# Manganese-Modified Asphalt Pavements: A Status Report

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#### ABSTRACT

This paper is a chronological account of the experimental asphaltic concrete highway sections that have been constructed using manganese-modified asphalt cements. Described are the potential performance improvements attainable with the chemical modifier and the changes that have been required in the way it is used to obtain benefits without undesirable side effects. The details of the laboratory testing before highway construction and the evaluations carried out with cores from highways after construction are related to the performance observed in experimental highway sections.

Modification of asphalt cements with soluble manganese can change the rheology of the cements so that the stability of resulting asphalt concrete mixtures at elevated temperatures is significantly increased. The liquid manganese compound can be easily blended with asphalt cements in storage tanks or before entering hot mix plants. The manganese-modified asphalt cements do not require any special handling or procedural changes in the highway building process. The chemical effect of the modifier takes place to some degree during hot mixing, but the major changes occur in the pavement after rolling and compaction.

The early field applications of manganese-modified asphaltic concrete mixtures indicated that the level of modification had to be carefully selected to prevent low-temperature cracking problems. In this paper, the field history of manganese-modified asphaltic concretes will be reviewed and the chemical and rheological changes in the asphalt cements in the pavements will be related to ultimate road performance as determined by observation and changes in the engineering properties of the asphalt concretes.

# EXPERIMENTAL PAVEMENT APPLICATIONS

During the period from January 1980 through August 1984, 44 projects were constructed throughout the United States using manganese-modified asphalts. Eleven projects were built in 1980, nine in 1981, ten in 1982, five in 1983, and nine to date in 1984. The locations are widely distributed throughout the country in a variety of climates.

From 1980 through September 1982 the modifier was marketed by the Chem Crete Corporation of Menlo Park, California. In October 1982 the Lubrizol Corporation of Wickliffe, Ohio, purchased the U.S. patent rights to produce and market the modifier. Chemkrete Technologies Incorporated was formed for this effort as a wholly owned subsidiary of Lubrizol.

During the 1980-1982 period, the modifier was manufactured at several locations in the United States by several processes using a variety of raw materials. In 1980 a liquid concentrate, containing 2.5 percent by weight manganese, was mixed at a 9 asphalt cement to 1 modifier ratio. The modified asphalt cement grade was generally an AC-20 or an AC-10. Asphalt was used as the carrier for the manganese in the concentrate.

Pavements constructed in 1980 exhibited marked increases in Marshall stability and tensile strength at 140°F over the control sections built during the same time period with unmodified control asphalt. The modified sections, however, cracked extensively. The cracking patterns and the loss of surface fines indicated that the modified pavements were much stiffer than the controls at low temperature.

In 1981 the amount of manganese in the concentrate was reduced to 2.0 percent by weight manganese and the concentrate was used to modify softer grades of asphalt (AC-10 or AC-5). The concentrate was added at a 9 asphalt cement to 1 modifier ratio. These 1981 pavements performed better than the 1980 projects but none were superior to adjacent control sections. Cracking occurred in the 1981 projects but not to the extent observed in the 1980 projects. In some instances, quality control problems during manufacture of the modifier and a lack of control during construction influenced the performance of the 1980 and 1981 projects. These factors will be discussed later.

In 1982 the modifier was changed considerably. It was manufactured with various petroleum oils as the carrier instead of an asphalt cement. The manganese in the modifier remained at the same level but the modifier was blended at a 15 asphalt cement to 1 modifier ratio. These changes were made to provide increased Marshall stability over the control without developing undesirable stiffness at low temperatures. The 1982 pavements have generally been superior to the 1980 and 1981 pavements. Table 1 gives

TABLE 1 Modifier Characteristics, 1980-1984

	1980	1981	1982	1983	1984
Manganese in modifier (%)	2.5	2,0	2.0	2.0	2.0
Asphalt cement to modifier ratio	9/1	9/1	9/1	15/1	25/1 33/1
Manganese in blended asphalt cement (%)	0.25	0.20	0.20	0.125	0.08
Grade of asphalt cement modified	AC-20 or AC-10	AC-20 or AC-10	AC-10 or AC-5	AC-10 or AC-5	AC-10 or AC-5

the details of the various versions of the modifier and how they were used.

