Physio-Chemical Evaluation of Asphalt-Aggregate Interactions
The durability of selected asphalt concrete components and mixtures from six projects were evaluated with the newly recommended net adsorption test and the more common ASTM D4867 (a modified Lottman), respectively. The net adsorption test was used to assess the durability of the adhesion of the asphalt to the aggregate surface in the presence of water. The ASTM D4867 method evaluated the retained strengths of compacted mixture resistance after freeze/thaw conditioning.

The net adsorption results indicated at least two of the six projects could be susceptible to moisture related adhesion problems. The test method was adjusted to use the full aggregate gradation rather than only the fine fraction. A comparison of these results to those originally reported by Strategic Highway Research Program (SHRP) researchers showed good agreement in both trends of results and within-laboratory test method variability (about 0.14 mg/g).

The mixture testing indicated that three of the six projects had tensile strength ratios of less than 70 percent and could be expected to show some evidence of moisture related damage. An evaluation of these results suggested that any moisture sensitivity could be due to mix design parameters such as lower film thicknesses, and lower initial strengths rather than a chemical loss of adhesion at the asphalt-aggregate interface. The influence of conventional mix design parameters on the moisture sensitivity of asphalt concrete mixtures should be more thoroughly investigated prior to any consideration of the use of additives.
PHYSIO-CHEMICAL EVALUATION OF ASPHALT-AGGREGATE INTERACTIONS

FINAL REPORT

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EXECUTIVE SUMMARY

The durability of selected asphalt concrete components and mixtures from six projects were evaluated with the newly recommended net adsorption test and the more common ASTM D4867 (a modified Lottman), respectively. The net adsorption test was used to assess the durability of the adhesion of the asphalt to the aggregate surface in the presence of water. The ASTM D4867 method evaluated the retained strengths of compacted mixture resistance after freeze/thaw conditioning.

The net adsorption results indicated at least two of the six projects could be susceptible to moisture related adhesion problems. This conclusion was based on an assessment of the original Strategic Highway Research Program (SHRP) research which indicated that asphalt-aggregate pairs with net adsorption results of less than 0.700 mg of asphalt per gram of aggregate would exhibit moisture damage; results above about 0.900 mg/g should not exhibit moisture related problems. The test method was adjusted to use the full aggregate gradation rather than only the fine fraction. A comparison of these results to those originally reported by the SHRP researchers showed good agreement in both trends of results and within-laboratory test method variability (about 0.14 mg/g).

The mixture testing indicated that three of the six projects had tensile strength ratios of less than 70 percent and could be expected to show some evidence of moisture related damage. An evaluation of these results suggested that any moisture sensitivity could be due to mix design parameters such as lower film thicknesses, and lower initial strengths rather than a chemical loss of adhesion at the asphalt-aggregate interface. The influence of conventional mix design parameters on the moisture sensitivity of asphalt concrete mixtures should be more thoroughly investigated prior to any consideration of the use of additives.
INTRODUCTION

CHAPTER ONE

Several mechanisms for the loss of asphalt mixture strength due to moisture damage have been suggested. These include loss of cohesive strength of the binder matrix, loss of adhesion of the asphalt to the aggregate surface, hydraulic scour, and emulsification of the binder. Of these mechanisms, loss of cohesion and adhesion are considered the major contributors to the loss of mixture strength in moisture susceptible asphalt concrete pavements. Laboratory tests have been developed over the last 10 years that identify moisture-related damage by either or both of these mechanisms.

Recently, the Minnesota Department of Transportation has reported an increasing number of premature pavement distresses that have been attributed to moisture damage of asphalt concrete pavements. Evidence of moisture susceptible mixtures includes a dry-looking (i.e., low asphalt cement content) surface on a young pavement surface with a tendency for ravelling and excessive pot-holing after freezing and thawing, and a general premature deterioration of the pavement due to a loss of strength. Loss of adhesion may be mitigated during construction with the use of anti-stripping additives such as hydrated lime or liquid chemical agents once a moisture sensitive mixture has been identified. However, the identification of moisture sensitive mixtures is a process that is not currently a part of traditional asphalt concrete mix designs.

The Strategic Highway Research Program (SHRP) considered the identification of moisture sensitivity one of several priorities in their recently completed asphalt research program. One of the final SHRP products for matching compatible asphalt-aggregate pairs for the optimum resistance to moisture sensitivity was the net adsorption test. Although this test was recommended, the final SHRP report stated that some developmental work remained. Also, a firm link between test results and pavement performance was needed before the test method could be implemented.

The net adsorption test is used to evaluate the ability of an asphalt cement to fully saturate an aggregate surface with a monolayer of asphalt molecules and the aggregate’s ability to retain the asphalt cement in the presence of water. The ability of the aggregate to retain the
INTRODUCTION

asphalt molecules in the presence of water is considered to be a measure of potential moisture damage due to loss of adhesion.

