that of powder calcium chloride deicer and ice melting performance was improved by mixing crude glycerin.
- 3) The steel corrosion test showed that the mass reduction rate was improved more by using the eco-friendly deicer than by using chlorine-based deicer.
- 4) The evaluation on snow melting performance showed that snow was completely removed after 35 min of spraying the eco-friendly deicer (D2).

In the present study, the applicability of the eco-friendly deicer was verified when mixing 10% of crude glycerin to calcium acetate mixture followed by making the solid at 30%. For future research, an evaluation on durability such as freeze-melting test and analysis on economic feasibility should be conducted.

Acknowledgment

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