Laboratory Performance Assessment of Sulfur-Modified Warm Mixes

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ABSTRACT: Since asphalt prices have escalated, a great deal of interest has been focused on using more reclaimed asphalt pavement or finding a material that can replace the asphalt binder in asphalt concrete (AC). Hot liquid sulfur was used to replace a portion of the asphalt binder in hot-mix asphalt (HMA) in the 1970s and 1980s. However, a sharp increase in the sulfur price, a significant amount of fumes, and problematic transportation of hot liquid sulfur brought its utilization in road paving to an end in the late 1980s. To replace the use of hot liquid sulfur in AC, a solid sulfur pellet technology was developed, known as Shell Thiopave[1]. The technology includes modified sulfur pellets and other additives designed to extend the asphalt binder, lower the mixing temperature to warm-mix asphalt (WMA) to reduce odors and fumes during production, and modify the properties of the asphalt mixture. In a comprehensive laboratory evaluation, performance properties of sulfur-modified WMA were determined and compared with those of a conventional Superpave HMA mixture. Results showed that the sulfur-modified WMA outperformed the HMA in terms of rutting resistance. The fatigue cracking resistance of the sulfur-modified WMA is closer to that of the conventional HMA at lower strain levels. However, the sulfur-modified WMA resistance to moisture damage may not be as good as that of HMA with certain mixtures without an effective anti-stripping agent and an appropriate mix design. Hence, a moisture susceptibility study including both laboratory and field evaluations is being conducted.

KEY WORDS: Asphalt concrete, sulfur, warm mix asphalt, laboratory performance testing.

1 INTRODUCTION

Use of sulfur in hot mix asphalt (HMA) (known as SEA or sulfur-extended asphalt) was originally tried in the 1970s and continued into the 1980s (Strickland et al. 2008). The hot liquid sulfur was used in HMA as a binder extender (replacing a portion of the asphalt binder) and a mixture modifier.

In a field evaluation of 26 SEA projects built between 1977 and 1982 in 18 states, Beatty et al. (1987) reported that the overall performance and level of distress in the SEA pavements were not significantly different from that of the control pavement sections. The mixtures used in the SEA pavements contained between 20 and 40 percent (by weight) of sulfur as a replacement for the asphalt binder. The material performance benefit was an increase in

[1] Shell Thiopave is a trade mark of the Shell Group of Companies

stiffness of the mixtures with a reduction in rutting susceptibility. The increase in stiffness of these mixtures also resulted in performance drawbacks. Bayomy and Khedr (1987) reported that the sulfur-modified mixtures were more prone to moisture damage than conventional asphalt mixtures.

In the late 1980s, a sharp rise in the price of sulfur in addition to the fact that the use of hot liquid sulfur during production generated a significant amount of fumes and odors brought its use in road paving to an end (Strickland et al. 2008).

To overcome the problems with hot liquid sulfur used in asphalt concrete (AC), a solid sulfur pellet technology, known as Shell Thiopave, was developed. The technology consists of small modified sulfur pellets that are added together with a compaction agent to the asphalt mixture during the mixing process. The technology is designed to lower the mixing temperature of the sulfur-modified mixture so that it can be produced as warm-mix asphalt (WMA) which reduces odors and fumes during production and placement. The modified sulfur pellets melt rapidly on contact with the heated mix and are dispersed throughout the asphalt mixture by aggregate shear during mixing (Deme and Kennedy 2004). Figure 1 shows the modified sulfur pellets and compaction agent used in the sulfur-modified WMA evaluated in this research project.

Figure 1: Modified sulfur pellets (left) and compaction agent (right) used in sulfur-modified WMA.

Technological improvements to the solid modified sulfur pellet technology have led to a resurgence in the exploration of the use of sulfur in asphalt concrete, and an extensive study has been conducted at the National Center for Asphalt Technology (NCAT) in Alabama, United States.