Another test method defined by the American Society for Testing and Materials (ASTM) D4867 measures the loss of mixture strength due to a combination of both cohesive and adhesive problems. Mixture tensile strength or resilient modulus is determined before and after exposure to water. The ratios of the after conditioned to before conditioned tensile strengths and resilient modulus are used to indicate a mixture that will show moisture-related pavement distress. This test method is commonly referred to as either the Root/Tunnicliff method when the freeze/thaw option is not included or the modified Lottman when this option is included. When the compacted sample is tested, the individual contributions of adhesive and cohesive loss can not be assessed.

Net Adsorption Test

Definitions of Terms

Common terms are defined prior to a discussion of the test method development to avoid any confusion on the part of the reader.

Absorbance: A turbidity measurement made with a spectrophotometer.

Absorptivity: The relationship between absorbance and the concentration of solute (i.e., dissolved asphalt cement) in solution.

Adsorption: The chemical attachment of asphalt to the surface of the aggregate. The attachment is a function of both the chemistry of the asphalt and aggregate. Adsorption equilibrium is defined as the maximum amount of asphalt molecules, one monolayer thick, that will be attached to a given aggregate surface.

Desorption: The release of asphalt from the aggregate surface. In this case, the release is due to a greater affinity of the aggregate for water than asphalt.
INTRODUCTION

Test Method Development

The net adsorption test is based on the concept that asphalt cement, dissolved in a solvent, will be removed from the solvent in the presence of aggregates due to a chemical attraction to the aggregate surface. Conversely, moisture sensitive aggregates should release adsorbed asphalt to solution in the presence of water if the aggregate has a greater affinity for the water molecules. Important factors that influence the asphalt-aggregate interactions include the asphalt chemistry, aggregate surface chemistry, and the aggregate surface area.

The amount of asphalt cement adsorbed from solution by the aggregate can be experimentally measured by using the basic concept expressed by Beer’s Law:

\[ A = abC \]

Where:

\( A \) = visible absorbance at a given wave length, experimentally measured (unitless)
\( a \) = absorptivity, an experimentally dependent constant cm\(^2\)/g
\( b \) = cell path length, a constant with units of lengths
\( C \) = concentration of asphalt cement in solution, g/L

Visible absorbance, \( A \), is measured with a spectrophotometer which is a device for measuring the amount of light that is absorbed by the solute (i.e., asphalt cement) dissolved in the reference solvent. Toluene was selected as the solvent for use with asphalt cement for this test (1).

Figure 1.1 shows that absorptivity, \( a \), is defined as the slope of the absorbance, \( A \), versus concentration, \( C \), in the solution (2). This figure also shows that absorptivity was dependent upon the wave length used to measure absorbance; it varied with the type of asphalt cement in solution. Absorptivity was 0.0062 and 0.00713 L/mg-cm (wavelength = 410 nm) for the SHRP AAM-1 (a West Texas Intercoastal crude AC-20) and AAK-1 (a Boscan crude AC-30), respectively.

Because both absorbance and absorptivity are a function of the wave length, it was
INTRODUCTION

necessary to select a standard wavelength for all measurements. Based on the information shown in Figure 1.2, a wavelength of 410 nm was selected as the standard wavelength (2). At this wave length, the absorbance of toluene, the solvent chosen for dissolving the asphalt cement, is approximately 0.0, therefore any changes in absorbance will be a function of the solute and not the solvent. At this wave length, absorbance readings were sensitive to different asphalt cement sources and/or grades; this can be seen in the change in the absorbance readings at the 410 nm wave length.

Figure 1.1a. AAM-1 Asphalt Cement.

Figure 1.1b. AAK-1 Asphalt Cement.

Figure 1.1. Dependence of Absorptivity on Absorbance and Solution Concentration (After Ref. 2).
Figure 1.2. Absorbance as a Function of Wavelength (After Ref. 2).

Once the test conditions were selected so that absorptivity could be considered a constant for a given asphalt-aggregate pair, Beer's law could be used to formulate a ratio of the final to initial test conditions to give:

\[
\frac{A_t}{A_o} = \frac{abC_t}{abC_o}
\]

Where:
- \(A_t\) = Absorbance at time, \(t\)
- \(A_o\) = Absorbance at start of test.
- \(C_o\) = Known concentration of asphalt cement in solution, mg/L
- \(C_t\) = Concentration of asphalt cement remaining in solution at time, \(t\), mg/L
INTRODUCTION

Cancelling the constants and rearranging the equation to solve for the only unknown, $C_t$:

$$C_t = C_o \frac{A_t}{A_o}$$

A decrease in the asphalt cement concentration in solution represents a corresponding increase in the asphalt cement concentration on the aggregate surface. In dilute solution, the amount of asphalt cement adsorbed, $B_t$ (in terms of mg of asphalt cement per gram of aggregate) after time, $t$, can be approximated by measuring the solute concentration decrease, $\Delta C$, caused by contacting a solution of known concentration and volume $V$ with a known mass of absorbent (i.e., aggregate), $M$:

$$B_t = \frac{V \Delta C}{M}$$

By defining $\Delta C$ as a positive increase in the asphalt cement concentration on the aggregate surface as:

$$\Delta C = C_o - C_t = C_o - \frac{C_o A_t}{A_o} = C_o \left( \frac{A_o - A_t}{A_o} \right)$$

