

Ice melting performance of deicers and their effect on stripping resistance of asphalt mixture

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Abstract: The ice melting performance of three types of deicers, including sodium chloride, calcium chloride and sodium acetate, were tested in laboratory under different temperature conditions, and their effects on asphalt mixture were evaluated from the point of the stripping resistance of asphalt mixture. Unsaturated Marshall samples were exposed to freeze-thaw cycling while immersed in the deicer solutions of different concentrations. After the freeze-thaw cycles, Cantabro tests were performed, and Cantabro loss was adopted to characterize the stripping resistance of asphalt mixture. The test results show that calcium chloride has the best comprehensive ice melting performance, and all deicers have detrimental effect on the stripping resistance of asphalt mixture at different degrees. The damage degree depends on deicer types and their concentration in the solution. Deicer solutions with about 2% concentration cause the greatest loss of stripping resistance due to serious freeze-thaw damage. Sodium acetate causes greater loss of stripping resistance than sodium chloride and calcium chloride at the same concentration.

Key words: deicer; ice melting performance; stripping resistance; freeze-thaw; Cantabro test

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Control of snow and ice plays a major role in the maintenance of cold region pavement during the winter months. As snow accumulates on the pavement surface, it will be compacted by vehicles and tightly bonded to pavement, making it slippery and leading to potential traffic accidents. Therefore, deicers are extremely critical for maintaining a high level of service and ensuring the safety of cars on highways in winter. Chloride salts are the most commonly used chemicals that serve as deicers for winter highway maintenance due to their abundance and low cost. While the heavy use of chloride-based deicers has caused a series of environmental problems, the dissolution of chloride-based deicers leads to the increase

of soil salinity, which may have detrimental effects on roadside vegetation and even people's health^[1-3]. In response to this problem, acetate- and formate-based deicers, also known as environment-friendly deicers, were introduced to the snow and ice control of pavement later. Application of these acetate- and formate-based salts effectively decreased the environmental pollution from deicers, but their negative effects on asphalt pavement increased at the same time.

As early as in 1990s, it was found that the durability of runway asphalt pavement in Nordic countries dropped dramatically after deicers were changed to acetate- and formate-based salts^[4]. Field investigations showed that acetate- and formate-based deicers tend to soften asphalt binders and accelerate the stripping and raveling of asphalt mixture^[5-6]. It was also proved that deicers increase the moisture susceptibility of asphalt mixture by enhancing its ability to absorb moisture from the atmosphere^[7]. The chemical reaction between acetate- and formate-based deicers and asphalt led to the deterioration of asphalt binder^[8]. Pan et al.^[9] verified emulsification of CH_3COO^- on asphalt binder through laboratory experiments. Moreover, it was identified that chloride-based deicers resulted in hardening of asphalt binder^[10-12]. Several laboratory studies have been carried out by researchers to evaluate the effects of different deicers on the performance of asphalt mixture. The effects of deicers on asphalt mixture during winter months were simulated through freeze-thaw cycling in deicer solutions, and dry-wet cycling was performed to simulate the damage of residual deicers on asphalt mixture during summer months^[13-14]. The test results of indirect tensile strength indicated that all deicers have some damaging effect on both aggregates and asphalt mixture, and the maximum damage depends on the deicer and its concentration in the solution.

The loss of indirect strength is not closely related to raveling and stripping, which are the main forms of deicer-induced damage of asphalt pavement. Raveling and stripping of asphalt mixture is caused by poor asphalt-aggregate adhesion. Therefore, it is necessary to characterize the effect of deicers on the stripping resistance of asphalt mixture. The Cantabro test is a standard test method specified in Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering (JTG E20—2011) of China to evaluate the stripping resistance and durability of open graded asphalt mixture. Similar to open

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graded mixtures, the deicer-induced raveling and stripping of normal dense graded asphalt mixtures are also caused by poor adhesion due to freeze-thaw damage and the erosion of deicers. Therefore, it is feasible to use the Cantabro test to characterize the stripping resistance of dense graded asphalt mixture.

