Research Article

Performance Damage Characteristics of Asphalt Binder Suffered from the Action of Sulfate

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Sulfate erosion is a threat to durability and sustainability of pavement structure. In this work, the performance degradation of asphalt binder under internal sulfate erosion was investigated. Different dosages of Na₂SO₄ (0 wt.%, 2.5 wt.%, 5 wt.%, and 10 wt.%) samples were prepared to investigate the effect of sulfate on the performance of the asphalt binder. The surface tension test and low-temperature rheological property test were carried out to evaluate the adhesion of sulfate-incorporated asphalt mastic. Rapid freezing and thawing test with different concentrations of sulfate solution was conducted to explore the effect of sulfate concentrations and freeze-thaw cycles on the softening point and force ductility of matrix asphalt. Phases of the asphalt binder were characterized by Fourier transform infrared (FTIR) spectroscopy. The results show that sulfate has a negative impact on the road performance of the asphalt binder. Internal sulfate erosion decreased the adhesion of the asphalt binder. Also, the low-temperature rheological property of asphalt binder was deteriorated. After the freeze-thaw cycles of external sulfate erosion, softening point and tensile force peak of matrix asphalt increased and the low-temperature ductility decreased. The main reason of performance deterioration of the asphalt binder is the "salt aging" effect causing by sulfate erosion. The research results can provide useful reference for the durability design of asphalt mixture in sulfate-enriched regions.

1. Introduction

Asphalt pavements are the main paving type of highway because of its advantages such as low noise, good skid resistance, improved comfort, convenience of maintenance, and recyclability. However, asphalt pavements are subjected to different levels of durability problems such as high-temperature rutting, low-temperature cracking, moisture damage, and fatigue under the effects of climatic conditions and repeated vehicle loading [1]. Actually, it should be noted that the real service environment for the asphalt pavement is more complex especially in the salt lakes and saline soil regions in western China and other similar regions, where the climate environment is relatively severe [2, 3]. Nowadays, the durability of the asphalt mixture has always been one of the important areas of concern. The erosive media, such as sulfate, enriched in the natural environment often makes road engineering materials suffer from damage to different extent, and freeze-thaw cycles further deteriorate the road performance of asphalt mixture. As a result, asphalt mixture shows severe durability problems [3]. At present, some studies have shown that chlorine salts have a continuing negative effect on asphalt mixture [4–9]. In addition, the adhesion of asphalt under salt action is also a hot research trend. Nowadays, the surface energy theory has been widely used to evaluate the adhesion properties of asphalt and aggregate [10, 11]. However, up to now, little research has been done on the durability of the asphalt binder exposed to sulfate erosion and freeze-thaw circles.
2. Materials and Methods

2.1. Asphalt. The SK-90# matrix asphalt was used for all experiments. Its physical properties were measured following the Standard Test Methods of Bituminous Mixtures for Highway Engineering of China (JTG E20-2011), presented in Table 1.

2.2. Filler. Limestone mineral filler (LMF) and sodium sulfate (\( \text{Na}_2\text{SO}_4 \)) powder were used in the test, whose technical indicators are shown in Tables 2 and 3, respectively.

Based on the plug-in method, the contact angles between the surface of asphalt binder and distilled water, glycerin, and glycol liquid were measured. The surface free energy parameters of the three liquids are shown in Table 4.

2.3. Preparation of Sulfate-Incorporated Asphalt Mastic. For practical asphalt pavement engineering projects in China, AC-13 is the most widely used surface paving material. The 0.075 mm sieve passing percentage of mineral aggregate gradations is usually around 5%, and the optimum asphalt content (OAC) is around 5% by the mass of mineral aggregate [12]. So, the filler-binder ratio of the asphalt mastic represented as

\[ \text{ASphalt content (OAC)} \approx 5\% \text{ by the mass of mineral aggregate} \]

The three-wall gravimetric method is mainly used to test the asphalt content. The HMA mixture was rolled out at a constant temperature of 130°C and 95°C, respectively. The asphalt was then cooled to 10°C and cut into a fixed size for later use.

2.4. Rheological Properties of Asphalt Binder Based on Viscoelastic Theory. The bending beam rheological (BBR) test can directly reflect the influence of ambient temperature and time on the low-temperature performance of asphalt materials. Asphalt is a typical viscoelastic material, and the most widely used viscoelastic model is the Burgers model which is a four-component viscoelasticity consisting of a set of Maxwell models and Kelvin models. The Burgers model can effectively describe the viscoelasticity of matrix asphalt, modified asphalt, aged asphalt, and recycled asphalt. The creep compliance formula of the Burgers model can be represented as

\[ J(t) = \frac{\varepsilon(t)}{\sigma_0} = \frac{1}{E_1} + \frac{t}{\eta_1} + \frac{1}{\eta_2} \left( 1 - e^{-\left( \frac{E_2 / \eta_2}{t} \right)} \right) = J_E + J_C + J_V, \]

(3)

where \( J_E \) is the instantaneous elastic compliance, \( J_C \) is the delayed elastic compliance, and \( J_V \) is the viscous creep compliance [14].

