# Engineering Properties of Manganese-Treated Asphalt Mixtures

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## ABSTRACT

An experimental program was conducted to evaluate the engineering properties and moisture susceptibility characteristics of manganese-treated asphalt mixtures over a range of temperatures. The experimental program involved three aggregates, two asphalt sources, three grades of asphalt cement, three levels of manganese treatment, and two air void contents. Tests were conducted at 32°F, 75°F, 104°F, and 140°F. The mixtures were cured 28 days at 140°F; however, resilient moduli were measured at various times during the 28-day curing period. Test methods were the static and repeated-load indirect tensile test, Marshall stability test, and Hveem stability test. Properties evaluated were tensile strength, resilient modulus of elasticity, Marshall stability and flow, and Hveem stability. In addition, the ratios of dry and wet tensile strengths and moduli were evaluated with respect to moisture susceptibility. On the basis of the results and conditions of this test program, it appears that the temperature susceptibility of the treated asphalt cement was reduced. Thus softer grades of asphalt cement treated with the manganese additive produced a mixture with less stiffness and strength at 32°F, higher strengths and stiffnesses at 104°F, and higher stabilities at 140°F compared to the untreated control mixtures containing a more viscous grade of asphalt cement. This should reduce the tendency for cracking at low temperatures and improve or maintain stability at higher temperatures. Stiffness increased with time during the curing period but appeared to be approaching a constant value after 28 days. An analysis of tensile strength or resilient modulus indicated no significant improvement in moisture or stripping resistance.

Chemkrete Technologies, Inc., produces an additive (CTI 101), an oil-based soap containing soluble manganese, that when mixed with asphalt cement and allowed to cure in thin films in the presence of oxygen modifies the asphalt causing increased viscosity and in some cases reduced temperature susceptibility as indicated by a flatter temperature-viscosity relationship. This suggests that, by using softer asphalts treated with the additive, adequate stabilities may be achieved at higher temperatures and more flexible and less brittle mixtures can be obtained at lower temperatures. Greater flexibility at the lower temperatures may increase resistance to reflection cracking and fatigue cracking in thinner pavement sections. It is also possible that increased viscosity could improve resistance to stripping or moisture damage.

The study summarized in this paper was part of a research program that was conducted at the University of Texas at Austin and the University of Nevada-Reno in order to evaluate and define needed improvements of the product. Before August 1982 a similar product had been used in field trials that often involved asphalts treated at high levels. These stiff asphalts and higher treatment levels produced mixtures with high stabilities but also mixtures that tended to be brittle. Beginning in August 1982, at the time the technology was acquired by the Lubrizol Company, changes were made in the additive and softer asphalts, treated at lower dosage levels, have been used. To date, minimal cracking, except for reflection cracking, has been reported (see paper by Moulthrop and Higgins in this Record) .

The objective of the study was to evaluate the

engineering properties and stripping or moisture susceptibility characteristics of manganese-treated asphalt mixtures and the effect of treatment levels using different types and grades of asphalt. The test results and a detailed analysis are available elsewhere (1,2). Other portions of the total research program were conducted at Pennsylvania State University, the Western Research Institute, and the University of Waterloo in Canada.

## TEST PROGRAM

The test program consisted of three aggregates, two asphalt sources, three grades of asphalt cement, three levels of treatment, and two air void contents. Mixtures were evaluated over a range of temperatures and in both the dry and wet condition.

# Aggregates

The aggregates are identified as Eagle Lake, Watsonville, and Helms. The Eagle Lake was a silicious river gravel and sand from Texas. Previous use and evaluation of this aggregate indicated that it is highly moisture susceptible. The Watsonville was a crushed granite from California and the Helms was a partly crushed river gravel and sand from Nevada. All three aggregates were dense graded  $(\underline{1,2})$ .

# Asphalt Cements

Two asphalt sources (Cosden Big Spring and Shell Wood River) were used. Three grades of asphalt ce-

ment were obtained from these sources. The asphalts were treated with 4, 6.25, and 10 percent of the manganese additive, which corresponds to 0.08, 0.125, and 0.2 percent manganese, respectively. For the Eagle Lake mixtures all three manganese contents were used. Untreated asphalts were used as controls for comparison purposes. The asphalts for the Watsonville and Helms mixtures contained 0.125 percent manganese. Both the treated and the untreated asphalt cements were supplied by the manufacturer. The basic combinations are given in Table 1.