Although the destructive effects of deicers on asphalt pavement are ignorable, its deicing performance is the most significant consideration in the selection and application of deicers. Thus, the ice melting test, which is one of the standard test procedures for the deicing performance of deicers specified by the Strategic Highway Research Program (SHRP), was introduced to test the ice melting performance at different temperatures, so as to evaluate deicers comprehensively and provide a guide for selecting deicers in practical applications.

1 Test Materials

1.1 Deicers

Although chloride-based salts may lead to many environmental problems, they are still widely used as pavement deicers. In order to comparatively evaluate traditional chloride-based deicers and new environment-friendly deicers, three types of deicers, namely sodium chloride (SC), calcium chloride (CC) and sodium acetate (SA), were adopted representatively in this study. All the deicers were commercial analytical reagents. Deicers were tested in the form of solid particles in the ice melting test, and deicer solutions were prepared in the adhesion and freeze-thaw test. Four different concentrations, 2%, 5%, 10% and 20%, were considered so as to investigate the influence of concentration. Distilled water (0% deicer solution) was set as the blank group.

1.2 Asphalt

Given that styrene butadiene styrene (SBS) modified asphalt is widely used in the surface course of asphalt pavement which is directly in contact with deicers, SBS modified asphalt was used in the laboratory tests of this study. The properties of SBS modified asphalt were tested according to Chinese specifications and test results are given in Tab. 1.

Tab.1 Properties of SBS modified asphalt

Index		Tested value	Requirement
Penetration at 25 °C/(0.1 mm)		63.6	>60
PI		0.08	> − 0.4
Softening point/°C		62.7	>55
Ductility at 5 °C/cm		30.5	>30
Kinematical viscosity at 135 °C/(mm ² · s ^{−1})		1.551	<3
Elastic recovery at 25 °C/%		83	>65
RTFOT	Mass loss/%	0.31	<1.0
	Residual penetration ratio at 25 °C/%	67.1	>60
	Residual ductility at 5 °C/cm	20.1	>20

1.3 Asphalt mixture samples

Crushed limestone was used as mineral aggregates in this study. Considering that asphalt concrete with nominal maximum aggregate size less than 13.2 mm, namely AC-13, was widely used in the construction of surface course of asphalt pavement in China, laboratory tests were conducted with AC-13 asphalt mixture samples. To ensure the representativeness of asphalt mixture samples, the mean value of gradation range specified in Specifications for Design of Highway Asphalt Pavement of China was chosen, and the aggregate gradation is shown in Tab. 2. Asphalt mixture was designed by the Marshall method. The optimal asphalt-stone ratio is determined to be 5.2%, and other technical parameters are shown in Tab. 3. All samples were prepared by the Marshall compaction method.

Tab.2 Gradation of aggregate

Sieve size/mm	13.2	9.5	4.75	2.36	1.18	0.6	0.3	0.15	0.075
Passing percent/%	95	76.5	53	37	26.5	19	13.5	10	6

Tab.3 Technical parameters of AC-13 asphalt mixture

Parameters	Tested value	Requirement
Bulk density/(g · cm ⁻³)	2.424	
VV/%	3.89	3 to 5
VMA/%	14.4	60 to 75
VFA/%	71.7	≥14
Marshall stability/kN	11	≥8
Flow/(0.1 mm)	32	20 to 40

2 Test Procedure

2.1 Ice melting test

The goal of this test is to evaluate the icing melting capacity of different deicers at different temperatures, and the ice melting test (see Fig. 1) also helps to compare the ice melting performance of a specific deicer with other deicers at a given temperature. The test follows the procedure of the Ice Melting Test of Solid Deicing Chemicals described in SHRP-H-332^[15], but the circular plexiglas dish was replaced by a 150 mm petri dish. To ensure the consistency of the ice thickness and deicer dosage, other testing parameters were converted accordingly.

