Effect of freezing and thawing cycle properties of cement-stabilized macadam materials with self-prepared early-strength agents

M Lin¹, Y C Guo¹, B S Tian² and Y L Song¹,*

¹School of Civil Engineering, Inner Mongolia University of Technology, Hohhot 010051, China
²Chang'an University, Xi'an 710064, China.

*E-mail: syllsj@sina.com

Abstract. Three types of cement-stabilized macadam materials and raw materials mixed with a self-made early-strength agent were prepared and subjected to freeze-thaw cycle tests. Based on the unconfined compression and freeze-thaw cyclic tests, the compressive strength and mass loss rate, and frost resistance coefficients of these samples were assessed and compared. The change of material properties caused by different content of early-strength agent was analyzed. The results show that three kinds of early-strength agents can improve the compressive strength and freezing resistance of cement-stabilized macadam. The compressive strength of cement-stabilized macadam with 2.0% anhydrous sodium sulfate and 1.0% triethanolamine is the best; the compressive strength is increased by 73.8%. Cement-stabilized macadam material with 1.5% anhydrous sodium sulfate and 1.0% triethanolamine has the best frost resistance, and its mass loss rate is reduced by 0.733%. The curves of mass loss rate and freeze-thaw cycle times of four groups of material are established, and the trend of positive correlation between the content of anhydrous sodium sulfate and the freezing resistance is obtained.

1. Introduction

At present, cement-stabilized macadam is used as subbase of most asphalt concrete pavement in China. This kind of material is between flexibility and rigidity, so it is called semi-rigid subbase. This subbase acts as main bearing structure, under the effect of reloading, fatigue performance of this material would significantly impact the pavement durability. Insofar as cement curing takes more than seven days to form the full strength, which seriously affects the construction progress, it is crucial to develop an early strength agent that can rapidly increase the strength of cement-stabilized macadam and reduce the curing time to speed up the construction progress. Zhang et al. [1] proved that the early-strength agents development which meet the low-temperature early strength requirements and get excellent operability is a vital direction of research now. [1]. Frigid zone (i.e., a zone between the Arctic Circle and the North Pole) in the North of China has as long as five months frost time in a year. This would make asphalt pavement cracking in this low-temperature environment. When the water permeates into the base from road surface course, the water freezes and expands at a temperature below 0°C, then internal structure of subbase course material would be damaged. Under repeated actions of vehicle load, the structure of semi-rigid subbase course material will be destroyed directly, mainly due to the temperature difference between day and night, and multiple freeze-thaw cycles during a day, the damage of semi-rigid subbase
course material becomes aggravated [2-5]. Numerous research studies were devoted to the performance of semi-rigid subbase course materials [6-8]. By mixing an ordinary silicate cement and other types of cement in different proportions, several researchers, such as Péra and Ambroise [9], Janotka [10], Czernin [11], and Chatterjee [12], successfully prepared plenty of early strength cement, that could make the forming strength of cement faster in varying degrees. Through a series of experiments, Berger et al. [13, 14] revealed that gypsum could improve the hydration rate of sulphoaluminate cement to some extent, and thus enhance the early strength of sulphoaluminate cement. At the same time, the hydration rate of sulphoaluminate cement after 24 hours could be slowed down. Clark and Brown showed that lithium salt could also play a vital role in hydration of sulphoaluminate cement. They found a small amount of lithium carbonate could significantly improve the early strength of sulphoaluminate cement, while the setting rate of cement was accelerated to a certain extent [15,16]. By studying the structure and mechanical properties of triethanolamine (TEA), Ma et al. found that there is a double critical amount of TEA. A proper amount of TEA can effectively improve the compressive strength of cement and control the setting time of cement [17]. Sha Aimin got different materials fatigue life prediction models through fatigue indoor experiment of all kinds of semi-rigid base materials. Then he explains the influence of material on fatigue performance [18, 19]. In this paper, to improve the frost resistance of cement-stabilized macadam material, an early strength agent was given, the best dosage of early strength agent based on the freezing-thawing experiment was also provided, which has best anti-frost property. The curve relation between the dosage of early strength agent and the anti-frost coefficient is fitted.