TABLE 1 Percentage Manganese—Cosden Big Spring and Shell Wood River

	Cosden Big Spring				Shell Wood River			
	0 <sup>a</sup>	0.08	0.125	0.2	Oa	0.08	0.125	0.2
AC-3	х	x	х	x	_	_	_	_
AC-5	X	X	X	X	X	X	X	X
AC-20	X	X	X	X	X	X	X	X

<sup>&</sup>lt;sup>a</sup>Untreated asphalt cement (control).

## Mixture Design

The Texas gyratory mixture design method was used to establish the optimum asphalt control for the Eagle Lake aggregate mixtures (3). The 50-blow Marshall design procedure was used for the Watsonville and Helms mixtures (4). All mixture designs were based on the use of the untreated Cosden AC-20.

The resulting asphalt contents were 4.6, 6.3, and 7.5 percent by weight of the dry aggregate for the Eagle Lake, Watsonville, and Helms mixtures, respectively. These values were used for all mixtures and defined the binder content (asphalt cement plus additive). Thus, in the specimens containing treated asphalts, 4, 6.25, or 10 percent of the asphalt cement, depending on manganese content, was replaced with the additive.

# Sample Preparation

Different procedures were used to prepare and compact the various asphalt-aggregate mixtures.

# Eagle Lake Mixtures

The aggregates and asphalt cement were preheated to  $275^{\circ}F$  before mixing. The asphalt cement and aggregate were mixed at  $275^{\circ}F$  for approximately 3 min in a Hobart mixer and were compacted at  $250^{\circ}F$  using the Texas Gyratory Shear Compactor (3). All samples were nominally 2 in. high and 4 in. in diameter.

Two compaction procedures were used to obtain approximately 3 and 7 percent air voids: the standard procedure specified by the Texas Department of Highways and Public Transportation, which normally would produce about 3 percent air voids in the design mixture containing the untreated AC-20, and a modified procedure with reduced compactive effort, which produced 7 percent air voids in the untreated AC-20 mixture. No correction to compaction procedure was made for mixtures containing either treated or less viscous grades of asphalt cement. Thus the samples containing less viscous asphalts probably had slightly lower air void contents.

#### Watsonville and Helms Mixtures

The aggregates and asphalt cements were mixed at 300°F and compacted at 280°F based on an analysis of the temperature-viscosity relationship for the Cosden AC-20. The two compaction procedures involved a Marshall compaction hammer using a variable number of blows. The standard 50 blows per side produced approximately 4 percent air voids for both aggregates. Twenty-five and 20 blows per side were used with the Watsonville and the Helms mixtures, respectively, to produce approximately 8 percent air voids.

## Curing and Conditioning

After compaction all samples were oven cured at 140°F for 28 days. Air was circulated in the oven throughout the curing period. After 28 days the samples to be tested dry were allowed to cool to room temperature and were then placed in chambers at the appropriate testing temperature for a period of 24 hr. Specimens to be tested wet were conditioned by vacuum saturating the specimens for 30 min using a vacuum equal to 26 in. of mercury and then soaking for an additional 30 min at room temperature. The specimens were then subjected to one freeze-thaw cycle consisting of 15 hr in water at 10°F and 24 hr (dry) at 140°F and subsequently soaked for 2 hr at 75°F before testing.

## Testing

Specimens were tested using the static and repeated-load indirect tensile tests  $(\underline{5})$ , the Marshall stability test (ASTM D 1559), and the Hveem stability test  $(\underline{3})$ . Properties measured were tensile strength, resilient modulus, Marshall stability and flow, and Hveem stability.

## Test Program Design

The experimental program consisted of full factorial designs with 2 or 3 replicate specimens per cell or test condition. All asphalts and treatment levels were coded and all tests were conducted blind. Subsequently the various combinations were identified and the final analysis of the results was conducted.

## DISCUSSION OF RESULTS

The primary objectives of this study were to (a) evaluate the engineering properties of asphalt mixtures containing manganese additive and (b) determine the effect of treatment levels over a range of temperatures for mixtures containing approximately 3 and 7 percent air voids.

Typical results are shown in the figures and are discussed next. A detailed analysis of all the data and a summary of test values are available elsewhere  $(\underline{1},\underline{2})$ .

# Tensile Strength

Tensile strengths were analyzed to determine the effect of temperature and manganese or additive content.