In the ice melting test, a layer of uniform thickness (3.175 mm) was prepared and equilibrated to testing temperature in a high-low temperature test box, then deicer particles were scattered uniformly over the surface of the ice and the test started. At the intervals of 10, 20, 30, 45, and 60 min, the melted deicer solution was collected by tilting the petri dish and withdrawing it through a syringe, then the collected deicer solution was reintroduced to the petri dish quickly after measuring its volume, so that the melting process could continue. Three

different temperatures were considered in this study, namely -5 , -10 , and -15 °C. At each temperature, three parallel tests were conducted for every deicer type, and the mean value of three parallel test results was taken as the final ice melting volume at a certain interval.

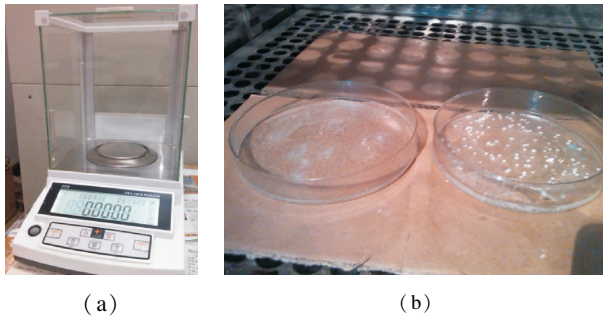


Fig. 1 Ice melting test. (a) Analytical balance; (b) Petri dishes

2.2 Freeze-thaw test in deicer solutions

Different from the normal freeze-thaw test, before freeze-thaw cyclings, all asphalt mixture samples were saturated by being immersed in deicer solutions for 20 h at room temperature, instead of being saturated under vacuum conditions. Then the samples were exposed to freeze-thaw cycling while immersed in deicer solutions of different concentrations. It took 48 h for one freeze-thaw cycle, including 36 h freezing in a -18 °C refrigerator and 12 h thawing at room temperature. Asphalt mixture samples were separated into two groups and subjected to 10 and 20 freeze-thaw cycles, respectively. There were three types of deicer solutions in each group, and five concentrations, 0%, 2%, 5%, 10% and 20%, were tested for each type of deicer. Deicer solutions were refreshed every five freeze-thaw cycles.

When freeze-thaw cycling was finished, samples in each group were subjected to the Cantabro test. The Cantabro test procedure used in this study was based on the test method for SMA mixture abrasion loss specified in Standard Test Methods of Bitumen and Bituminous Mixtures for Highway Engineering (JTG E20—2011). A standard Marshall sample was placed in the drum of a Los Angeles Abrasion testing machine without steel spheres and subjected to 300 revolutions. Then, the largest portion of the tested sample was removed from the drum, lightly brushed off with a wet towel and weighed. The mass of the sample was recorded before and after the test, and the loss in the sample mass during the test reported as a percentage of the original mass was obtained as Cantabro loss.

Prior to testing, samples were immersed in a 20 °C thermostat water bath for 12 h. The sample surface was dried with a wet towel before weighing, and then it was put into the drum of the Los Angeles Abrasion testing machine, in which the residual of last sample was moved.

3 Results and Discussion

3.1 Ice melting performance of deicers

The deicing mechanism of deicers is that the addition of deicers decreases the freezing point of water, causing ice or snow to melt at temperatures below zero. However, the freezing point of the deicer solution depends on its concentration, when the deicer solution type is the same. The greater the density, the lower the freezing point. Fig. 2 shows the freezing point of the sodium chloride solution^[16].

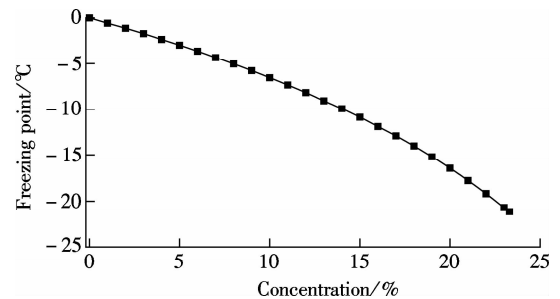


Fig. 2 Freezing point of the sodium chloride solution^[16]

Fig. 3 shows the results of the ice melting test. The whole ice melting process in the test can be divided into