2.Materials

2.1 Cement

We chose cement material according Technical Norm for Construction of Highway road bed (JTG-T-F20-2015) [20]. The result measured by testing all parameters of cement is recorded in Table 1.

| Project | Setting time, min | Compression strength, MPa | Rupture strength, MPa |
|---------|-------------------|---------------------------|----------------------|
| Initial setting time | Final setting time | 3d | 28d | 3d | 28d |
| Technical requirements for cement raw materials | ≥180 | ≥360 and≤600 | ≥16 | ≥32.5 | ≥3.5 | ≥5.5 |
| Experimental result | 245 | 420 | 17.8 | 43 | 4.4 | 8.7 |

2.2 Aggregate, triethanolamine (TEA) and anhydrous sodium sulfate: Table 2

| Material name | Source | Reagent content |
|---------------|--------|-----------------|
| aggregate | Mount Daqing stone plant in Hohhot | |
| TEA | Tianjin Chemical Co., Ltd. (China) was adopted | ≥85% |
| anhydrous sodium sulfate | Tianjin Chemical Co., Ltd. (China) was adopted | ≥99% |

3.Empirical method

3.1 Unlimited compression test
We chose 3 effective implantation volume, which specific compounding ratio recorded in table 3, by doing complex hardening accelerator experiments. And compared them with control group. The testing period is 12h, 24h, 48h, 72h, 168h and 672h. Every testing period needs one specimen.

| Name                  | anhydrous sodium sulfate | TEA   | Quantity |
|-----------------------|--------------------------|-------|----------|
| Volume I pressure     | 2.0%                     | 1.0%  | 13       |
| Volume II pressure    | 2.0%                     | 0.75% | 13       |
| Volume III pressure   | 1.5%                     | 1.0%  | 13       |

Table 3 Each dosage group

Through unconfined compression strength test, we find that the compressive strength of cement-stabilized macadam materials could be significantly improved by cement early-strength admixture of three trial groups, no matter the difference between three admixture [21]. During 24 hours, the strength results of unconfined compressive strength test respectively increased by 74% (dosage I), 62% (dosage II), 58% (dosage III), compared with the blank group compressive strength test. We used Friedman statistical analysis by SPSS software in order to study the difference of compressive strength between three admixture groups.

To analyze the difference between each group and eliminate the influence of the variation within the group, the data of each group was examined by the two-way grade variance analysis. Independent of the data of each group, the principal features in each group were ranked, the differences within the group were eliminated, and any differences between various dosage groups were checked. The statistical analysis of the compressive strength of 312 samples was carried out by using the SPSS software. The results showed no significant difference. If the probability (P) value was less than a given significance level of 0.05, the original hypothesis would be rejected. Therefore, it could be considered that there was a significant difference in the rank of each group of samples and that the distribution of the plurality of paired samples was significantly different; otherwise, the original hypothesis could not be rejected, and it could be considered that there was more or less same in the rank of each group of samples [22].

The statistical calculations are provided as in [22]

\[ N^2 = \frac{12}{b(k+1)} \sum_{i=1}^{k} (R_i - \frac{b(k+1)}{2})^2 \]  

where \( N^2 \) represents the chi-square statistic, \( b \) is the number of sample observations, \( k \) is the number of samples, and \( R_i \) is the sum of ranks of the \( i \)th sample.

Table 4 shows the statistics for the groups with different admixtures and their compressive strengths.

Table 4. Descriptive statistics and test statistics

|                  | N  | mean value | Std | minimum (min) | maximum (max) | Rank mean | \( x^2 \) | df | Sig. |
|------------------|----|------------|-----|----------------|----------------|-----------|----------|-----|------|
| Volume 0 pressure| 78 | 5.46       | 2.13| 2.69           | 9.84           | 1.05      |          |     | 163.75 3 0.00 |
| Volume I pressure| 78 | 6.59       | 2.28| 2.83           | 11.06          | 3.48      |          |     |       |
| Volume II pressure| 78 | 6.40       | 2.07| 2.32           | 10.51          | 3.13      |          |     |       |
| Volume III pressure| 78 | 6.16       | 1.91| 3.07           | 10.07          | 2.34      |          |     |       |

In Table 4, \( N \) is the number of samples; the number of samples is the four mixed groups, with 78 samples in each group and a total of 312 samples; \( r \) is the rank of data; \( df \) is the degree of freedom; \( Sig. \) is significant level (P).