The equation can be rewritten:

$$B_t = \frac{V}{M} C_o \left( \frac{A_o - A_t}{A_o} \right)$$

In order to use this final equation experimentally, $C_o$ as well as the time at which to obtain the final measurements needed to be defined. The initial concentration, $C_o$, was selected by the SHRP researchers so that an aggregate surface could be completely saturated with asphalt molecules. This minimum was defined as the concentration above which absorbance readings did not change with increasing concentrations of asphalt cement. Figure 1.3 shows that absorbance values did not change substantially for an initial concentration greater than 0.5 g/L. The results shown in Figure 1.3 were typical for a wide range of asphalt cements and aggregate
INTRODUCTION

sources (2). Based on these results, the SHRP researchers selected 0.6 g of asphalt cement per liter of solvent as a standard initial concentration, \( C_0 \).

The time, \( t \), at which to obtain the final absorbance reading was selected as the time needed to achieve equilibrium at the selected concentration, \( C_0 \). Figure 1.4 shows that equilibrium was reached after about 6 hours. The same criterion was also used to set the time at which to obtain the absorbance reading for the desorption phase of the test method. Figure 1.4 shows that the relatively stable calculations were obtained after 2 hours.

![Graph showing the relationship between equilibrium concentration and amount adsorbed](image)

**Figure 1.3.** Typical Relationship Between Adsorption of Asphalt Cement and the Initial Concentration of Asphalt Cement in Solution (After Ref. 2).
INTRODUCTION

Figure 1.4. Concentration versus Time With and Without the Presence of Water (After Ref. 2).

Results Reported by SHRP

Figures 1.5 through 1.7 show typical results obtained by Auburn University and University of Nevada, Reno researchers during the development of the original and the up-scaled version of the net adsorption test. The original method proposed by Auburn used only 5 g of one-sized aggregate; the University of Nevada, Reno method used in this research allows for the evaluation of the full fine [i.e., minus 4.75 mm (No. 4)] aggregate gradation. These figures show that while there is a difference in the magnitude of all of the results, trends between combinations of aggregates and asphalts are similar. These figures also indicate that there was little difference between different asphalt cement sources but substantial differences between aggregate sources.
Figure 1.5. Adsorption Results Reported by SHRP Researchers (After Ref. 2).

Figure 1.6. Desorption Results Reported by SHRP Researchers (After Ref. 2).
ASTM D4867 - Effect of Moisture on Asphalt Concrete Paving Mixtures

This test method is a combination of two commonly used test methods referred to as the Lottman and Root/Tunnicliff methods. In 1982 Lottman reported two variations of a moisture conditioning program intended to reflect short (less than 4 years) and long-term (from 4 to 12 years) performance, depending upon the influence of other factors (3,4). Short-term performance is estimated by compacting a set of six samples to anticipated in-place voids, separating these into two groups of three, and determining both resilient modulus and tensile strength (i.e., unconditioned group). The second group is subjected to vacuum saturation at 26 in. Hg for 30 minutes, which results in the full saturation, then tested. Long-term performance is estimated by adding a freeze/thaw cycle to the conditioning process. Lottman established a relationship between test results and pavement performance up to 5 years with projects in 6 different states (3). Results indicated that retained tensile strengths of greater than 70 percent represented good performance without evidence of moisture sensitivity distresses. Other researchers confirmed the reasonableness of the 70 percent criterion for defining moisture
sensitive mixtures (5, 6).

Root and Tunnicliff suggested the level of saturation be reduced to between 55 and 80 percent to prevent damage to the samples (4,7). They also suggested that a 24 hour warm water soak (60°C (140°F)) was all that was required to condition samples; they felt that the freeze/thaw portion was not needed to identify moisture sensitive mixtures. Specific limits for test results that have been related to pavement performance are currently under investigation.

The ASTM test method uses the saturation level proposed by Root and Tunnicliff with an optional Lottman-recommended freeze-thaw conditioning procedure.