2.5. Freeze-Thaw Cycle Test Exposed to \( \text{Na}_2\text{SO}_4 \) Solution. The freeze-thaw cycle test exposed to \( \text{Na}_2\text{SO}_4 \) solution in this study mainly focuses on the effect of sulfate concentration and freeze-thaw cycles on the performance change of the asphalt binder. First, the asphalt sample is placed in a square pan, and a sufficient amount of sulfate solution is poured on its surface. Adopting the rapid freeze-thaw test method of cement concrete, the freezing temperature of asphalt is set as \(-18^\circ\text{C}\) lasting for 2 h and then the melting temperature is as \(5^\circ\text{C}\) lasting for 2 h, which is a whole procedure (one time). The concentration of \( \text{Na}_2\text{SO}_4 \) solution is selected as 0% (distilled water), 2.5%, 5%, and 10%. The number of freeze-thaw cycles is set as 7 times, 14 times, 21 times, and 28 times. The performance of asphalt exposed to \( \text{Na}_2\text{SO}_4 \) solution was evaluated through the softening point and force ductility test. The freeze-thaw cycle test exposed to \( \text{Na}_2\text{SO}_4 \) solution is shown in Figure 2.

3. Results and Discussion

3.1. Sulfate-Incorporated Asphalt Mastic

3.1.1. Contact Angle Test. The results of the contact angle for the matrix asphalt and sulfate-incorporated asphalt mastic versus above three liquids (distilled water, glycerin, and ethylene glycol) are shown in Table 5, which satisfies the
accuracy requirement. In the case of sulfate-incorporated asphalt mastic, the contact angle between asphalt and different liquids increases to some extent along with the increase of age. SU_hat is, the “salt aging” effect increases the hydrophilicity of the asphalt mastic. At the same tested liquid condition, the contact angles between the sulfate-incorporated asphalt mastic and the liquids are greater than that of matrix asphalt and the liquids. Based on the wetting theory, in the presence of sulfate, the wettability of the asphalt to the aggregate is reduced to some extent, and further weakens with the increase of age, which directly leads to the decrease of the adhesion between asphalt and aggregate, thereby affecting the road performance of asphalt mixture.

SU_he contact angle values in Table 5 are brought into the above formulato obtain the dispersion component \(c_d\), the polar acid component \(c_p\), and the polar base component \(c_\pm\) of various asphalt mastics. Then, the surface free energy can be calculated. The results of surface free energy and its components of matrix asphalt and asphalt mastics are shown in Figure 3.

It can be seen from Figure 3, compared with the matrix asphalt, the surface free energy and polar components of the LMF asphalt mastic are improved while the nonpolar component is significantly reduced at 30 d and 120 d ages, indicating that the incorporation of LMF enhances the polarity of the asphalt and improves the surface tension. Compared with the LMF asphalt mastic, the surface free energy of Na\(_2\)SO\(_4\) asphalt mastic decreased significantly at 30 d and 120 d ages. The surface free energy of the Na\(_2\)SO\(_4\)
asphalt mastic shows a downward trend. According to the calculated cohesive and adhesion power, sulfate incorporation reduces the free energy and dispersion component of the asphalt surface, which in turn adversely affects the water sensitivity of asphalt mixture.

3.1.2. BBR Test. The test results of stiffness modulus \( S \) and creep rate \( m \) of various asphalt mastics at the temperature of \(-6^\circ C, -12^\circ C, -18^\circ C, \) and \(-24^\circ C\) are shown in Figure 4.

It can be seen from Figure 4 that, at the same temperature, compared with the matrix asphalt, the stiffness modulus of the sulfate-incorporated asphalt mastic increases greatly, and the creep rate decreases, indicating that the sulfate deteriorates the low-temperature performance of the asphalt binder. As the age increases, performance of the sulfate-incorporated asphalt mastic continues to deteriorate. In addition, the incorporation of sulfate hardens the asphalt to a certain extent, forming the “salt aging” effect as mentioned before. Meanwhile, under low-temperature conditions, the asphalt is in a glassy state, and the asphalt molecular chain is difficult to be rapidly oriented or moved.

Then, the results of the BBR test were fitted by Origin 8.5 software. The elastic moduli \( E_1 \) and \( E_2 \), viscosity coefficients \( \eta_1 \) and \( \eta_2 \), the relaxation time \( \lambda \), and delay time \( \tau \) of the Burgers model were obtained at different temperatures, shown in Table 6.

It can be seen from Table 6, the variation of delay time \( \lambda \) of the asphalt mastics at different ages in the temperature range of \(-12^\circ C \sim -6^\circ C\) shows that the matrix asphalt has the smallest change, and the \( \text{Na}_2\text{SO}_4 \) asphalt mastic changes the most. At the same temperature, the longer the age, the worse low-temperature performance of the sulfate-incorporated asphalt mastics. As the temperature decreases, the relaxation time of various asphalt mastics is gradually prolonged. On the one hand, the movement of the asphalt molecular chain is subject to increasing internal frictional resistance, and the stress relaxation is slowed down. On the other hand, the temperature reduction reduces the energy consumption rate and increases the relaxation time. Within the entire test temperature range, the stress relaxation ability
of the sulfate-incorporated asphalt mastic is inferior to the LMF asphalt mastic.