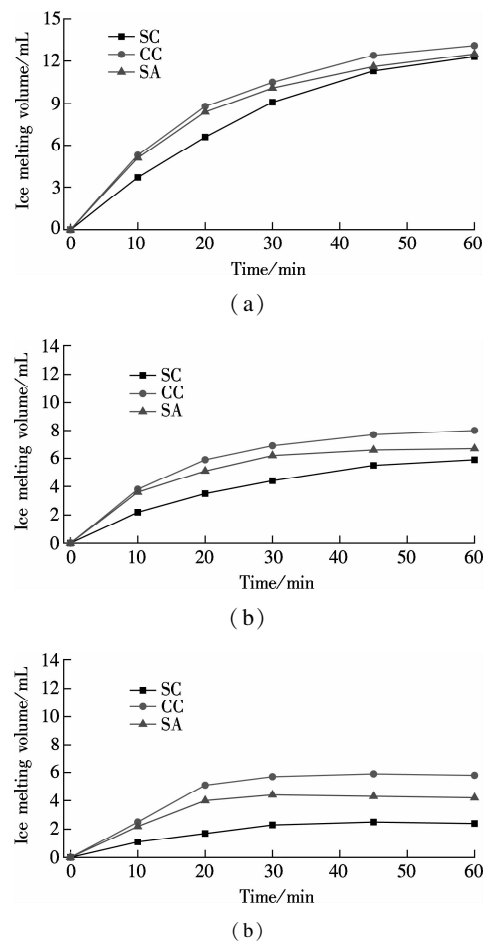


Fig. 3 Ice melting performance of deicers at different temperatures. (a) -5 °C; (b) -10 °C; (c) -15 °C

two stages: the dissolution of solid deicers and dilution of deicer solutions. At the first stage, the concentration of deicer solutions were kept at a high level and the ice melting rate was very fast, then the ice melting rate slowed down gradually with decreasing concentration at the second stage. At the end of the second stage, the ice melting volume curve became flat due to the poor ice melting ability of low-concentration deicer solutions. Heat of solution generated in the dissolution process of the deicer also helps to accelerate melting of the ice sample. Obviously, at the beginning of the test, the ice melting volume of SC was far less than those of CC and SA at all temperatures, which is because both the dissolution processes of CC and SA are exothermic but the dissolution of SC is an endothermic process.

The integrated ice melting capacity can be reflected by the total ice melting volume in 60 min. The results show that CC had the best ice melting performance among three types of deicers, and it melted the most amount of ice at all three temperatures in 60 min. SA had the medium ice melting capacity among SC, CC and SA. The performance of SC was largely dependent on temperature conditions. It showed considerable ice melting capacity with SA at -5°C , but appeared to have far less ice melting capacity than SA and CC at -10°C and -15°C .

3.2 Effect of deicers on stripping resistance of asphalt mixture

The results of the Cantabro test after 10 and 20 freeze-thaw cycles are shown in Fig. 4. Compared with unfrozen samples, of which the Cantabro loss was only 5.1%, the Cantabro loss of samples suffered freeze-thaw cycling increased dramatically, and the more freeze-thaw cycles samples that suffered, the larger the Cantabro loss. Fig. 4 shows that Cantabro loss of asphalt mixture samples was greatly influenced by the concentration of deicer solution during freeze-thaw cycles. For all three types of deicers, Cantabro loss of samples freeze-thaw cycled by 2% deicer solutions was the highest among all five testing concentrations, indicating that the deicers critically affected the freeze-thaw damage of asphalt mixture, and 2% was the most destructive concentration.

Deicer seems to affect freeze-thaw damage by influencing water absorption of the asphalt mixture. Fig. 5 shows the water absorption of asphalt mixture samples measured after 10 and 20 freeze-thaw cycles. It can be supposed that the maximum water absorption exists between 2% and 5%. Freeze-thaw damage is caused by the icing pressure which is produced in the freezing process of void water within asphalt mixture samples. Therefore, for distilled water, the more water samples that have been absorbed, the higher the icing pressure that will be produced during the freezing process. Nevertheless, the freezing process of the deicer solution in void is different from

