The influence of water on the oxidation of asphalt cements

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HIGHLIGHTS

- The interaction between water oxygen molecules and asphalt changes the asphalt properties.
- Increases in the asphalt stiffness and viscosity are observed after immersion in distilled water for one year.
- The consistency of the binder changes and its stiffness increases in the presence of water.
- Aging and oxidation are caused by the air–asphalt or air–water–asphalt interaction and by the oxygen from the water.

ARTICLE INFO

ABSTRACT

Two grades of paving asphalt, AC 80-100 and AC 60-70, were studied to determine changes in their physical and chemical properties caused by exposure to water. This experimental study's primary hypothesis is that the interaction between the water oxygen molecules and asphalt, known as oxidation, changes the asphalt properties, resulting in increased damage from mechanisms such as humidity and aging for mixtures in service. The chemical responses of both asphalts were measured, and the flow activation energy concept was used to understand the resulting changes in the physical and rheological properties after immersion in distilled water for one year.

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1. Introduction

In a flexible pavement structure, the primary causes of damage to asphalt mixtures in service include moisture, aging, oxidation, fatigue and rutting [1]. In the literature, the damage to asphalts caused by moisture and aging are correlated primarily with changes in their physical properties when the binder is oxidized. For example, when an asphalt ages or is oxidized, its viscosity and stiffness increase. In addition, the damage to asphalts by moisture and aging generates a decrease in the adherence between the mineral aggregate and the binder, thus increasing the probability of the occurrence of asphalt stripping. This type of damage also causes a transformation from a ductile behavior to a fragile behavior for the asphalt and the asphalt mixture, making them brittle and susceptible to cracking.

According to Brock [2], oxidation is the process of combining or causing the combination of a specific substance with oxygen. In asphalt pavements, oxidation is generally associated with the reaction between the asphalt and the oxygen in air and/or moisture. As the temperature and the exposure time of the asphalt in air increase, the oxidation rate and aging rate also increase. From the perspective of pavement engineering, no studies have been performed on the effect of the oxygen in water on the properties and behaviors of asphalts because asphalt is considered to be a material with extremely low permeability. However, oxygen is an essential component of water. It can produce oxidation and short- and long-term changes in the chemical and physical properties of asphalt, particularly when the asphalt layer that covers the mineral aggregate is thin, such as in asphalt mixtures. Therefore, the effects of water on the physical, chemical and rheological properties of two types of asphalt cements (ACs), AC 80-100 and AC 60-70 (AC 80-100 and AC 60-70 refer to ACs with American Society for Testing and Materials (ASTM) D-5 penetration test values between 80 and 100 tenths of a millimeter and between 60 and 70 tenths of a millimeter, respectively), are evaluated in this study. To evaluate these properties, the following tests were performed: the penetration test (ASTM D-5), the softening point test (ASTM

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D-36), the ductility test (ASTM D-113), the absolute viscosity test (ASTM D-2171), the viscosity test at 135 °C (American Association of State Highway and Transportation Officials (AASHTO) T-316), rheological characterizations at intermediate and high temperatures using an AASHTO T 315-05 dynamic shear rheometer (DSR) and column liquid chromatography to quantify the chemical composition of the asphalts through the determination of the saturate, aromatic, resin and asphaltene (SARA) fractions in asphalt samples immersed in distilled water for 12 months. The mathematical parameter flow activation energy (E_f) is used in this study to estimate changes in the physical properties of asphalt that are only produced by chemical reactions. The flow activation energy is an estimate of the energy required by the asphalt to produce a chemical reaction. It is determined from the viscosity at the temperature of the binder. Because the material is not performing mechanical work in the proposed experiments, the estimated activation energy corresponds to the chemical work that is generated by the oxygen in the distilled water reacting with the asphalt molecules.

Khalid [3] concluded that oxidation, which has been considered to be the dominant process in the deterioration of binders in asphalt pavements, is an irreversible chemical reaction that involves asphalt components and atmospheric oxygen. Bocci and Cerni [4] suggested that the *in situ* oxidation mechanisms are primarily dependent on an increase in temperature (which increases the degree of oxygen diffusion and accelerates chemical reactions), the exposure time, the thickness of the asphalt layer exposed to the oxygen and the amount of the air flow. With respect to the physical changes, laboratory results (e.g., [5,6]) have shown that when asphalt oxidizes, the penetration and the ductility both decrease and the softening and ignition point temperatures both increase. From the mechanical and dynamic points of view, an incremental change is observed in the modulus ratio after aging or oxidation, which is primarily from asphalt hardening [7,8]. Similarly, the chemical changes corresponding to the rearrangement of the asphalt molecules from volatilization and oxidation effects generate changes in the SARA groups [9]. SARA fractions are molecular moieties that share an affinity with some solvents; oxidation from reactions with air and moisture changes that affinity. The nature of the affinity is also affected by changes in temperature. An increase in asphaltene moieties and the formation of carbonyl and sulfoxide functional groups have been widely reported as indicators of oxidation in asphalt cements [10,11]. Despite several studies addressing the mechanisms associated with specific asphalt oxidation and transformation during aging [12–15], the phenomena are not fully understood. Asphalt oxidation is a complex phenomenon not only because of the complex molecular composition of the asphalt cement but also because of the complex reaction kinetics.