As mentioned previously, quality control problems during manufacture of the modifier and poor control of construction procedures had an adverse effect on performance. During the period 1980-1982, the modifier was blended with asphalt cement before the asphalt was mixed with the aggregate at the hot mix plant. In most instances the blending was accomplished by placing the modifier and the asphalt cement in a heated asphalt storage tank at the hot mix plant site and then recirculating the contents of the tank for 24 hr before hot mixing with aggregate. On several occasions, blending was done at a terminal or refinery and the blend was then delivered to the hot mix plant in a conventional manner. The several pavements constructed during the 1980-1982 period exhibited a great degree of variation in performance. This variation leads the authors to conclude that blending of large volumes by recirculation alone is neither efficient nor acceptable. This type of blending can be done properly but it is not cost-effective because of the long time period required to obtain a uniform blend. Table 2 gives data from a project in Oregon that indicate excessive modifier level, which must have been due to a nonuniform blend of modifier.

TABLE 2 Actual Versus Target Manganese Level, Klamath Falls, Oregon, Project

Asphalt cement grade	AR 2000
Target percentage of manganese	0.125
Actual percentage of manganese from core analyses	0.73

In the spring of 1983 a volume proportioning blending device was developed and it has been used to blend the modifier and the asphalt cement on those projects for which terminal or refining blending was unavailable. This device, which is portable, meters both asphalt and modifier at the proper ratio using an air-actuated ratio control device connecting both meters. Blending takes place in line before the mixture is pumped into the hot mix plant asphalt storage tank.

# MANUFACTURING

As noted earlier, the modifier was manufactured at various locations from 1980 to 1982 and several materials were used as vehicles for the manganese. On more than one occasion during this period, the manganese level in the modifier was higher than specified. For example, the modifier used on the 1981 New Hampshire project had a manganese content of 3.5 percent not the specified 2.0 percent. Since 1982 the modifier has been produced under strict quality control procedures at plants in Painesville, Ohio, and Bayport, Texas, using a single carrier of consistent quality.

# CASE HISTORIES

Detailed performance information is not available from each project constructed to date. However, to describe the changes that have taken place and the attendant performance, a typical project will be discussed from each of the 4 years previously noted.

#### 1980, New Hampshire

An experimental overlay project was constructed in October 1980 on Interstate 93 north of Thornton, New Hampshire, using a manganese-modified bituminous mixture. Table 3 gives placement details.

TABLE 3 Pertinent Field Data, New Hampshire I-93

Date constructed	October 1980
Existing base Modified flexible	
Base condition	Transverse thermal cracks
Type of placement	Overlay
Thickness	1½-in. wearing course
Modified asphalt cement	AC-10
Asphalt/modifier ratio	9/1
Target percentage of manganese	0.25
Control asphalt	AC-10

After the first winter the modified pavement had twice as many cracks as the control section. A block crack pattern developed and, with time, has become extensive. A minor loss of fines was noted as well. Thermal cracks also occurred after the first winter on the control section. However, there was no loss of fines, and the block crack pattern was not present.

#### 1981, Maine

A 4,400-ft-long overlay was placed in June 1981 on two lanes of Interstate 95 near Benton, Maine. Table 4 gives the pertinent project facts. Both the control section and the modified section are performing well except for transverse cracks in both sections. The modified section had no cracks until sometime between March 7 and April 7, 1983, at which time cracking developed in the 4-ft shoulder section.

TABLE 4 Pertinent Field Data, Maine I-95

Date placed	June 1981	
Existing base 5-in, penetrated base		
Base condition Cracked in outside v		
Type of placement Overlay		
Thickness	21/4-in, binder course	
Modified asphalt cement	AC-10	
Asphalt/modifier ratio	9/1	
Target percentage of manganese	0.2	
Control asphalt AC-10		

# 1982, West Virginia

A modified pavement was constructed on state route 97 near Pineville. Table 5 gives the pertinent project details. Two separate control and modified sections were constructed. This highway carries a large volume of heavily loaded coal trucks. Cores drilled in 1983 from one of the control sections indicated that the base course in this section was badly cracked. Cores from the adjacent modified section

TABLE 5 Pertinent Field Data, West Virginia Rt. 97

Date placed	August 1982
Existing base	Bituminous pavement
Base condition	Badly cracked
Type of placement	Full depth
Thickness	6-in. BCBC, 1-in, wearing course
Modified asphalt cement	AC-10
Asphalt/modifier ratio	9/1
Target percentage of manganese	0.125
Control asphalt	AC-20

were intact. In addition, shoving was noted on curves in the same control section. Short (3-ft) longitudinal cracks in both the control and the modified sections were noted in the spring of 1984.