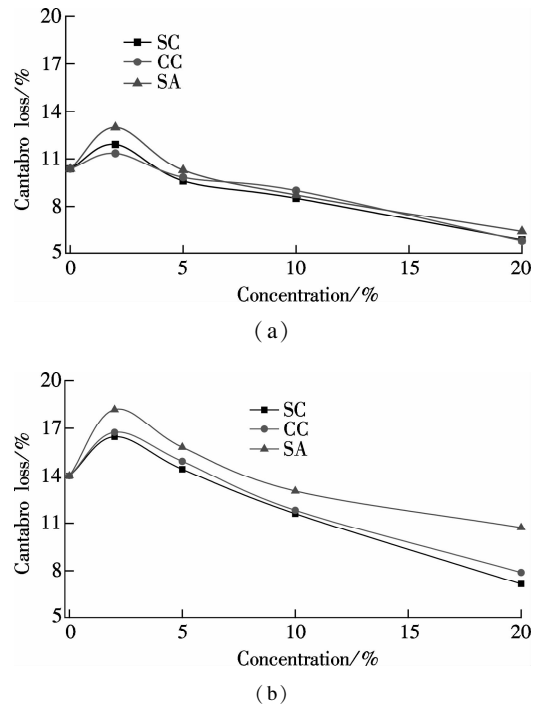


Fig. 4 Results of Cantabro test after freeze-thaw cycling. (a) 10 cycles; (b) 20 cycles

that of distilled water. According to Raoult's law, water might crystallize first during the freezing process of the deicer solution in void, resulting in that the concentration of unfrozen solution is increased and its freezing point decreased. While the testing temperature was limited, the volume of frozen water in void decreased with the concentration rising when water absorption was fixed.

Moreover, the freezing point of the solution in capillary pores was lower than that in voids under the same concentration conditions according to the Kelvin equation. Therefore, the increase of water absorption cannot effectively increase the volume of frozen water when the water absorption was close to saturation level. Based on these two reasons, concentration leading to the maximum water absorption was not in accordance with the concentration that caused freezing of the maximum volume of void water in the freezing process. Although the maximum water absorption was obtained at a concentration between 2% and 5%, the maximum volume of frozen water, which means the maximum icing pressure, was achieved at a concentration around 2%. In brief, through the influencing freezing point of the deicer solution and water absorption of samples, the concentration of deicer solution affected the volume of frozen water at the end of freezing stage of a freeze-thaw cycle, and finally determined the magnitude of icing pressure.

From the Cantabro test results after 10 freeze-thaw cycles, the impact of the deicer type on the Cantabro loss is not very clear. Under the most destructive concentration, the effect of SA appeared to be the largest, but the difference among three types of deicers diminished as concen-

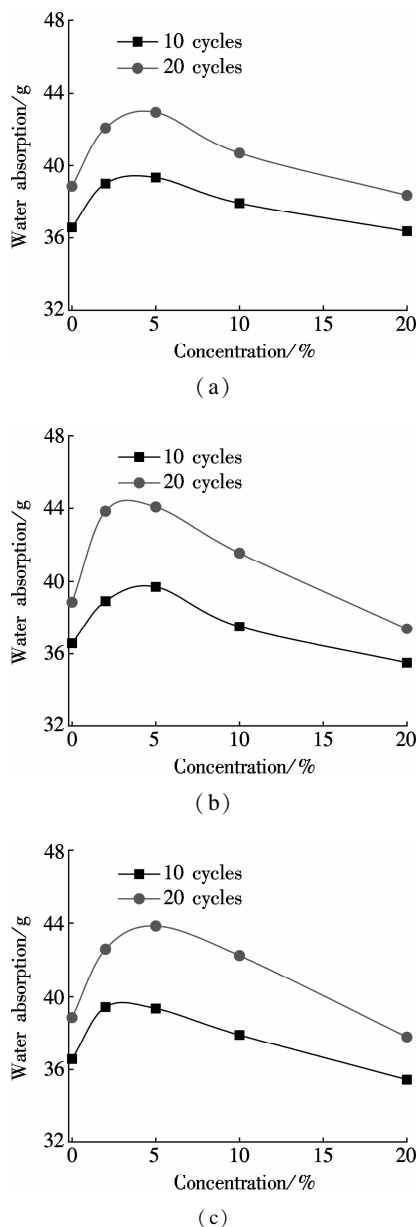


Fig. 5 Variation of sample water absorption with concentration. (a) SC; (b) CC; (c) SA

tration rose. However, after 20 cycles, it can be found that deicer type had an evident effect on the freeze-thaw damage of asphalt mixture, particularly the considerable difference between SA and the other two chloride-based deicers (SC and CC).