The purpose of this paper is to present a performance evaluation (moisture susceptibility, mixture stiffness, rutting, and fatigue cracking) of two sulfur-modified WMA mixes relative to the performance of a control HMA mixture in the laboratory. Complete details of this laboratory evaluation were documented in a comprehensive report (Timm et al. 2009). A field evaluation of the three mixes is underway at the NCAT Pavement Test Track (hereinafter referred to as “the Test Track”) in Alabama, United States.

2 LABORATORY EXPERIMENT

Three asphalt mixtures were evaluated in the laboratory experiment. The three mixtures were using the same 19 mm aggregate gradation (Figure 2) and PG 67-22 asphalt binder. The differences in these mixtures were the percentage of sulfur used to replace a portion of the base binder and the design air void content.

- The control HMA mixture did not contain sulfur and was designed to have 4 percent design air voids. The control mixture was based on a mix design used in the bottom two asphalt layers of section S11, and its performance was well documented in the third (2006-2009) research cycle at the Test Track (Willis et al. 2009). This mix design was used again in the bottom asphalt layer of the control test section (S9) in the fourth (2009-2012) research cycle at the Test Track.

- The second mixture was a sulfur-modified WMA containing 30 percent sulfur (by the weight of the total binder) and was designed to have a design air void content of 2 percent to obtain more flexibility with more total binder content. This mixture was used in the bottom asphalt layers of two sulfur-modified test sections, N5 and N6, in the fourth Test Track research cycle. It is referred to as "rich bottom" mix in this paper.
- The third mix was a sulfur-modified WMA mixture containing 40 percent sulfur and was designed at 3.5 percent air voids to obtain slightly more total binder content. This mixture was used in the binder (middle) asphalt layers of two test sections, N5 and N6, in the fourth Test Track research cycle and is referred to as "binder layer" mixture in this paper.

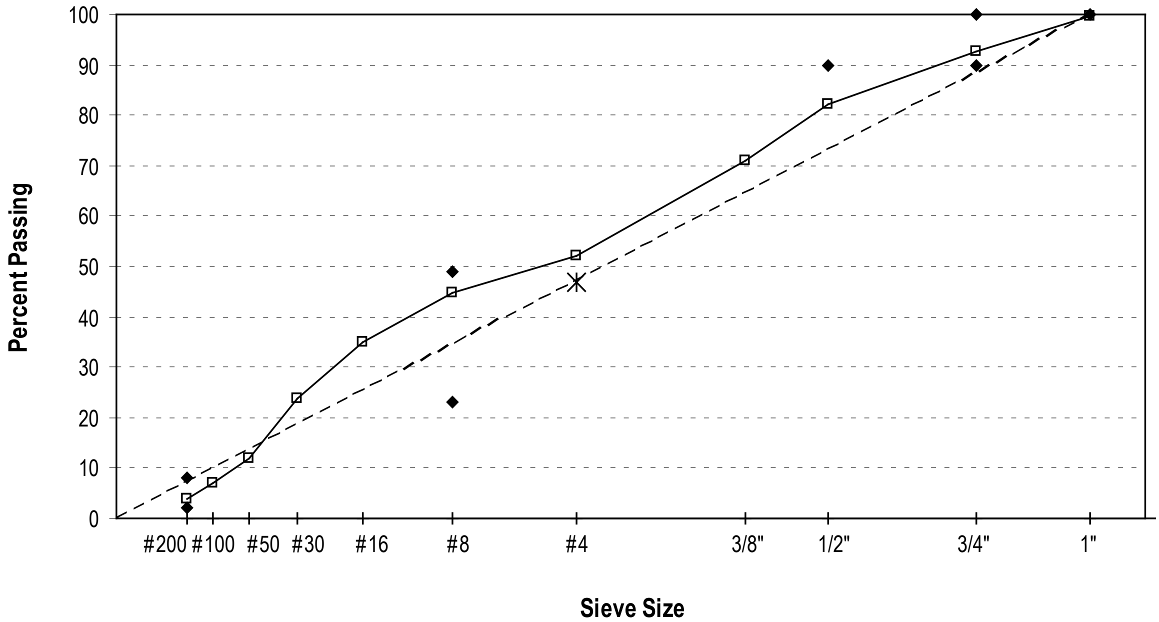

Figure 2: Aggregate gradation for the three mixtures evaluated in the laboratory.