3.2. Freeze-Thaw Cycle Test Exposed to Na$_2$SO$_4$ Solution

3.2.1. Softening Point. The softening point of the matrix asphalt sample with 7, 14, 21, and 28 times of freeze-thaw cycles was tested, respectively, exposed to 0%, 2.5%, 5%, and 10% Na$_2$SO$_4$ solution. The results are shown in Figure 5.

It can be seen from Figure 5 that, for the same concentration of sulfate solution, as the freeze-thaw cycles increases, the softening point of the matrix asphalt increases with different degrees. Under the same freeze-thaw cycles, the higher the concentration of the sulfate solution, the greater the softening point of the asphalt. When the concentration of sulfate solution is small, the increase of freeze-thaw cycles has little effect on the softening point value. When the concentration reaches 10%, the increase of freeze-
thaw cycles will increase the softening point significantly. Compared with distilled water, the sulfate solution has a certain enhancement effect on the softening point. After different freeze-thaw cycles, the asphalt gradually changes from the sol-type structure to the gel-type structure, and the proportion of asphaltenes becomes higher while the outer film of the micelles becomes thinner. The macro-performance is that the asphalt becomes more harden and brittle.

3.2.2. Force Ductility. The force ductility tester was used to test the change of low-temperature ductility, maximum tensile force of asphalt at 5°C under different sulfate solution concentrations and different freeze-thaw cycles. The results are shown in Figure 6.

It can be seen from Figure 6 that, for the matrix asphalt under the condition of freeze-thaw cycles with distilled water, the increase of freeze-thaw cycles has little effect on the maximum tensile force. When the concentration of sulfate solution is 2.5% and 5%, the maximum tensile force of asphalt goes up with the increase of freeze-thaw cycles. The maximum pull force is quite different. For the 0% and 2.5% sulfate solutions, the fracture ductility of asphalt decreases with the increase of freeze-thaw cycles, and for the 5% and 10% sulfate solutions, the ductility between 7 and 14 times is quite different. In addition, as the freeze-thaw cycles increase, the asphalt elongation changes little. When the tensile force reaches the peak, it quickly enters the stress relaxation phase, and the tensile force decreases rapidly.

The maximum tensile force value of asphalt after freeze-thaw cycles is shown in Figure 7.

It can be seen from Figure 7 that, as the freeze-thaw cycles increases, the peak value of asphalt tensile force increases. When the concentration of the sulfate solution is 2.5%, the peak value of the tensile force is the largest. After
the freeze-thaw cycles, the brine evaporates and the sulfate accumulates on the surface and invades gradually, changing the continuous state of the asphalt.

3.3. Mechanism Analysis of the Action of Sulfate Erosion. Fourier-transform infrared (FTIR) spectroscopy was used to analyze the changes of the absorption peaks of the main functional groups of the matrix asphalt and the above several asphalt mastics (30 d and 120 d). The results are shown in Figure 8.

It can be seen from Figure 8 that the change of the absorption peak of the Na$_2$SO$_4$ asphalt mastic at 30 d and 120 d age is that the peak of 1110.63 cm$^{-1}$ is stronger. Compared with the LMF, the Na$_2$SO$_4$ has a great influence on the absorption peak of 1605 cm$^{-1}$ for aromatic hydrocarbons and the benzene ring substitution region of 900–650 cm$^{-1}$, which is the main change of asphalt performance caused by Na$_2$SO$_4$. That can be called the aforementioned "salt aging" effect.

4. Conclusions

Due to the prevalence of the sulfate environment in China, this paper aims at exploring the performance damage characteristics of the asphalt binder under the action of sulfate (Na$_2$SO$_4$) from internal and external pathways. Some interesting conclusions can be drawn as follows:

(i) For the sulfate-incorporated asphalt mastic, due to the "salt aging" effect, the contact angle of the asphalt binder is obviously increased, and the surface free energy of the sulfate-incorporated asphalt mastic is reduced. Thereby, the adhesion is decreased correspondingly. Meanwhile, the creep rate decreases with the increase of age, and the delay time increases, causing the low-temperature rheological property deteriorate.

(ii) For the matrix asphalt exposed to the freeze-thaw cycle of Na$_2$SO$_4$ solution, as the freeze-thaw cycles increase, the asphalt elongation decreases overall while the maximum tensile force increases gradually. Compared with distilled water (control sample), the presence of Na$_2$SO$_4$ makes the low-temperature plasticity of the asphalt get worse.

(iii) Sulfate has a negative impact on the road performance of the asphalt binder. The effect of sulfate on the durability of asphalt and asphalt mixture should be taken into full consideration in sulfate-enriched regions.

Data Availability

The authors would like to declare that all the data in the manuscript were obtained by experiment and the data are true and effective in the manuscript.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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