OBJECTIVE

The three objectives of this research were to:

1. Evaluate asphalt-aggregate interactions for typical Minnesota paving mixtures.
2. Determine key aggregate physical and chemical properties that influence adhesion of the asphalt cement to the aggregate surface.
3. Develop recommendations and guidelines for the implementation of the net adsorption test as a screening test for asphalt-aggregate compatibility for Mn/DOT.
INTRODUCTION

SCOPE

Materials were obtained from six construction projects built in the summer of 1992. Both raw materials and behind the paver samples were obtained from all six projects. The raw materials were used to evaluate adhesion-related moisture sensitivity; the behind the paver materials were compacted and used to evaluate mixture moisture sensitivity.
CHAPTER TWO

Materials were obtained from southeastern Minnesota and nearby Wisconsin projects:

1. Project 92-3604 near Scandia, Minnesota.
2. TH 63 near Lake City, Minnesota in Wabasha county.
3. Project No. CP-26-20W in Dakota county.
4. The Mn/ROAD 5-Year Main Line test facility construction on I 94 near Albertville, Minnesota.
5. Two sections of a demonstration project constructed on I 94 from U.S.H. 12 to the Warrens interchange in Tomah, Wisconsin, near the Minnesota - Wisconsin state line. Materials were obtained from both the SHRP gap-graded (SHRP SPS-9) and the Mathey Construction stone matrix asphalt (SMA) test sections.

Aggregates

Aggregate samples were used to determine properties and prepare samples for the net adsorption test. The University of Minnesota laboratory determined the aggregate gradations and the bulk specific gravities of the aggregates for each project. These tests were conducted on the as-received materials. Information on the aggregate sources and stockpiles, and blending percentages were obtained from Mn/DOT records. Table 2.1 shows the aggregate properties; Figure 2.1 shows the range of aggregate gradations for the projects selected for this research.

Once the aggregate properties had been determined, all aggregate stockpiles were sieved into individual fractions. Aggregate samples for the net adsorption test were individually recombined according to the as-received gradation.
Figure 2.1. Aggregate Gradations.
Table 2.1. Aggregate Properties.

<table>
<thead>
<tr>
<th>Test</th>
<th>Scandia</th>
<th>Dakota</th>
<th>Wabash</th>
<th>Mn/ROAD</th>
<th>SHRP</th>
<th>SMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Specific Gravity</td>
<td>2.601*</td>
<td>2.611</td>
<td>2.590*</td>
<td>2.627</td>
<td>2.657</td>
<td>2.502</td>
</tr>
<tr>
<td>Water Absorption Capacity, %</td>
<td>2.1'</td>
<td>2.0</td>
<td>2.2'</td>
<td>Not Available</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>Target Gradation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.0 mm (3/4 in.)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>12.5 mm (1/2 in.)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>95</td>
<td>92</td>
</tr>
<tr>
<td>9.0 mm (3/8 in.)</td>
<td>96</td>
<td>88</td>
<td>92</td>
<td>84</td>
<td>85</td>
<td>70</td>
</tr>
<tr>
<td>4.75 mm (No. 4)</td>
<td>77</td>
<td>66</td>
<td>68</td>
<td>70</td>
<td>59</td>
<td>32</td>
</tr>
<tr>
<td>2.00 mm (No. 10)</td>
<td>59</td>
<td>47</td>
<td>51</td>
<td>57</td>
<td>29</td>
<td>16</td>
</tr>
<tr>
<td>1.00 mm (No. 20)</td>
<td>---</td>
<td>37</td>
<td>---</td>
<td>43</td>
<td>19</td>
<td>14</td>
</tr>
<tr>
<td>0.45 mm (No. 40)</td>
<td>23</td>
<td>17</td>
<td>16</td>
<td>26</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>0.25 mm (No. 80)</td>
<td>---</td>
<td>9</td>
<td>---</td>
<td>8</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>0.075 mm (No. 200)</td>
<td>4</td>
<td>3.2</td>
<td>4</td>
<td>4.3</td>
<td>3.6</td>
<td>8.2</td>
</tr>
<tr>
<td>Blends</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90% Barton Scandia RA 1/2 in.</td>
<td>45% Inver Grove Heights Screened Sand</td>
<td>30% Moyer Coarse</td>
<td>10% Meridian CA-50</td>
<td>35% 3/4 in. Clear</td>
<td>60% 5/8 in. Clear</td>
<td></td>
</tr>
<tr>
<td>10% Bryan-Bayport 1/2 in. minus</td>
<td>28% Fisher Motor Seal</td>
<td>60% Cement</td>
<td>24% Crow River Coarse</td>
<td>10% 5/16 in. Clear</td>
<td>20% 3/4 in. Clear</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27% Shiply 1/2&quot; Limestone, Clear</td>
<td>10% Moyer Fines</td>
<td>66% Crow River Fines</td>
<td>10% 3/8 in. Minus</td>
<td>19% 3/8 in. Dirty</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: U of M results; tests run with less than ASTM required sample size due to limited amount of material on hand.
MATERIALS AND TESTING

Asphalt Cement

The original asphalt cement viscosities and penetration values were obtained by the University of Minnesota and are shown in Table 2.2. The Scandia, Dakota, and Wabasha binders were neat binders obtained from Ashland (120/150 pen), a Koch-Pine blend (85/100 pen), and Midland (85/100 pen) refineries, respectively. Both 120/150 and 85/100 pen grades of binder were obtained from the Koch refinery in Inver Grove Heights, Minnesota for use with the Mn/ROAD aggregate. While the 85/100 penetration grade binder was not used in the construction project, it was included in this study in order to provide a comparison for the other 85/100 pen grade binders.