2.1 Material Preparation and Laboratory Mixing

The 19 mm aggregate gradation used for the three mixtures consisted of four different aggregate stockpiles. Two limestone coarse aggregate materials used in the three mixes were from Martin Marietta Quarry in Auburn, Alabama. Two fine aggregate materials were fine granite from Vulcan Materials Barin Quarry in Columbus, Georgia, and natural sand from Martin Marietta Sand and Gravel in Shorter, Alabama. The percentages of each stockpile were generated from the original laboratory mix design used in the third Test Track research cycle.

A PG 67-22 binder blended with 0.5 percent (by weight of the bitumen binder) of an anti-stripping agent was used for the three mixes evaluated in this study. For the sulfur-modified WMA, the bitumen binder was further modified with 1.52 percent by the bitumen binder weight of a compaction agent, as shown in Figure 1. This compaction agent, consisting of fine wax, aids in the compaction of sulfur-modified WMA mixes to the target air voids at the lower compaction temperatures that are necessary to control sulfur emissions.

To prepare the sulfur-modified mixtures in the laboratory, the modified sulfur pellets were added to the heated aggregate and asphalt binder immediately after the start of the mixing process. The mixing process using the sulfur materials was conducted in a well-ventilated mixing room. The target mixing temperature was 138-143°C. The mixes were visually inspected after the mixing process to ensure that the modified sulfur pellets had melted and been distributed throughout the mix. All the samples were then short-term aged in the oven at a temperature of 140°C for two hours before compaction. These sulfur-modified mixes were aged at a lower temperature to control emissions. The control HMA mixture was short-term aged for two hours at 157°C.

2.2 Mix Design

For this study, a mix design was conducted for each of the control and sulfur-modified asphalt mixtures. These mix designs were conducted in accordance with AASHTO M323-07 and AASHTO R35-04.

For the control mix, the optimum binder content was determined corresponding to 4 percent air voids. For each sulfur-modified mix, the binder content of combined sulfur and asphalt binder materials was determined according to Equation 1, which is a simplified version of that developed by the Bureau of Mines (McBee, et al. 1980), to account for the presence of sulfur materials in the mixture. The optimum content of combined sulfur and asphalt binder materials for the sulfur-modified binder layer mix (40 percent of sulfur) was determined at 3.5 percent air voids, and the optimum content for the rich bottom mixture (30 percent of sulfur) was determined at 2 percent air voids. The mix designs were carried out using a spreadsheet provided by Shell for use with this project that incorporates Equation 1.

$$Sulfur + Binder\% = A * \frac{100R}{[100R - P_{sulfur}(R - G_{binder})]} \quad (1)$$

where:

- A = weight percentage of binder in conventional mix design
- R = G_{Sulfur}/G_{Binder} (R = 1.90 for this study)
- P_{sulfur} = weight percentage of sulfur in sulfur-blended binder
- G_{binder} = specific gravity of the virgin binder

The design pills were compacted to an N_{des} level of 60 gyrations and a target height of 115 ±5 mm. The bulk specific gravity of the compacted specimens was determined according to AASHTO T166, and the maximum theoretical specific gravity of the loose mixtures was determined in accordance with AASHTO T209. A summary of the volumetric properties is given in Table 1. The equivalent binder content is the binder content by mass of a sulfur-modified mixture with the volume of sulfur modifier replaced by the volume of base binder or the conventional binder content at the appropriate level of air voids.

2.3 Laboratory Performance Testing

A wide array of performance testing was utilized for this study to compare the laboratory performance properties of the two sulfur-modified WMA mixtures with those of the control HMA. The testing plan was designed so that there would be multiple tests, if possible, used to assess the performance characteristics of the sulfur-modified WMA mixtures. A full performance testing plan was documented in the final report for this laboratory study (Timm et al. 2009). Due to the limitation of this paper, only four laboratory performance tests for characterizing the moisture susceptibility, mixture stiffness, rutting and fatigue cracking resistance are presented.