It can be seen from Table 4 that 0-admixture group has the minimum rank mean, so it has the minimum compressive strength. The samples mixed with early strength agent are all greater than the 0-admixture group. The rank’s mean value of admixture I group is the largest, and its compressive strength is the highest. As shown in Table 4, the original hypothesis was rejected, because the progressive significance was 0.000 < 0.05. So, there was a significant difference in the compressive strength of each mixed group.
It can be seen from figure 1 that the slopes of the four lines were almost identical, indicating that none of the three admixtures could change the time of intensity change. However, the admixture could improve the compressive strength of cement-stabilized macadam material. The admixtures with three kinds of dosages could all enhance the strength of cement-stabilized macadam material, and admixture I showed the best performance.

3.2. Frozen-thawing test

3.2.1 Preparation of the samples and preliminary procedure for the experiment.

The sample was prepared following the method of making the cylindrical sample of the stable material in the standard [23], and the concrete single side freeze-thaw test machine was used to conduct the freeze-thaw test.

There are four experimental groups: groups with the admixture of I, II, III and the control group. Each group has nine samples, numbered from 1 to 9. The mass of each sample was m0. The sample was placed in a freezer at a temperature of -18°C. After being frozen for 16h, the sample was taken out. The mass at each time was recorded. Then the sample was melted in a water tank for 8h at a constant temperature of 20°C. The water surface height in the same tank was 2.5 cm higher than the top of the sample. Afterward, the sample was removed, and the surface moisture was wiped with a wet cloth and the mass was weighed and recorded. This was the first freeze-thaw cycle. Then the sample was put into the freezer for the next freeze-thaw cycle. Finally, all the samples were subjected to five freeze-thaw cycles. A universal test machine was used to detect the maximum pressure (N) of samples submitted to compression failure after five freeze-thaw cycles, and to calculate the unconfined compressive strength.

3.3 Freeze-thaw mass loss rate

After five freeze-thaw cycles, the mass loss rates of the four experimental groups were recorded. To facilitate the analysis and summary of the experimental results, it would be convenient to compare the different experimental groups. The mean value of each experimental group was calculated. The mass loss rate of the first five freeze-thaw cycles of all samples was analyzed by Friedman statistics to further examine the difference in the mass loss rate of each group. Limited by the times of experiment, to further investigate the effect of this kind of early strength agent on the freeze-thaw resistance of cement-stabilized macadam material, the polynomial linear equation fitting was carried out from the existing five groups of data. According to the development trend of each set of fitting results, two freeze-thaw cycles were carried out. The mean mass loss rate of each group is shown in Table 5. The fitting equation is shown in Table 8. The relationship between the mean mass loss rate and the number of freeze-thaw cycles, and the two freeze-thaw cycles after the fitting is shown in Figure 1.

| Circulation | 1 | 2 | 3 | 4 | 5 |
|-------------|---|---|---|---|---|
| Group 0     | 0.20 | 0.42 | 0.93 | 1.61 | 2.35 |
| Group I     | 0.15 | 0.36 | 0.74 | 1.16 | 1.75 |
| Group II    | 0.17 | 0.41 | 0.79 | 1.37 | 1.98 |
| Group III   | 0.14 | 0.31 | 0.59 | 1.07 | 1.62 |

By analyzing Table 5, it could be concluded that zero-admixture group has the most considerable mass loss after five test cycles, with the loss rate of 2.353%. For the three groups with admixtures, the mass loss rate of the I-admixture group was 1.75%, and the loss rate of the II-admixture group was 1.98%. The mass loss rate of the III-admixture group was only 1.62%. And from Table 3, it was found that in the first two freeze-thaw cycles, the difference in mass loss rates among the four groups was very small. By the end of the second freeze-thaw cycle, the difference between the highest mass loss rate and the lowest mass loss rate in the four groups was 0.11%. After the end of the 5th cycle, the difference between the
highest mass loss rate and the lowest mass loss rate reached 0.73%. This indicated that the admixture could improve the freeze-thaw resistance of cement-stabilized macadam during the repeated freezing and thawing process.