More information regarding advancements in the aging of asphalts and asphalt mixtures is detailed in the studies of Rondón [16] and Fernández et al. [10,17].

2. Materials and methods

2.1. Material characterization

The ACs were tested to obtain physical properties, parameters and rheological characterization using a DSR (AASHTO T 315-05). The results of these tests are shown in Tables 1–3. In Tables 2 and 3, the temperatures used in the evaluation of the asphalts correspond to the performance grade (PG) method at high and intermediate temperatures for selecting the appropriate binder for pavement performance in terms of rutting and fatigue cracking, according to the AASHTO Performance Graded Binder Specification (MP1).

2.2. Experimental phase

Sheets of AC 80-100 and AC 60-70, approximately 2 mm in thickness, were immersed in distilled water for a period of time (t) of twelve months. This thickness was the smallest thickness that could be produced in glass containers with a rectangular area (30 cm × 30 cm) and a height of approximately 1 cm. Ideally, the production of sheets with smaller thicknesses may have been sufficient because the effect of water occurs primarily on the asphalt surface. The water was distilled to eliminate minerals and chemicals that may affect the results. In this way, the chemical changes generated in the asphalt are primarily attributed to interactions with the water, particularly with the oxygen molecules (oxidation). The water was replaced on a weekly basis to prevent contamination or skewed results. Every two months, the asphalt layers were removed from the distilled water to perform the penetration test (ASTM D-5), the softening point test (ASTM D-36), the ductility test (ASTM D-113), the absolute viscosity test (ASTM D-2171) and the viscosity test at 135 °C (AASHTO T-316) to evaluate changes in consistency when immersed in water. In summary, these tests were performed on samples at $t = 0$ (not immersed or neat asphalt) and at $t = 2, 4, 6, 8, 10$ and 12 months (immersed). Three samples were used for each test performed. A phase of rheological characterization was also performed (AASHTO T 315-05) using a DSR on the immersed sheets of AC 80-100 and AC 60-70. The temperatures used in the rheological evaluation of asphalts correspond to the PG method at high and intermediate temperatures for selecting the appropriate binder for pavement performance in terms of rutting and fatigue cracking, according to the AASHTO Performance Graded Binder Specification (MP1). In the rheological tests, three samples for each temperature were used, and the shear modulus and phase angle were measured ten times for each sample. These tests were performed on samples at $t = 0$ (not immersed or neat asphalt) and $t = 12$ months (immersed). Prior to the tests, the surfaces of the AC sheets were carefully dried with tow. Subsequently, the AC was separated from its support with a spatula. The absolute viscosity test (60 °C) and the Brookfield viscosity test at 135 °C were performed using a vacuum capillary viscometer and a rotational viscometer, respectively. Each test used an independent sample, i.e., no AC samples were reused. In the previously mentioned tests, the asphalts only experienced changes in their physical properties from reactions or chemical work done by water–asphalt interactions. Therefore, an Arrhenius mathematical expression [18] was used to evaluate the chemical kinetics of the water–asphalt interactions in the ACs. Using this equation and the laboratory results of the asphalt viscosity *versus* temperature tests, E_f, which represents the energy required to perform the chemical work generated by the physical changes discussed in the following section, was obtained.

To evaluate the chemical responses of the asphalts immersed in water for 12 months, which occur during the separation of the asphalt binder in asphaltenes and maltenes by precipitation with n-heptane and subsequent fractionation of the maltenes through an alumina column with solvents of increasing polarity, the SARA fractionation test was performed according to ASTM D-4124 specifications. A detailed description of this test, which was performed on both a non-immersed ($t = 0$ or neat asphalt) sample and a sample immersed for $t = 12$ months, can be found in the literature [19].

3. Results and discussion

Figs. 1–5 show the evolution of the penetration, softening point, ductility and viscosity with immersion time of the ACs analyzed (AC 80-100 and AC 60-70). The asphalt penetration decreases with immersion time in distilled water (refer to Fig. 1). At $t = 12$ months, the penetration decreases by 26% and 34% for AC 80-100 and AC 60-70, respectively. This decrease in penetration corresponds with the results obtained for the other measured parameters (increase in the softening point and viscosity and decrease in the ductility).

At $t = 12$ months, increases in the softening points of 8% and 7% are observed for AC 80-100 and AC 60-70, respectively. The increases in viscosity for this immersion time are 20% and 31% at 60 °C and 40% and 38% at 135 °C for AC 80-100 and AC 60-70, respectively; the decreases in ductility were 17% and 21%, respectively.

Tables 4 and 5 show the results of the rheology tests performed on the asphalts immersed in distilled water for 12 months. Compared with the results shown in Tables 2 and 3 (non-immersed asphalts), the shear modulus G^* for AC 60-70 and AC 80-100 increased between approximately 5% and 15% when the sheets were immersed in distilled water for 12 months. The elastic component of the asphalts increased (shown by a decrease in the phase angle δ), which predicts that the asphalt elastic response will increase more rapidly than the viscous response from the presence of oxygen during the oxidation. The molecular agglomerates lose mobility, the phase angle decreases, and the viscosity increases, changes that are reflected in the rheological properties [20–23].