Both of the binders used in the Wisconsin demonstration sections were polymer modified binders. The SHRP SPS-9 test section used a 158 penetration asphalt with an EMA (ethylene methacrylate) modifier (Polybilt 503 supplied by Exxon Chemical) at about 5 percent by weight of asphalt cement. The SMA test section used an EMA modified 85/100 penetration grade binder.

Table 2.2. Asphalt Cement Properties.

<table>
<thead>
<tr>
<th>Test</th>
<th>Scandia Ashland 120/150</th>
<th>Dakota Koch-Pine Blend 85/100</th>
<th>Wabasha Midland 85/100</th>
<th>Mn/ROAD Koch 85/100</th>
<th>Mn/ROAD Koch 120/150</th>
<th>SHRP 158 Pen. EMA Mod.</th>
<th>SMA 85/100 Pen EMA Mod.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity, Poise 60°C (140°F)</td>
<td>923</td>
<td>1,423</td>
<td>1,349</td>
<td>1,588</td>
<td>846</td>
<td>10,942</td>
<td>12,922</td>
</tr>
<tr>
<td>Viscosity, cSt 135°C (275°F)</td>
<td>276</td>
<td>306</td>
<td>347</td>
<td>362</td>
<td>271</td>
<td>1,432</td>
<td>1,287</td>
</tr>
<tr>
<td>Penetration, dmm 25°C (77°F)</td>
<td>127</td>
<td>94</td>
<td>90</td>
<td>92</td>
<td>130</td>
<td>69</td>
<td>88</td>
</tr>
</tbody>
</table>

1: shown as reported in Ref. 7.
MATERIALS AND TESTING

Mixtures

Behind the paver samples obtained during construction were used to prepare laboratory-compacted samples for testing with the ASTM D4867 test method. Mix design information was obtained from both Mn/DOT records and the Wisconsin demonstration project open house presentation information (8). A summary of optimum binder contents, mix design methods, and binder sources is given in Table 2.3. All of the mixtures had similar binder contents of around 6.0 percent except for the SHRP gyratory design method with an optimum binder content of 5.4 percent.

Table 2.3. Mixture Information.

<table>
<thead>
<tr>
<th>Project</th>
<th>Asphalt Cement</th>
<th>Mix Design Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Source/Grade</td>
<td>Opt. AC by Total Wt. Mix., %</td>
</tr>
<tr>
<td>Scandia</td>
<td>Ashland, 120/150 pen</td>
<td>5.8</td>
</tr>
<tr>
<td>Dakota</td>
<td>Koch-Pine Blend, 85/100 pen</td>
<td>6.1</td>
</tr>
<tr>
<td>Wabasha</td>
<td>Midwest, 85/100 pen</td>
<td>6.0</td>
</tr>
<tr>
<td>Mn/ROAD</td>
<td>Koch, 120/150 pen</td>
<td>6.1</td>
</tr>
<tr>
<td>SHRP</td>
<td>EMA Modified 158 Pen</td>
<td>5.4</td>
</tr>
<tr>
<td>SMA</td>
<td>EMA Modified 85/100 Pen</td>
<td>6.0</td>
</tr>
</tbody>
</table>

¹: Optimum binder content based only on voids analysis.
MATERIALS AND TESTING

TESTING PROCEDURES

Net Adsorption

The original SHRP net adsorption test specified the use of recirculating columns as the reaction chamber. Further work on the test method by the original developers suggested that a batch-type reaction chamber could be used and that this approach was easier and possibly more reliable. Both methods were evaluated in this research program.

Column Method

The equipment used in this test is shown in Figure 2.2. Fifty grams of aggregate were placed in a large chromatography column and a peristaltic pump was used to continuously circulate 134 ml of a 0.6-g/L solution of toluene and asphalt cement through the column for 6 hours. A set of three columns were run simultaneously. Four milliliters of solution were removed from each column for an initial determination of asphalt cement concentration (initial spectrophotometer reading). Fifty grams of graded aggregate were then added to each column and the solution circulated through the column for 6 hours. Another 4 ml was removed from each column and the amount of adsorbed asphalt determined with a second spectrophotometer reading. Water (1150 µl) was added, and the solution and water recirculated for another 2 hours. The third and final reading was obtained at this time. The within-laboratory standard deviation was reported by SHRP as 0.14 mg/g for either washed or unwashed minus 4.75 mm (No. 4) to 0.075 mm (No. 200) fraction gradations. The full procedure is shown in Appendix A.