All the specimens for moisture susceptibility testing were compacted to a height of 95 mm and an air void level of 7 ± 0.5 percent as specified in AASHTO T283 to represent field compaction. Within each set of specimens, three specimens were tested with no moisture conditioning while the other three specimens were conditioned and then tested according to AASHTO T283. Calculation of the failure load, splitting tensile strength, and tensile strength ratio (TSR) was done as specified in the AASHTO procedure.

Table 1: Volumetric Properties

Mix Type	%Sulfur by total binder weight	%Design Air Voids	%(Sulfur + Binder)	%Equivalent Binder	%Voids in Mineral Aggregate	%Voids Filled with Asphalt	Dust Proportion
Control	0	4.0	5.30	5.30	15.3	74.2	0.82
Rich Bottom	30	2.0	6.30	5.48	13.9	86.0	0.69
Binder Layer	40	3.5	6.15	5.07	14.5	75.9	0.71

An Asphalt Mixture Performance Tester (AMPT) was used for dynamic modulus (E*) testing for characterizing the mixture stiffness and flow number (Fn) testing for evaluating the mixture resistance to rutting according to AASHTO TP79. These tests were conducted on specimens that were 150 mm high and 100 mm in diameter cored and cut from gyratory compacted specimens (170 mm high and 150 mm in diameter). The specimens were prepared in the laboratory with a target air void level of 7 ± 0.5 percent. The specimens were tested for dynamic modulus (E*) before they were used for Fn tests. Dynamic modulus tests were conducted at three temperatures (4.4, 21.1, and 46.1^{o}C) and six frequencies (10, 5, 1, 0.5, 0.1, and 0.01 Hz) to generate master curves for comparing mixture stiffness over a wide range of temperature and frequency and to provide inputs for a mechanistic-empirical pavement analysis.

All Fn tests were conducted at a temperature of 58^{o}C, which was close to the 50 percent reliability pavement temperature for the Opelika, Alabama area where the Test Track is located. The specimens were tested at a deviator stress of 70 psi and unconfined, and the tests were terminated when the specimens reached 10 percent axial strain. Calculation of the Fn was done using the AMPT software according to AASHTO TP79.

Bending beam fatigue (BBF) testing was performed in accordance with AASHTO T321 to determine the fatigue limits of the three mixes. Six beam specimens were tested for each mix. Within each set of six, two beams each were tested at 200, 400, and 600 microstrain. The specimens were originally compacted in a kneading beam compactor then trimmed to the dimensions of 380 ± 6 mm in length, 63 ± 2 mm in width, and 50 ± 2 mm in height. Additionally, the orientation in which the beams were compacted was marked and maintained for the fatigue testing as well. Testing was performed at 20 ± 0.5°C. According to AASHTO T321, the fatigue failure point for each beam was the number of cycles at which the initial modulus of the beam has been reduced by 50%.

For the above performance tests, all the test specimens prepared from the two sulfur-modified WMA mixtures were allowed to cure at room temperature for 14 days prior to testing to allow for sufficient crystallization of the sulfur materials.

3 RESULTS AND ANALYSIS

3.1 Moisture Susceptibility

Tables 2 shows the moisture susceptibility testing results conducted according to AASHTO

T283. The sulfur-modified mixes had lower splitting tensile strength and TSR values than the control mixture. The TSR value for the binder layer mix fell below the commonly accepted failure threshold of 0.8 and there are numerous factors that contribute to this low value, such as less bitumen in the total binder and less anti-stripping agent with the sulfur-modified WMA. A comprehensive moisture susceptibility study including both laboratory and field evaluations is being conducted. The moisture susceptibility study will better quantify the potential reduction in laboratory moisture resistance of sulfur-modified WMA mixes that occurs in certain cases and better explore ways to mitigate this negative impact through the use of more effective anti-stripping agents, other additives, or mix design modifications.