## Effect of Temperature

Typical relationships between tensile strength and temperature for modified compacted specimens (7 per-

cent air voids) are shown in Figures 1-4. It is evident that the tensile strength decreased with increased temperature and that the slope of these relationships varied. Although a direct comparison is not provided, the strengths of the modified compacted specimens were significantly less than the strengths of the standard compacted specimens (3 percent air voids).

In most cases there was a crossover between the treated and untreated (control) asphalt mixtures. Thus the strength of the mixtures containing the treated asphalt often was less than the strength of the untreated asphalt cement at 32°F while the reverse was true at 104°F.

## Effect of Manganese Content

The relationships between tensile strength and manganese content for the standard and modified compacted Eagle Lake mixtures containing Shell and Cosden asphalts are shown in Figure 5. It should be noted that the additive content also increased with increased manganese content.

At higher temperatures there appeared to be a manganese or additive content for maximum tensile strength. The optimum is well defined at 75°F. At 104°F the trend is not as evident. At 32°F, however, the relationships are varied, which suggests the possibility that strength decreased with increased manganese or additive content.

Similar behavior also occurred for the modified compacted specimens (7 percent air voids), although the trends were not as pronounced except at 32°F, at which temperature strength decreased with increased manganese content.

## Resilient Modulus

Resilient moduli were analyzed with respect to testing temperature, manganese or additive content, and curing time.

#### Effect of Temperature

Typical relationships between resilient modulus of elasticity and temperature for the modified compacted Eagle Lake mixtures with manganese contents of 0.08 and 0.125 percent are shown in Figures 6 and 7.

As did tensile strength, the resilient modulus decreased with increased temperature and the slope of these relationships varied and there was a cross-over between the treated and untreated (control) asphalt mixtures. Thus the resilient modulus or stiffness of the mixtures containing the treated asphalt cements often was less than that of the untreated asphalt cements at 32°F and greater at 104°F. In addition, the resilient moduli of the modified compacted specimens were significantly less than the moduli of the standard compacted specimens (3 percent air voids).

## Effect of Manganese Content

The relationships between resilient modulus and manganese or additive content for Eagle Lake mixtures containing Shell and Cosden asphalts are shown in Figure 8.

A manganese or additive content for maximum stiffness occurred at about 0.125 percent manganese

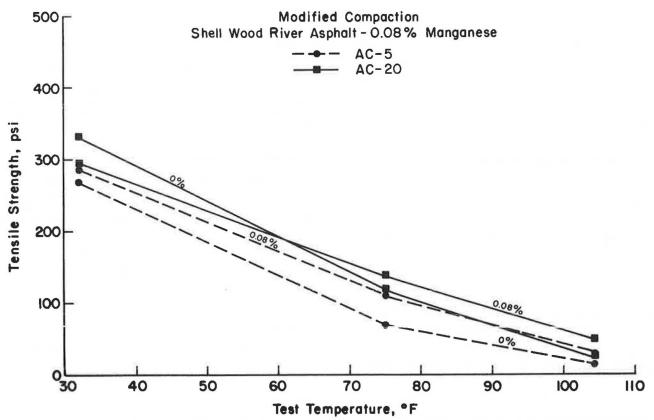


FIGURE 1 Relationships between tensile strength and test temperature for Eagle Lake mixtures with untreated and treated (0.08% Mn) Shell asphalts.

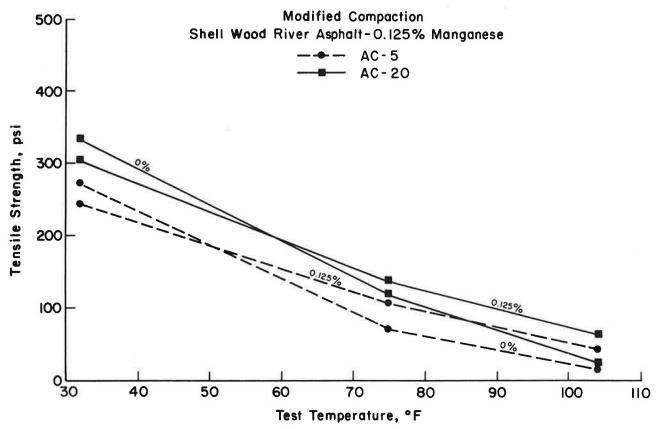


FIGURE 2 Relationships between tensile strength and test temperature for Eagle Lake mixtures with untreated and treated (0.125% Mn) Shell asphalts.