One change was made in the original SHRP procedure. This was to use 50 g of the full aggregate gradation rather than limit the test to only the minus 4.75 mm (No. 4) to 0.075 mm (No. 200) fraction. This change was made in order to assess the influence of the combined aggregate properties on moisture sensitivity. A portion of the original developmental testing was repeated in order to confirm that the change in aggregate gradation did not require corresponding
changes in critical test parameters as well as to determine if changes in the desorption phase were indicated.

Figure 2.2. Equipment Set-Up for the Net Adsorption Test (Column Method).

Batch Method
MATERIALS AND TESTING

The batch method as reported by Dr. Curtis, used only washed aggregate of one size. It was felt that restricting the test to a one-size fraction was not truly representative of the of the full gradation aggregate chemistry. Therefore, the batch procedure was modified to use the full gradation using the same up-scaling parameters as were used with the column method.

This variation used the same quantity of aggregate, solvent, and asphalt cement but placed the materials in a 300 ml Erlenmeyer flask. The mixture was then agitated for one hour on an orbital shaker table, the materials were allowed to settle for 1 hour, 4 ml of solvent were removed and used to determine the asphalt cement concentration in the flask. The sample was agitated again for another 10 minutes, allowed to settle for 50 minutes, and a second reading was taken. This procedure was repeated again after allowing the sample to stand overnight. Water was then added to the flask, and the agitation/standing sequence was repeated two times prior to the final desorption reading. The full test method is shown in Appendix B.

ASTM D4867 (Modified Lottman)

Six samples were prepared using a reduced compactive effort (20 blows/side) in order to produce samples with air voids in the specified 6 to 8 percent range. Briefly, the test method requires that these six samples be separated into two sets of three. The air voids, resilient modulus and tensile strengths were determined for the first set, referred to as the unconditioned set. The second set was partially saturated (55 - 80 percent), wrapped, frozen for a minimum of 15 hours, unwrapped and thawed for 24 hours in a 40°C (140°F) water bath. The samples were then brought to the 25°C (77°F) test temperature by storing in a water bath for 2 hours prior to testing. The results from this set of samples are referred to as the conditioned results. Moisture sensitivity is expressed as both the absolute values, before and after conditioning, for resilient modulus and tensile strength as well as the ratios of conditioned to unconditioned values.

Resilient modulus was determined at the 0.1 second load duration with the measurements taken over the full diameter of the sample (ASTM D4123), and test frequencies of 0.33, 0.5,
1.0 Hz. Tensile strengths were determined at a loading rate of 50 mm/min (2 in/min).
RESULTS AND ANALYSIS

CHAPTER THREE

Net Adsorption

Changes in Column Method

The change in the aggregate gradation from the minus No. 4 fraction to the full gradation required that several of the original test parameters be verified. An initial testing program was completed to ensure that the test method parameters originally developed for the test were applicable to the new gradation range. Figures 3.1 and 3.2 show that adsorption results were generally stable after 4 to 6 hours for a range of aggregate sources with two typical Minnesota asphalt cements. Based on these results, the original SHRP test procedures were used with the full aggregate gradations for the remainder of the research program.

The full net adsorption was not completed at this time as only the adsorption versus time characteristics were to be evaluated with this particular experiment. However, these results can be tentatively evaluated based on the limited data presented in the final SHRP report (2). While not specifically stated in the final SHRP report, results presented indicated that asphalt-aggregate pairs with net adsorption values less than 0.700 mg/g (washed aggregates) could be expected to show moisture-related pavement distresses while pairs with net adsorptions greater than approximately 0.900 mg/g (washed aggregates) were associated with mixtures that did not have a history of moisture sensitivity (2). Data between 0.700 and 0.900 were not presented in the final SHRP report. Since the net adsorption values are always less than the amount of initially adsorbed asphalt cement, and the amount of initially adsorbed asphalt cement for the pairs shown in Figures 3.1 and 3.2 are generally around or below 0.007 mg/g, it is possible that these materials would show some tendency for adhesion-related moisture sensitivity.
RESULTS AND ANALYSIS

Figure 3.1. Adsorption Over Time for Various Aggregates Sources and Koch 85/100 Pen Asphalt Cement (Column Method).

Figure 3.2. Adsorption Over Time for Various Aggregate Sources and Koch 120/150 Pen Asphalt Cement (Column Method).
RESULTS AND ANALYSIS

Influence of Fines and Aggregate Surface Area

Another test parameter that was evaluated after the change in gradation was the influence of the minus 0.075 mm (No. 200) material on test results. Table 3.1 shows the results for tests conducted using both the full gradation and one without the minus 0.075 mm (No. 200) sieve. Neither gradation was washed as it was felt the surface coating on the aggregate could have a significant influence on the adsorption/desorption properties of the aggregates. While the gradations including the minus 0.075 mm (No. 200) material showed generally higher adsorption and desorption values, the trends appear to be consistent between both gradations. These observations agree with the finding presented in the SHRP A-003B final report (1).