Table 2: Moisture Susceptibility Testing Results

Mix Type	**Treatment**	**Average Specimen Air Voids (%)**	**Saturation (%)**	**Splitting Tensile Strength (kPa)**	**TSR**
Control	Conditioned	6.6	73.1	792.9	0.87
	Unconditioned	6.8	N/A	917.0	
Rich Bottom* (30% sulfur)	Conditioned	6.9	71.3	539.2	0.84
	Unconditioned	6.9	N/A	638.5	
Binder Layer* (40% sulfur)	Conditioned	7.1	74.5	562.6	0.73
	Unconditioned	7.0	N/A	769.5	

*Using plant-produced mix

3.2 Mixture Stiffness

To compare stiffness of the three mixtures, a master curve for each mixture (Figure 3) was developed according to AASHTO PP 62 by fitting a sigmoidal function to the E* data tested at three temperatures (4.4, 21.1, and 46.1^{o}C) and six frequencies (10, 5, 1, 0.5, 0.1, and 0.01 Hz). There was a distinct separation between the master curve of the control mix and those of the sulfur-modified mixtures. This separation is evident across the range of testing temperatures and frequencies, with the sulfur-modified mixtures showing less of an increase at low temperatures (high frequency) but much greater improvement in the higher temperature (low frequency) range, which relates to rutting resistance. The sulfur-modified binder layer mix (40 percent sulfur, 3.5 percent design air voids) exhibited higher stiffness values than the rich bottom mixture (30 percent sulfur, 2 percent design air voids), followed by the control mix. This behavior was anticipated because the rich bottom mix was intentionally designed with more asphalt binder to improve fatigue cracking resistance.

3.3 Rutting/Permanent Deformation

One of the primary benefits of utilizing a sulfur-modified asphalt mixture is increased resistance to loading deformation. For this study, three tests were performed to quantify the rutting resistance of the various sulfur-modified mixtures as well as the control mixture. These tests include flow number test in the AMPT, the Asphalt Pavement Analyzer (APA), and the Hamburg Wheel-Track Device (also used to evaluate moisture susceptibility). However, due to the limitation of this paper, only results from flow number tests are presented. Details about results from other test methods were presented in the final report for this laboratory study (Timm et al. 2009).

Figure 4 shows the average flow numbers for each of the three mixes tested. From these results, it appeared that the binder layer mix (40 percent sulfur, 3.5 percent air voids) had the highest resistance to rutting, given these specimens took the greatest number of cycles to fail.

All the sulfur-modified mixtures showed significant improvement in deformation resistance compared to the control mixture. This trend is in the agreement with those from APA and Hamburg tests (Timm et al. 2009). This finding is consistent with the results of the dynamic modulus testing which showed that the sulfur-modified mixes had a much stiffer behavior under loading than the control, especially at higher temperatures.