Using the mass loss rate data of five freeze-thaw cycles in the four groups of samples (180), data enlisted in Table 6 were obtained by the Friedman statistics.

| Group  | N   | Mean value | Std  | Minimum | Maximum | Rank mean | x²      | df   | Sig. |
|--------|-----|------------|------|---------|---------|-----------|---------|------|------|
| Group 0| 45  | 1.10       | 0.80 | 0.19    | 2.38    | 3.91      |         |      |      |
| Group I| 45  | 0.83       | 0.58 | 0.14    | 1.76    | 2.00      |         |      |      |
| Group II| 45  | 0.94      | 0.66 | 0.16    | 1.99    | 3.09      |         |      |      |
| Group III| 45  | 0.75     | 0.54 | 0.13    | 1.63    | 1.00      |         |      |      |

In Table 6, N is the number of samples, which includes 45 samples in four mixed groups and equals to a total of 180 samples; x² is the chi-square statistic; df is the degree of freedom of the data; Sig. is significant level (P).

Because of the increasing significance of freeze-thaw cycle was 0.000<0.05, the original hypothesis was rejected, indicating that there were significant differences in the mass loss rate of the groups with different admixtures. It can be seen in Figure 1 that the mass loss rate increased with the increase of the number of freeze-thaw cycles, and the difference between the zero-admixture group became more and more apparent, showing that the anti-freezing performance was improved.

![Figure 1. The difference of mass loss rate between the test and control groups](image)

| Group  | Fitting relation y=ax²+bx+c | Correlation coefficient: R²  |
|--------|-----------------------------|-------------------------------|
| Group 0| y=0.0868x²+0.0291x+0.0602   | 0.9982                        |
| Group I| y=0.0572x²+0.0548x+0.0371   | 0.9993                        |
| Group II| y=0.0676x²+0.0517x+0.0448  | 0.9992                        |
| Group III| y=0.0685x²-0.0392x+0.1097 | 0.9994                        |

Table 7 tabulates the fitting formulas for the four admixture groups, which results are plotted in Figure 2. The obtained correlation coefficients R² for all fitting curves and the respective test results are above 0.99, suggesting their close correlation. The fitting curves also show the trend of the test results. After fitting two freeze-thaw cycles, the most significant mass loss rate was still in the zero-admixture group, and the mass loss rate was the lowest in group I. According to five tests and two fitting freeze-thaw cycles, it could be concluded that the admixture could not only improve the antifreeze property of materials at the initial stage of the cycle but also show a better trend of anti-freeze-thaw with the increase of freeze-thaw times. This occurs because TEA and ASS could enhance the antifreeze property of
materials, and the antifreeze property could be further greatly improved on the original basis. Admixture III performed better in reducing the mass loss rate in the first five cycles. But the slope of the admixture I curve was the slowest, revealing that in a certain range in the case of equal dose, TEA and ASS dosage would directly affect the antifreeze property of the material.

To verify the conclusions presented above, partial correlation analysis was performed on the data of the first five freeze-thaw cycles of 180 samples by the SPSS software. Time variables were controlled. The correlation between admixture group and mass loss rate was analyzed, and the correlation data were calculated by Eq. (2) [22]. The analysis results are listed in Table 8.

\[ r = \frac{\Sigma XY - \frac{\Sigma X \Sigma Y}{N}}{\sqrt{\left( \Sigma X^2 - \frac{\Sigma X^2}{N} \right) \left( \Sigma Y^2 - \frac{\Sigma Y^2}{N} \right)}} \]  

where \( r \) is the correlation coefficient between the admixture group and the mass loss rate; \( X \) is the number of admixture groups (four, in this study); \( Y \) is the mass loss rate of each sample in each admixture group; \( N \) is the number of samples.