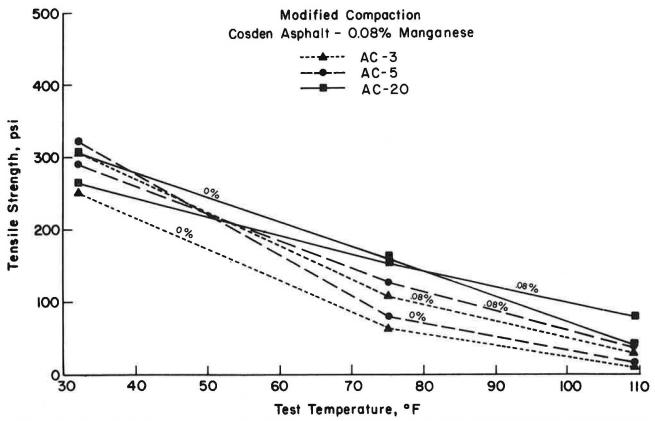


FIGURE 3 Relationships between tensile strength and test temperature for Eagle Lake mixtures with untreated and treated (0.08% Mn) Cosden asphalts.

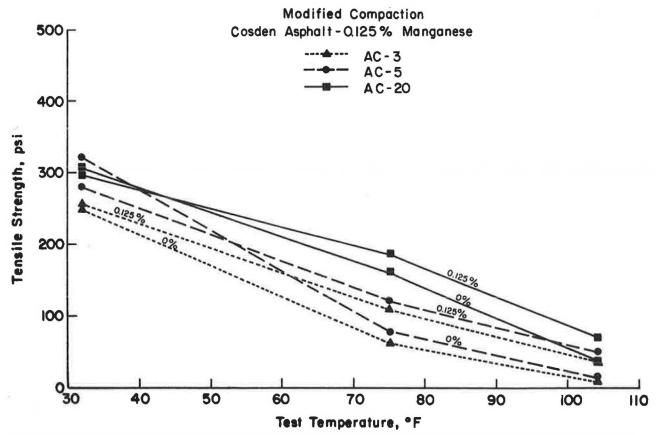


FIGURE 4 Relationships between tensile strength and test temperature for Eagle Lake mixtures with untreated and treated (0.125% Mn) Coeden asphalts.

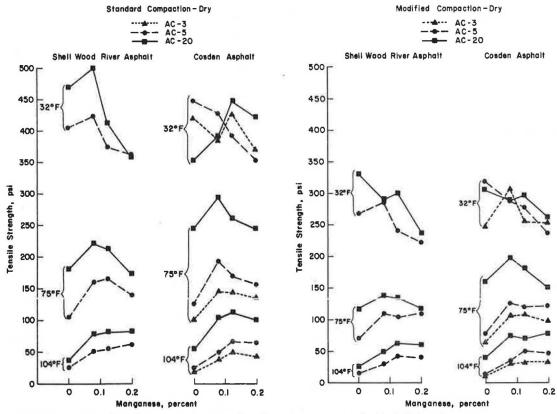


FIGURE 5 Relationships between tensile strength and manganese content for Eagle Lake mixtures.

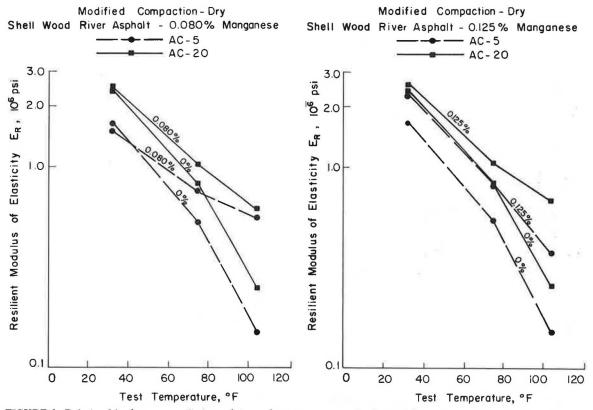


FIGURE 6 Relationships between resilient modulus and test temperature for Eagle Lake mixtures with untreated and treated Shell asphalts.