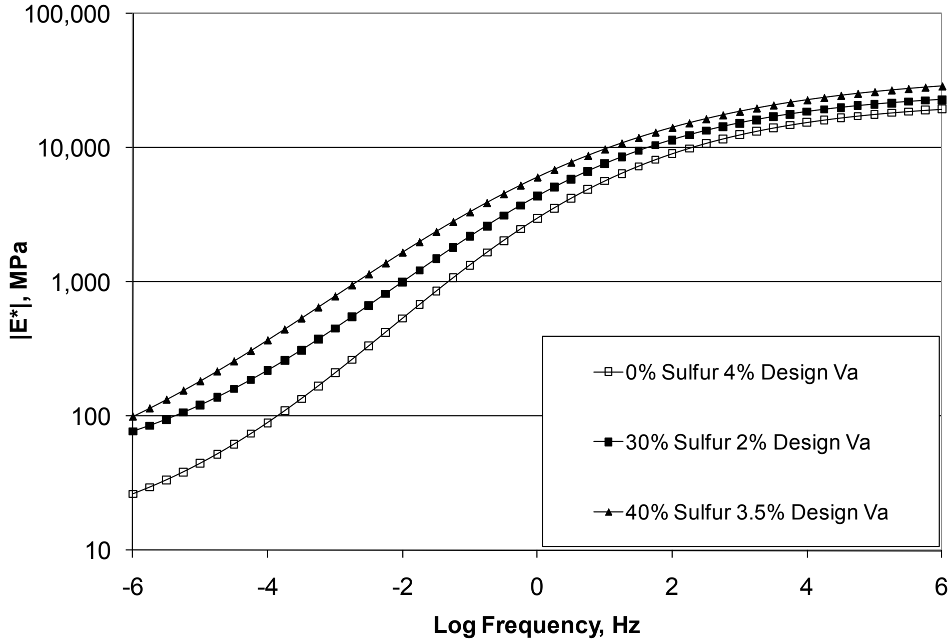

Figure 3: Dynamic modulus master curves for the three mixtures.

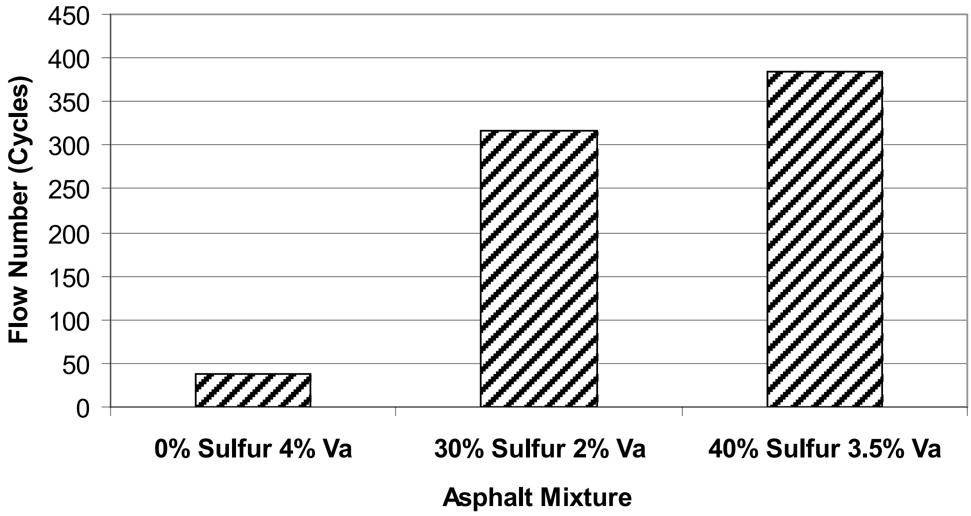

Figure 4: Average flow numbers for the three mixtures.

3.4 Fatigue Cracking

Despite adherence to the specification and tight control of specimen air voids (7 ± 1 percent), dimensions, and beam orientation in BBF testing, significant variability was observed in the duplicate results for a given mixture at a given strain level. This variability was especially evident for testing performed at the lowest strain level (200 microstrain). Figure 5 compares the fatigue cracking resistance of the three mixtures determined in accordance with AASHTO T 321. The control mix had higher numbers of cycles to failure at the high and intermediate train levels (600 and 400 microstrain), followed by the rich bottom mix (30 percent sulfur, 2 percent air voids). However, at the low strain level (200 microstrain), the numbers of cycles to failure for the rich bottom mix exceeded that of the control mix which were higher than that of the binder layer mix.