The damage of asphalt mixture during freeze-thaw cycles consists of freeze-thaw damage and erosion of deicer solutions. Due to the variation in freezing point with concentration, the deicer solutions with a high concentration cannot freeze at the test temperature. Fig. 6 shows the icing condition of SC solutions with different concentrations at the end of 36 h freezing. Similarly, there is a parallel situation in respect of CC and SA. Obviously, 20% deicer solutions did not freeze during the whole freeze-thaw cycle, while samples conditioned by 20% deicer solutions were still tested and damaged to a certain degree after 20

freeze-thaw cycles compared to the unfrozen samples which were immersed in distilled water for 40 d at 20 °C. It demonstrates that erosion of the deicer also contributes to the destruction of the asphalt mixture during freeze-thaw cycles. In Fig. 3 and Fig. 4, the Cantabro test results of samples conditioned by 20% deicer solutions after 20 freeze-thaw cycles show that the erosion of SA is far stronger than that of SC and CC, indicating emulsification of SA solution.

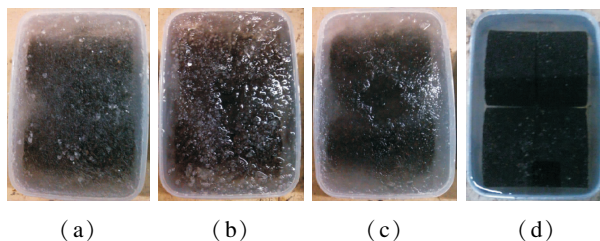


Fig. 6 Icing condition of SA solutions at different concentrations. (a) Frozen completely and tightly (2%); (b) Frozen completely (5%); (c) Partially frozen (10%); (d) Unfrozen (20%)

4 Conclusion

In this study, three types of deicers including sodium chloride, calcium chloride, and sodium acetate were evaluated combining ice melting performance and its damage to asphalt mixture. Among all three types of deicers tested in this study, calcium chloride shows the most outstanding ice melting performance at all temperatures with relatively small damage to asphalt mixture. Asphalt mixture samples exposed to freeze-thaw cycling while immersed in deicer solutions experience loss of stripping resistance. The damage degree depends on deicer types and their concentration in the solution. Deicer solution is the most destructive to asphalt mixture when its concentration is around 2%, and sodium acetate causes the maximum loss of stripping resistance. Water absorption of asphalt mixture, which is largely influenced by deicer concentration, is the main factor that leads to freeze thaw damage and causes loss of stripping resistance.

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融雪剂融冰能力及其对沥青混合料抗剥落性能的影响

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摘要:选取氯化钠、氯化钙和醋酸钠 3 种融雪剂,通过室内融冰试验测试融雪剂的融冰性能,并从抗剥落性能的角度评价融雪剂对沥青混合料的破坏.试验中将未饱水马歇尔试件浸入不同浓度的融雪剂溶液中进行冻融循环,冻融循环结束后进行肯塔堡飞散试验,以飞散损失作为沥青混合料抗剥落性能的评价指标.试验结果表明:氯化钙的综合融冰性能最强,冻融循环过程中 3 种融雪剂均对沥青混合料造成不同程度的抗剥落性能损失,其破坏程度与融雪剂的种类和溶液浓度有关.融雪剂溶液的质量分数为 2% 左右时,破坏最为严重,沥青混合料的抗剥落性能损失最大;在质量分数相同的条件下,醋酸钠引起的抗剥落性能损失大于氯化钠和氯化钙.

关键词:融雪剂;融冰性能;抗剥落性能;冻融;肯塔堡飞散试验

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