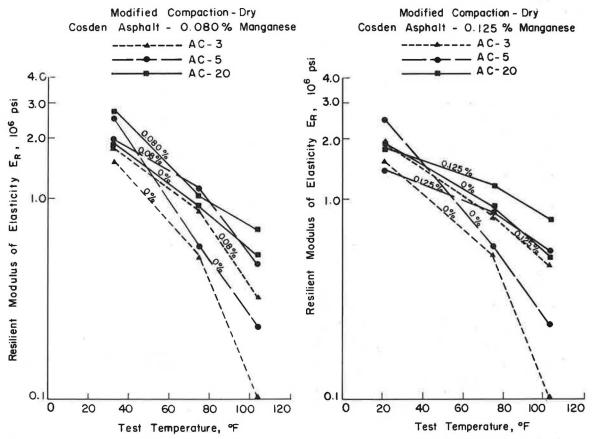


FIGURE 7 Relationships between resilient modulus and test temperature for Eagle Lake mixtures with untreated and treated Cosden asphalts.

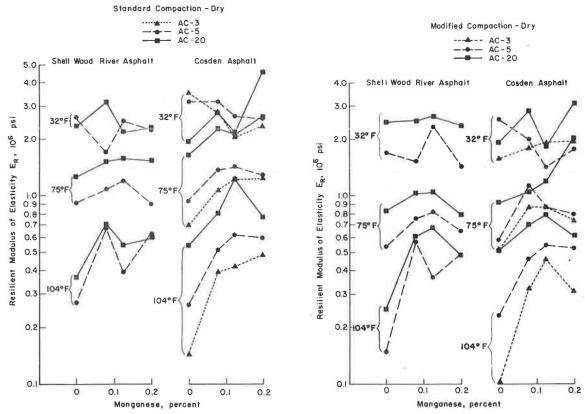


FIGURE 8 Relationships between resilient modulus and manganese content for Eagle Lake mixtures with Shell and Cosden asphalts.

for test temperatures of 75°F and 104°F. At 32°F the relationships were not as consistent and erratic behavior indicated that the effect of manganese was quite small. Unlike tensile strength, there was no indication that stiffness decreased with increased manganese content.

# Effect of Curing Time

The relationships between resilient modulus and time for the Watsonville and Helms mixtures made with AC-20 untreated and treated asphalts are shown in Figure 9. At 77°F the treated mixtures initially had lower resilient moduli (stiffness) than the untreated mixtures. After curing, however, the stiffness of the treated mixtures exceeded the stiffness of the untreated mixtures. In addition, it appears that, although the stiffness of both mixtures continues to increase after 28 days, the rate of increase is relatively small.

Treated samples with higher void contents exhibited a higher rate of stiffness increase. For Watsonville aggregate mixtures, the crossover between treated and untreated asphalt occurred after about 5 to 8 days of curing whereas for the Helms mixtures, which had approximately 2 percent more voids, the crossover occurred after about 3 days (Figure 10).

Figure 11 shows a typical relationship between mixtures containing AC-20 untreated asphalt and AC-5 treated asphalt. The mixtures containing the treated AC-5 asphalt had lower initial resilient modulus as measured at 77°F. Within 28 days the resilient modulus of the mixture containing the treated AC-5 asphalt approached or exceeded the modulus value of mixtures containing the untreated AC-20 asphalt cement.

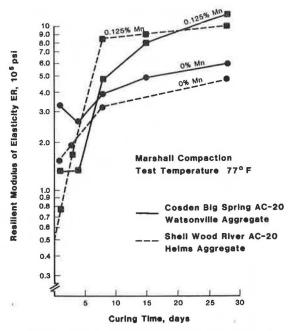


FIGURE 9 Relationships between resilient modulus and curing time for mixtures with untreated and treated asphalts.

## Marshall Stability and Flow

Relationships between Marshall properties at 140°F and manganese content for standard compacted Eagle Lake mixtures are shown in Figure 12. Marshall stabilities increased with increased manganese or additive content with many of the relationships for the

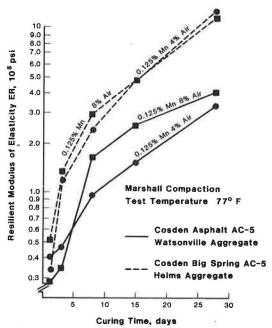


FIGURE 10 Relationships between resilient modulus and curing time for treated asphalt mixture with 4 and 8 percent air.