### Table 8. Correlation of each group and its mass loss rate

| Controlled variable | Mass loss rate | Admixture group |
|---------------------|---------------|-----------------|
| Mass loss rate       | Relativity    | 1.00            |
| Time                | Sig.          | 0.00            |
| Admixture group      | Relativity    | -0.51           |
|                      | Sig.          | 0.00            |

According to the analysis of Table 8, the partial correlation between the admixture group and the mass loss rate was \(-0.512\). The relationship of each admixture group’s mass loss rate was: group 0 > group I > group II > group III, in which the content of TEA in group I was the same as that in group III, but the amount of ASS in group I was higher than that in group III. It could be concluded that more ASS led to better antifreeze property of the material when the amount of TEA was between 0% and 1.25%.

### 3.4 Antifreeze coefficient

The antifreeze coefficient reflects the unconfined compressive strength of cement-stabilized macadam after many freezing-thawing cycles. The larger the antifreeze coefficient was, the smaller the strength loss caused by freezing-thawing of the cement-stabilized macadam material. Therefore, the antifreeze coefficient reflects the freezing-performance of materials on a certain level. According to the standards
[23], 72 samples were prepared and subdivided into four groups, with 18 samples in each test group. Nine samples of each test group were subjected to five freeze-thaw cycles, and then unconfined compression tests were conducted. Nine remaining samples of the same test group were subjected to unconfined compression tests without freezing and thawing.

According to the formula of antifreeze coefficient, the antifreeze coefficient of each group of cement-stabilized macadam was calculated and listed in Table 9. The calculation method is given by

$$BDR = \frac{R_{nc}}{R_c} \times 100\%$$

where $BDR$ is the loss rate of compressive strength after $n$ freeze-thawing cycles (%), $R_{nc}$ and $R_c$ are unconfined compressive strength values of samples of the same test group either subjected to $n$ cycles of freezing and thawing or not, respectively (MPa).

Table 9. Antifreeze coefficients of samples after five freeze-thaw cycles (%)

| Group   | Pressure after five freeze-thaw cycles, MPa | Non-freeze-thaw cycle pressure, MPa | The coefficient of freeze resistance |
|---------|-------------------------------------------|-------------------------------------|-----------------------------------|
| Group 0 | 7.92                                      | 9.34                                | 84.80                             |
| Group I | 9.76                                      | 10.82                               | 90.20                             |
| Group II| 8.97                                      | 10.14                               | 88.46                             |
| Group III| 9.16                                     | 9.56                                | 95.82                             |

Through the data analysis and calculation results in Table 9, four admixture groups could be obtained after five freeze-thaw cycles of the unconfined compression test. The mass loss rate of zero-admixture in control group 0 was the maximum, namely 15.20%, and the antifreeze coefficient was 84.80%. The mass loss rate of admixture in the test group I was 9.80%, with the antifreeze coefficient of 90.20%. The mass loss rate of admixture in group II was 11.54%, with the antifreeze coefficient of 88.46%. The mass loss rate of admixture in group III was only 4.18%, with the antifreeze coefficient of 95.82%. Thus, group III showed the largest antifreeze coefficient.

2. Conclusions

- All 3 new early-strength agents can make improvement on the compressive strength and frost resistance of cement-stabilized macadam material. The compressive strength also can be enhanced by TEA and ASS significantly within a short period.
- From the analysis of compressive strength and freeze resistance coefficient, it can be found that adding admixtures of compressive strength and frost resistance properties were superior to the control group. Thus, under the same conditions, with 2.0%-ASS and 1.0%-TEA, the cement-stabilized macadam material compressive strength values in all agents were optimal. Meanwhile, with 1.5%-ASS and 1.0%-TEA cement-stabilized macadam material antifreeze performance in five cycles were optimal.
- In the freeze-thaw cycle - mass loss curve, the slope growth rate of curve III is higher than that of curve I with the increasing times of freezing and thawing. It can be observed that 2.0% ASS and 1.0% TEA early strength agent has the best development prospects.
- Through the index of compressive strength and freezing resistance coefficient, it was found that when the content of TEA was 0.75, the effect of the three groups was worse than that of 1.0% TEA. The quality loss of rate of each dosage group was lower than that of the control group, and the freezing-performance of each dosage group was better than that of the control group.

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