In the summer of 1984 these experimental pavements were again evaluated. Cores were taken for physical testing and deflection tests were run by West Virginia highway personnel. The test data are given in Table 6.

TABLE 6 1984 Test Data from West Virginia 1982 Pavement— Marshall Stability and Flow (140°F)

		Stability (lb)	Flow (0.01 in.)
Surface course	Control	2,582	8
	Mn-modified	3,738	10
Base course	Control	1,236	15
	Mn-modified	2,247	27

These data indicate the beneficial effect of manganese modification on asphalt concrete properties. During the 2-year life of this West Virginia pavement, the softer AC-10 asphalt, because of manganese modification, has produced a pavement that is much more stable than the control pavement produced with the harder AC-20 asphalt. The degree of improvement due to manganese modification over the control is 82 percent in the base course and 45 percent in the surface course.

The following deflection data also indicate the benefit of manganese modification on overall performance of asphalt concrete. In the control section deflection has increased significantly whereas that of the manganese-modified pavement has not changed after 2 years.

Deflections	(mils)
1983	1984
0.63	0.718
0.69	0.78
0.61	0.58
0.65	0.62
	0.63 0.69 0.61

There is no thermal cracking in the manganesemodified pavement after 2 years of service. This is an example of how to properly use manganese modification to obtain higher strength pavements without inducing thermal cracking.

# 1983, Ohio

An experimental section was placed on Interstate 70 just east of Springfield. After 1 year the control and the modified sections were performing equally well. Table 7 gives the pertinent project details.

## CURRENT PRECONSTRUCTION EVALUATION PROCEDURES

The early paving experiences with manganese-modified asphalt cements indicated the need for several changes. The modifier should be used with the softest grade of asphalt that, when modified, will provide initial stability and improved high-temperature strength. The manganese level should be reduced to a level commensurate with these requirements so that low-temperature properties will be equal to or better than those of the control. This also does not reduce the asphalt binder level to any significant extent. Earlier treatment levels decreased asphalt

TABLE 7 Pertinent Field Data, Ohio I-70

Date placed	July 18-26, 1983
Existing base	Portland cement concrete
Base condition	Joint failures, scaling
Type of placement	Overlay
Thickness	1½ in.
Modified asphalt cement	AC-10
Asphalt/modifier ratio	15/1
Target percentage of manganese	0.125
Control section	AC-20

binder levels as much as 10 percent, which could have been partially responsible for poor pavement performance. It was also apparent that a more detailed preconstruction analysis was required for each project. This analysis includes the evaluation of aggregates, mix design, control asphalt cement, and a softer asphalt cement with several levels of manganese modification.

At the present time highway and transportation departments include manganese-modified sections in new construction or in maintenance work as part of established highway building programs. This makes it possible to directly compare manganese-modified pavements to conventional asphalt pavement compositions in a variety of applications. This is being done nationwide and, for each project involving manganese-modified pavements, the following preconstruction analysis is being carried out in order to specify the optimum manganese level in the modified sections:

- 1. When the highway engineers have decided on a specific asphalt, aggregate composition, and mix design for the control section, samples of the asphalts (usually AC-20 or AC-10 grades for the control sections and a softer grade, usually an AC-5 for manganese modification) are obtained. The grades of asphalt for a specific test section are usually from the same source. Samples are also obtained of the aggregates, and the mix design is established for the control section.
- 2. In the initial laboratory analysis nine cylindrical (2-in.-long by 4-in.-diameter) specimens are prepared on the basis of the established mix design for the control. The specimens are compacted to 7 percent air voids for each of the following compositions: (a) AC-20 or AC-10 control, (b) AC-5 containing 0.04 percent manganese, (c) AC-5 containing 0.08 percent manganese, and (d) AC-5 containing 0.12 percent manganese. In all systems the asphalt-to-aggregate ratio is the same as that established in the original mix design for the control.
- 3. Immediately after preparation, three specimens of each variable are tested for stability by either Marshall or Hveem procedures. These data allow anticipation of the relative stabilities of modified and control sections at the time the new construction is opened to traffic. The modifier develops increased strength in asphalt concretes over a period of several weeks after application. However, the modified system must produce the required stability to support immediate traffic.
- 4. The remaining six specimens of each variable are cured for 9 days at 140°F to produce the oxidative and chemical changes that will occur over extended periods in both control and modified highway sections. After accelerated curing, three specimens of each variable are tested for stability by either Marshall or Hveem procedures. Three specimens are subjected to indirect tensile testing at 39.2°F.
- 5. The data developed are analyzed and a modified AC-5 system is selected that will provide significant high-temperature strength improvement over the control at 140°F and, at the same time, equiva-

lent or better low-temperature flexibility at 39.2°F. Three specimens are prepared with each the modified AC-5 and the AC-20 control. They are compacted to 3 percent voids for Marshall or Hveem stability as related to state specifications. The modifier makes it possible to use softer grades of asphalt to obtain better low-temperature properties in asphalt concrete and still provide improved resistance to rutting, shoving, and other forms of instability at high temperatures. The amount of modifier must not only provide improved properties over extended periods but also adequate stability in the modified pavement early on when the road is first opened to traffic.

6. At the job site engineers obtain liquid samples of the modified asphalt cement entering the hot mix plant. They also obtain samples of hot mix before it is applied. These samples are analyzed for manganese content in the asphalt and for asphalt content in the mix to assure proper composition in the entire length of the modified test section. If for some reason there has been a blending or mixing error, the records will show the error and it will be known when the highway sections are inspected later.

#### CONSTRUCTION CONSIDERATIONS

The manganese modifier, when combined with asphalt cement, will initially reduce the viscosity. The data given in Table 8 indicate the amount of viscosity reduction that was obtained by modification of several AC-5 grades from various parts of the country with a commonly used modifier level.

TABLE 8 Viscosity Reduction of AC-5 Asphalt Cements With Manganese Modifier<sup>a</sup>

Asphalt	Viscosity (140°F, poise)	Reduction (%)
A	463	
A modified	247	47
В	572	
B modified	303	47
C	570	
C modified	315	47
D	497	
D modified	255	49
E	481	
E modified	241	50

<sup>&</sup>lt;sup>8</sup>All modified asphalts contain 0.08 percent Mn.

As noted earlier, modified asphalt cement usually is made with an asphalt cement that is softer than the grades normally used. As a result, the temperature required in the hot mix plant is lower because of the lower viscosity of the softer grade. Lower temperatures in the hot mix plant reduce fuel costs. In addition, the modified softer asphalts generally tend to compact with less effort. Mixing temperature should not be indiscriminately lowered; this should be done on the basis of a study of the temperatureviscosity curve for the modified asphalt cement. When modified asphalt concrete is in place, compaction proceeds as with a conventional mix. If the modified mix is at the proper temperature, breakdown, intermediate, and finish rolling proceeds routinely. Special equipment and procedures are not required for manganese-modified asphalt concretes.

#### POSTCONSTRUCTION PAVEMENT EVALUATIONS

After construction the comparative performance of the control and the modified-asphalt concrete sections is monitored by visual inspection and by analysis of road core components in the laboratory. In many cases changes in the properties of the road sections are not visually obvious and some apparent differences may be misleading because they are due to factors other than the asphalt cements. Local conditions such as subgrade variations, application differences, or differences in traffic volume or patterns may cause changes unrelated to the asphalt cements. Therefore changes in the engineering properties of road cores taken at random locations over a wide area must be studied to evaluate the relative merits of conventional and manganese-modified pavements.