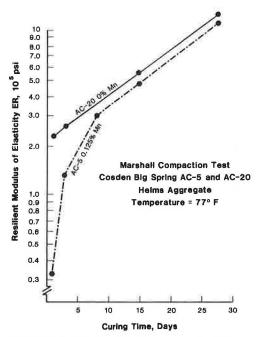


FIGURE 11 Relationships between resilient modulus and curing time for Helm mixtures with treated AC-5 and untreated AC-20 Cosden asphalts.

standard compacted mixtures indicating a manganese content for maximum stability. Stabilities were substantially greater for the standard compacted specimens. It is also evident that the stability of mixtures with 0.08 percent manganese was greater than that of the control (no manganese) asphalt mixtures containing the next grade of asphalt. For the Cosden asphalts, 0.125 percent manganese was required for the AC-3 to achieve a stability greater than the stability of the control AC-20 mixture.

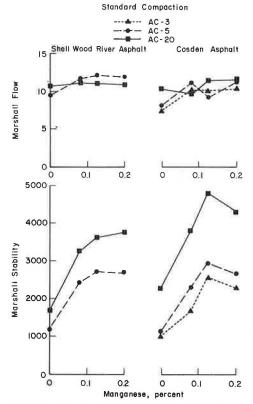


FIGURE 12 Relationships between Marshall properties and manganese content for standard compacted Eagle Lake mixtures with Shell and Cosden asphalts.

Flow values did not exhibit consistent relationships although flow values may have increased slightly with increased manganese contents. Nevertheless, the difference for the various mixtures was small. In addition, there were essentially no differences between the standard and the modified compacted mixtures.

## Hveem Stability

Relationships between Hveem stability and manganese or additive content for standard compacted Eagle Lake mixtures are shown in Figure 13. There were no consistent relationships. For the modified compacted mixtures, stability increased with increased manganese or additive content. It should also be noted, however, that the stabilities of the treated asphalt cement mixtures generally were equal to or greater than the stability of the control with no manganese. For the Cosden asphalts, the AC-20 (control) had higher stabilities than the mixtures with treated AC-3 asphalt. The small effects produced by the additive probably are not unexpected because the Hveem stabilities, unlike the Marshall stabilities, are relatively insensitive to the binder.

# Moisture Susceptibility

The tensile strength ratios and the resilient modulus ratios for Eagle Lake mixtures with various manganese contents indicated a substantial loss in strength and modulus. Only about 15 to 25 percent of the dry tensile strength and 10 percent of the dry resilient modulus were retained and were essentially

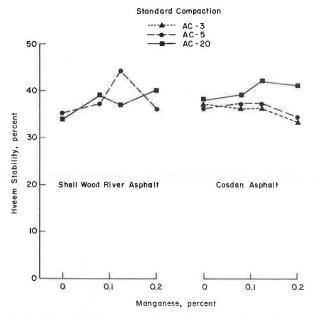


FIGURE 13 Relationships between Hveem stability and manganese content for standard compacted Eagle Lake mixtures with Shell and Cosden asphalts.

equal at all levels of manganese. In addition, there were no apparent benefits relative to the absolute values of strength and modulus. This suggests that the treatment did not improve the moisture susceptibility of these mixtures.

Similar results are shown for the Watsonville and Helms mixtures (Figures 14 and 15). The ratios for the Watsonville mixture, although not acceptable, were greater for the treated asphalt (Figure 15).

Thus, on the basis of these test results, it must be concluded that the use of manganese-treated asphalts did not improve moisture resistance to an acceptable level as measured by the indirect tensile test. Previous testing using the Texas boiling test had shown substantial improvement; the benefits measured by the Texas pedestal test were questionable (6).

## CONCLUSIONS

The following conclusions are based on the findings of this study and the conditions evaluated.

## Tensile Strength

 The tensile strengths of the untreated and the treated mixtures decreased significantly with increased testing temperature.

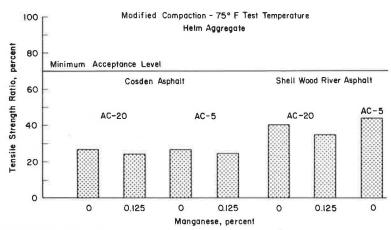


FIGURE 14 Tensile strength ratios for Helm mixtures with untreated and treated Shell and Cosden asphalts.