Table 3.1. Net Adsorption Results (Paired Asphalt Cement and Aggregates).

<table>
<thead>
<tr>
<th>Test Time</th>
<th>Scandia</th>
<th>Dakota</th>
<th>Wabasha</th>
<th>Mn/ROAD</th>
<th>Mn/ROAD</th>
<th>SHRP</th>
<th>SMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphal cement</td>
<td>120/150</td>
<td>85/100</td>
<td>85/100</td>
<td>120/150</td>
<td>85/100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>With Minus 0.075 mm (No. 200)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>1.254</td>
<td>1.015</td>
<td>1.169</td>
<td>NA</td>
<td>1.534</td>
<td>0.664</td>
<td>0.584</td>
</tr>
<tr>
<td>± 0.063</td>
<td>± 0.142</td>
<td>± 0.166</td>
<td>± 0.208</td>
<td>± 0.353</td>
<td>± 0.062</td>
<td>± 0.158</td>
<td></td>
</tr>
<tr>
<td>Desorption</td>
<td>0.155</td>
<td>0.975</td>
<td>0.197</td>
<td>NA</td>
<td>0.206</td>
<td>0.293</td>
<td>0.164</td>
</tr>
<tr>
<td>± 0.015</td>
<td>± 0.008</td>
<td>± 0.094</td>
<td>± 0.070</td>
<td>± 0.180</td>
<td>± 0.053</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Adsorption</td>
<td>1.099</td>
<td>0.040</td>
<td>0.972</td>
<td>NA</td>
<td>1.496</td>
<td>0.371</td>
<td>0.416</td>
</tr>
<tr>
<td>± 0.057</td>
<td>± 0.118</td>
<td>± 0.138</td>
<td>± 0.042</td>
<td>± 0.238</td>
<td>± 0.193</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Without Minus 0.075 mm (No. 200)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>0.895</td>
<td>0.879</td>
<td>0.832</td>
<td>1.350</td>
<td>1.457</td>
<td>0.680</td>
<td>0.234</td>
</tr>
<tr>
<td>± 0.087</td>
<td>± 0.104</td>
<td>± 0.046</td>
<td>± 0.228</td>
<td>± 0.082</td>
<td>± 0.018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desorption</td>
<td>0.273</td>
<td>0.089</td>
<td>0.159</td>
<td>0.209</td>
<td>0.177</td>
<td>0.330</td>
<td>0.164</td>
</tr>
<tr>
<td>± 0.089</td>
<td>± 0.008</td>
<td>± 0.107</td>
<td>± 0.063</td>
<td>± 0.065</td>
<td>± 0.026</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Net Adsorption</td>
<td>0.622</td>
<td>0.790</td>
<td>0.673</td>
<td>1.141</td>
<td>1.280</td>
<td>0.350</td>
<td>0.070</td>
</tr>
<tr>
<td>± 0.111</td>
<td>± 0.104</td>
<td>± 0.107</td>
<td>± 0.244</td>
<td>± 0.022</td>
<td>± 0.019</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1: Average of three columns. NA: data not available
RESULTS AND ANALYSIS

The original SHRP research found that within-laboratory precision for both adsorption and net adsorption values was about 0.14 mg/g for either washed or unwashed aggregates (minus 4.75 mm (No. 4) fraction). The average within-laboratory precision for a set of three columns for this testing program was 0.16 and 0.13 for adsorption and net adsorption, respectively, for the full gradation. The precision was 0.09 and 0.15 for the 0.075 mm (No. 200) and above gradation. Both sets of results agree very well with the SHRP within laboratory precision with the gradation missing the minus 0.075 mm (No. 200) material showing the most precise measurements of adsorption.

The decrease in the adsorption testing variability when the minus 0.075 mm (No. 200) fraction was excluded was attributed to the differences in aggregate surface area between the with and without the minus 0.075 mm (No. 200) material. The hypothesis was that the number of chemically active aggregate sites should increase with increasing surface area. In order to investigate this hypothesis, a simple estimate of aggregate surface area was made by assuming a spherical shape for the aggregate with an average particle diameter equal to the size of the screen on which the aggregate was retained. The surface area of the minus 0.075 mm (No. 200) fraction was based on a hydrometer particle size analysis. The total surface area was estimated, based on the equation presented by Aljassar and Haas as (9):

$$\Sigma A_{s,i} = \Sigma \frac{6 \ W_i \ d_i}{G_s \ \rho_w \ d_i}$$

Where:

- $A_s$ = Aggregate surface area for a given aggregate fraction, cm$^2$
- $W$ = mass of aggregate retained on a given sieve size, grams
- $G_s$ = specific gravity of aggregate
- $\rho_w$ = unit weight of water, 1 g/cm$^3$
- $d$ = diameter of sieve opening, cm

The combined gradation and hydrometer results are shown in Table 3.2, and the surface
RESULTS AND ANALYSIS

area calculation results are given in Table 3.3. The SMA and Mn/ROAD aggregates had estimated surface areas of 1.5 and 4.2 m²/kg, respectively, for material excluding the minus 0.075 mm (No. 200) fraction. This is sensible in that the SMA gradation was coarser than the Mn/ROAD gradation. When the material finer than 0.075 mm (No. 200) was included, the surface area increased to 27.0 and 36.4 m²/kg, respectively. This emphasizes the important contribution of the fine aggregate fraction to the overall surface area of the mixture.