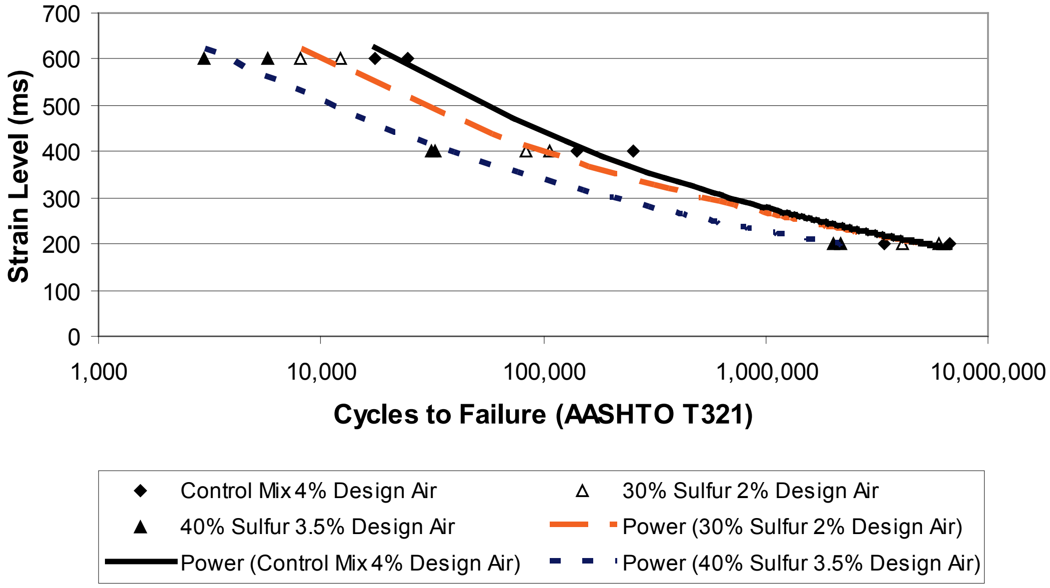

Figure 5: Average flow numbers for the three mixtures.

Given the cycles to failure for three different strain levels, the fatigue endurance limit (the strain level at which the number of cycles to failure is greater than 50 million, indicating indefinite service life in terms of fatigue) was then calculated for each mix. Using a proposed procedure developed under NCHRP 9-38 (Prowell et al. 2009), the endurance limit for each of the five mixes was estimated using Equation 2 based on a 95 percent lower prediction limit of a linear relationship between the log-log transformation of the strain levels (200, 400, and 600 microstrain) and cycles to failure. All the calculations were conducted using a spreadsheet developed under NCHRP 9-38.

$$\text{Endurance Limit } = \hat{y}_0 - t_\alpha s\sqrt{1 + \frac{1}{n} + \frac{(x_0 - \bar{x})^2}{S_{xx}}} \tag{2}$$

where:

$\hat{y}_o$	= log of the predicted strain level (microstrain)
t_α	= value of t distribution for n-2 degrees of freedom = 2.131847 for n = 6 with α = 0.05
s	= standard error from the regression analysis
n	= number of samples = 6
S_{xx}	= $\sum_{i=1}^{n}(x_i - \bar{x})^2$ (Note: log of fatigue lives)
x_o	= log (50,000,000) = 7.69897
$\bar{x}$	= log of average of the fatigue life results

Table 3 shows the 95 percent one-sided lower prediction of endurance limit for each of the three mixes tested in this study based on the number of cycles to failure determined in accordance with AASHTO T 321. The rich bottom mix (30 percent sulfur, 2 percent design air voids) had a significantly higher predicted endurance limit among the three mixes tested in this study. The control mix and the sulfur modified binder mix had similar endurance limits within the range of the determination error.

Table 3: Endurance Limits for the Three Mixtures

Mix Type	Sulfur Content (%)	Design Voids (%)	Endurance Limit (Microstrain)*
Control	0	4	102
Rich Bottom	30	2	119
Binder Layer	40	3.5	98

Note: * 95% one-sided lower prediction limit

4 CONCLUSIONS

The purpose of this paper is to present the effects of using modified sulfur pellets to replace a portion of the asphalt binder on the performance of asphalt mixtures utilizing three asphalt mixtures. The control mixture was a 19 mm Superpave mix using a PG 67-22 binder with a liquid anti-strip (0.5 percent by the weight of binder). This control mix was designed with 4 percent air voids. This mix was utilized in the third (2006-2009) and fourth (2009-2012) research cycles at the NCAT Pavement Test Track.