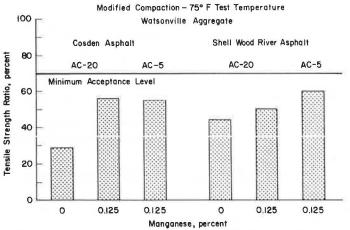


FIGURE 15 Tensile strength ratios for Watsonville mixtures with untreated and treated Shell and Cosden asphalts.

- 2. Tensile strengths of treated asphalt mixtures at all temperatures generally were greater than tensile strengths of untreated asphalt mixtures containing the same asphalt type and grade.
- 3. The effect of temperature on the tensile strengths of treated asphalt mixtures was less than on untreated mixtures (i.e., the slope of the temperature-tensile strength relationship was flatter).
- 4. Tensile strengths of the treated asphalt mixtures were less at 32°F and greater at 140°F than the tensile strength of the untreated control mixtures that contained the same type but a higher viscosity grade of asphalt.
- 5. The crossover in strength generally occurred at about 80°F to 90°F.
- 6. An optimum manganese content for maximum tensile strength at 75°F and 104°F occurred for both asphalts and void contents although the optimum was more pronounced for the low void content specimens (standard compacted).

#### Resilient Modulus of Elasticity

- 1. The resilient moduli of the untreated and the treated mixtures decreased significantly with increased testing temperature.
- Resilient moduli of treated asphalt mixtures at all temperatures generally were greater than moduli of untreated asphalt mixtures containing the same asphalt type and grade.
- The effect of temperature on the resilient moduli of treated asphalt mixtures was less than the effect on that of untreated mixtures.
- 4. Resilient moduli of the treated asphalt mixtures were less at 32°F and greater at 140°F than the moduli of the untreated control mixtures that contained the same type but a higher viscosity grade of asphalt.
- 5. The crossover in moduli generally occurred at about 80°F to 90°F for the Shell Wood River asphalt mixtures but was not as consistent for the Cosden asphalt mixtures.
- 6. An optimum manganese content for maximum resilient modulus occurred for a few mixtures at the higher testing temperatures; however, there was no consistent relationship at 32°F.
- 7. The resilient moduli of the treated mixtures initially were lower than those of the untreated mixtures, presumably because of the increased amount of additive; however, after curing, the stiffness of the treated mixtures exceeded the stiffness of the untreated mixtures.
- 8. The resilient moduli of the higher void content mixtures increased more rapidly than did the moduli of the mixtures with low voids.

# Marshall Stability and Flow

- 1. An optimum manganese or additive content for maximum stability occurred for the standard compacted (low void) mixtures.
- Stabilities increased with increased manganese content for the modified compacted (high void) mixtures.
- The treated mixtures had higher stabilities than the untreated control mixtures containing the same type but a higher viscosity grade asphalt.
- 4. There was no significant relationship between manganese content and flow value although for the modified compacted (high void) mixtures the flow values increased slightly.

# Hveem Stability

There was no significant effect of manganese content on Hveem stability.

## Moisture Susceptibility

There was no improvement in moisture or stripping resistance of mixtures produced using treated asphalts. All moisture-conditioned Eagle Lake mixtures, both treated and untreated, retained only about 15 to 25 percent of the dry tensile strength and only about 10 percent of the dry resilient modulus. Similar results occurred for the Watsonville and Helms mixtures, although the Watsonville mixtures with the additive did show a substantial improvement.

#### Summary

On the basis of the results and conditions of this test program, it appears that the temperature susceptibility of the treated asphalt cement is reduced. Thus use of the manganese additive with softer grades of asphalt cement will produce a mixture with less stiffness and strength at 32°F, higher strengths and stiffnesses at 104°F, and higher stabilities at 140°F compared to the untreated control mixtures containing a more viscous grade of asphalt cement. This should reduce the tendency for cracking at low temperatures and improve or maintain stability at higher temperatures. Additional work is required to determine the significance of the observed behavior in terms of pavement performance. This should involve theoretical estimates of performance as well as additional field trials.

An analysis of tensile strength and resilient modulus indicated that there was no significant improvement in moisture or stripping resistance as measured by the retained strength or modulus or the absolute values of wet strength and modulus. However, previous evaluations on other mixtures using the boiling test have shown significant improvements. Additional work will be required to ascertain the effect of manganese-treated asphalts on the moisture susceptibility of mixtures.

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