To study the properties of road cores and their components, the following procedures have been adopted:

- If the cores are intact, indirect tensile values at 39.2°F and Marshall stabilities at 140°F are determined.
- 2. The tested cores (or cores that could not be tested because of a lack of integrity) are extracted with a solvent (1,1,1 trichloroethylene) to separate the aged asphalt cement from the aggregate.
- 3. The solvent is removed from the extract under heat and vacuum to recover the "neat" aged asphalt.
- 4. On the basis of the weight of recovered asphalt and isolated aggregate, the asphalt content of the road core is determined.
- 5. The asphalt is analyzed for manganese content. If any error was made in blending the modifier or in the aggregate-asphalt hot mixing operation the values obtained will pinpoint the error or errors.
- The penetration of the asphalt is determined at a series of temperatures from 39.2°F to 140°F.
- 7. The viscosities of the asphalts are determined at 140°F by either the Schweyer Rheometer method or kinematically (ASTM D2170-83). These consistency measurements will define and confirm the oxidative and chemical changes that increase viscosity in the modified asphalts.
- 8. The recovered aged asphalts are also evaluated by means of the thermal mechanical analyzer (TMA). This instrument provides information on the glass transition point (Tg), the coefficients of linear expansion at low temperatures (where asphalts are solids), and the moduli of elasticity at low temperatures. These values are related to low-temperature performance properties of asphalt concrete highways.
- 9. The differential scanning colorimeter (DSC) is used to determine the liquefication temperature of the aged asphalt cements. This can be related to the degree of flexibility of the asphalt concrete binder at low temperatures.

These tests provide a picture of the changes that take place in the control and in the manganese-modified asphalt cements in the liquid and solid states as the pavement ages. The test data relate to either high- or low-temperature properties of the asphalt cements and indirectly to the engineering properties of the pavement as it ages. These data define the state of the road before any apparent visual changes do so.

## SUMMARY

The results, as they have evolved to date, indicate that, for a specific road application, improved

high-temperature stability and strength plus equivalent or improved low-temperature flexibility are possible by replacing a given conventional asphalt cement with a manganese-modified, softer asphalt cement from the same source. The modification must be based on a thorough study of each asphalt-aggregate combination. In general, if an AC-20 grade is specified, it should be replaced with an AC-5 grade from the same source containing enough modifier to give a 0.06 to 0.08 percent manganese content. The modified system does not require any significant changes in construction procedures and, generally, the modified asphalt will tend to compact with less

effort. The use of modified asphalt may decrease energy consumption in compaction and in the hot mix plant by allowing the plant to run at lower than normal temperatures. Future reports on the specifics of property changes in experimental highway projects will be forthcoming.

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# Sensitivity of Flexible Pavement Performance to Bituminous Mix Properties

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# ABSTRACT

Modulus (stiffness) characterization that may be predicted is a crucial factor in the design of pavement structures. Locally produced and used bituminous materials, when not characterized correctly and statistically within an allowable significant range, will result in pavements of unreliable design thicknesses and performance. Crushed stone-, gravel-, slag-, and sand-asphalt mixes were evaluated by the dynamic modulus laboratory test in the study. Tests conducted in the Civil Engineering Department of the University of Maryland and previous tests conducted by the Asphalt Institute were combined to formulate an extensive data base of 131 different mix types and 1,179 mix-temperature-frequency data point combinations. The variables and coefficients used in the model are both statistically significant and rational from an engineering point of view. On the basis of this modulus model, a sensitivity analysis for the selected variables was done on the typical simulated pavement life models for fatigue, rutting for three layers, and rutting for full-depth sections. Some newly incorporated variables like coarse-grained materials were found to be significant in the sensitivity analysis for both the modulus model and the life models. Because of the extreme ranges in the material types and properties considered in the study, it is believed that the final regression equation is applicable to most commonly used bituminous mixtures. The development of this accurate prediction model should obviate the need for design agencies to use time-consuming and expensive laboratory testing to characterize the dynamic response of bituminous materials in pavement design.

Two general approaches to the design of pavement systems are in practice today: (a) an empirical approach such as the AASHTO method of design, which relies on the experience of the user and subsequent correlation with performance and (b) the rational or mechanistic approach, which is primarily based on theoretical concepts of modeling structural behavior. The modulus characterization of materials is important in both approaches.

One of the major properties of bituminous materials in pavement performance is the dynamic modulus, which is a function of many variables. These include aggregate type, aggregate size and gradation, aggregate shape, asphalt content, asphalt viscosity, void ratio, temperature, and frequency of loading. The development of models to predict performance on the basis of improved material characterization in the laboratory under dynamic load sim-