The other two asphalt mixtures were modified with the Shell Thiopave pellets. The binder layer mix was modified with 40 percent sulfur (by the weight of binder) and designed at 3.5 percent air voids. The rich bottom mix was modified with 30 percent sulfur and designed with 2 percent air voids. The aggregate gradation and base binder utilized in these two mixes were the same as those for the control mixture, except that the binder was modified with an additional compaction agent to facilitate the compaction of the sulfur-modified mixtures at lower temperatures. The results of the laboratory study can be summarized as follows:

- The moisture susceptibility of the three mixtures used for this study was quantified by TSR testing according to AASHTO T283. The AASHTO TSR results showed an increase in the moisture susceptibility of the sulfur-modified mixtures in relation to the control mixture, when using similar binder contents. The TSR value for the binder layer mix fell below the commonly accepted failure threshold of 0.8. However, the rich bottom mix had nearly an equivalent passing TSR as the control mix, which demonstrates the impact of mix design changes on moisture susceptibility. A comprehensive moisture susceptibility study including both laboratory and field evaluations is being planned to further explore this behavior and develop practical solutions.
- Dynamic modulus testing was performed for each of the three mixes. Dynamic modulus tests were conducted at multiple temperatures on test specimens that had been cured for 14 days to develop the master curves. A distinct separation between the master curves showed that the sulfur-modified mixes were stiffer than the control mix, especially at the high testing temperatures.
- The flow number results showed a significant increase in the rutting resistance of the sulfur-modified mixtures versus the control mix. These results agreed with observations reported in the literature and with the increase in stiffness at the high test temperatures observed in the E* testing.
- Based on the BBF test results, the control mix had longer fatigue lives at 600 and 400 microstrain than both sulfur-modified mixes. However, the rich bottom sulfur-modified

mix (30 percent sulfur, 2 percent design air voids) exhibited a fatigue life longer than that of the control mixture at 200 microstrain. The control mix displayed a longer fatigue life than the sulfur-modified binder layer mix at 200 microstrain.

- Among the three mixes tested in this study, the rich bottom sulfur-modified WMA mix had the highest predicted endurance limit, followed by the control HMA mix and the binder layer sulfur-modified WMA mix, which were similar.

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REFERENCES

Bayomy, F., and S.A. Khedr, 1987. *Sulfur as a Partial Replacement for Asphalt in Pavement,* Journal of the Transportation Research Board: Transportation Research Record No. 1115, pp. 150-160, Washington, D.C., USA.

Beatty T., K. Dunn, E.T. Harrigan, K. Stuart, and H. Weber, 1987. *Field Evaluation of Sulfur-Extended Asphalt Pavements,* Journal of the Transportation Research Board: Transportation Research Record No. 1115, pp. 161-170, Washington, D.C., USA.

Deme, I., and B. Kennedy, 2004. *Use of Sulfur in Asphalt Pavements*. Presented at the 5th International Symposium on Pavement Surface Characteristics, Roads and Airfields, Toronto, Canada.

McBee, W.C., T.A. Sullivan, and J.O.Izatt, 1980. *State-of-the-Art Guideline Manual for Design, Quality Control, and Construction of Sulphur-Extended-Asphalt (SEA) Pavements*, Report, Bureau of Mines, Boulder City, Nevada, USA.

Prowell, B. et al 2009. *Endurance Limit of Hot Mix Asphalt Mixtures to Prevent Fatigue Cracking in Flexible Pavements*. Draft Final Report for NCHRP 9-38, NCAT, Alabama, USA.

Strickland, D., J. Colange, M. Martin, and I. Deme, 2008. *Properties of Sulphur Extended Asphalt Mixtures with Modified Sulphur Pellets*, Proceedings of the International Society for Asphalt Pavements.

Timm, D., N. Tran, A.J. Taylor, M.M. Robbins and R.B. Powell 2009. *Evaluation of Mixture Performance and Structural Capacity of Pavements Using Shell Thiopave.* Final Report, National Center for Asphalt Technology, Auburn University, USA.

Willis, R., D. Timm, R. West, B. Powell, M. Robbins, A. Taylor, A. Smit, N. Tran, and M. Heitzman 2009. *Phase III NCAT Test Track Findings*, NCAT Auburn University, Alabama, USA.