Table 3.2. Combined Aggregate Gradations.

<table>
<thead>
<tr>
<th>Test</th>
<th>Scania</th>
<th>Dakota</th>
<th>Wabashia</th>
<th>Mn/ROAD</th>
<th>SHRP</th>
<th>SMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieve Analysis for 0.075 mm (No. 200) Material and Above:</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>19.0 mm (3/4 in.)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>95</td>
<td>92</td>
</tr>
<tr>
<td>12.5 mm (1/2 in.)</td>
<td>96</td>
<td>88</td>
<td>92</td>
<td>84</td>
<td>85</td>
<td>70</td>
</tr>
<tr>
<td>9.0 mm (3/8 in.)</td>
<td>77</td>
<td>66</td>
<td>68</td>
<td>70</td>
<td>59</td>
<td>32</td>
</tr>
<tr>
<td>6.35 mm (No. 4)</td>
<td>59</td>
<td>47</td>
<td>51</td>
<td>57</td>
<td>29</td>
<td>16</td>
</tr>
<tr>
<td>3.15 mm (No. 10)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>43</td>
<td>19</td>
<td>14</td>
</tr>
<tr>
<td>1.00 mm (No. 20)</td>
<td>23</td>
<td>17</td>
<td>16</td>
<td>26</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>0.45 mm (No. 40)</td>
<td>---</td>
<td>9</td>
<td>---</td>
<td>8</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>0.25 mm (No. 80)</td>
<td>4</td>
<td>3.2</td>
<td>4</td>
<td>4.3</td>
<td>3.6</td>
<td>8.2</td>
</tr>
<tr>
<td>0.075 mm (No. 200)</td>
<td>Hydrometer Analysis</td>
<td>4</td>
<td>2.40</td>
<td>4</td>
<td>3.53</td>
<td>3.6</td>
</tr>
<tr>
<td>0.025 mm</td>
<td>1.80</td>
<td>1.50</td>
<td>1.88</td>
<td>3.23</td>
<td>2.30</td>
<td>5.25</td>
</tr>
<tr>
<td>0.015 mm</td>
<td>1.28</td>
<td>1.12</td>
<td>1.36</td>
<td>2.84</td>
<td>1.76</td>
<td>4.02</td>
</tr>
<tr>
<td>0.0095 mm</td>
<td>1.04</td>
<td>0.93</td>
<td>1.20</td>
<td>2.28</td>
<td>1.69</td>
<td>3.20</td>
</tr>
<tr>
<td>0.0085 mm</td>
<td>1.02</td>
<td>0.90</td>
<td>1.16</td>
<td>2.15</td>
<td>1.37</td>
<td>2.95</td>
</tr>
<tr>
<td>0.0075 mm</td>
<td>1.00</td>
<td>0.86</td>
<td>1.08</td>
<td>2.11</td>
<td>1.26</td>
<td>2.79</td>
</tr>
<tr>
<td>0.0065 mm</td>
<td>0.88</td>
<td>0.83</td>
<td>1.04</td>
<td>2.06</td>
<td>1.22</td>
<td>2.54</td>
</tr>
<tr>
<td>0.0055 mm</td>
<td>0.84</td>
<td>0.80</td>
<td>1.00</td>
<td>2.02</td>
<td>1.15</td>
<td>2.46</td>
</tr>
<tr>
<td>0.0045 mm</td>
<td>0.80</td>
<td>0.77</td>
<td>0.96</td>
<td>1.98</td>
<td>0.97</td>
<td>2.38</td>
</tr>
<tr>
<td>0.0035 mm</td>
<td>0.76</td>
<td>0.74</td>
<td>0.88</td>
<td>1.94</td>
<td>0.94</td>
<td>2.13</td>
</tr>
<tr>
<td>0.0025 mm</td>
<td>0.72</td>
<td>0.70</td>
<td>0.84</td>
<td>1.85</td>
<td>0.86</td>
<td>1.97</td>
</tr>
<tr>
<td>0.0015 mm</td>
<td>0.68</td>
<td>0.67</td>
<td>0.76</td>
<td>1.63</td>
<td>0.79</td>
<td>1.80</td>
</tr>
</tbody>
</table>

When the material finer than 0.075 mm (No. 200) was included, the estimated surface
RESULTS AND ANALYSIS

areas for the coarser SHRP and SMA mixtures were greater than those for the Scandia, Dakota, and Wabasha projects. This indicates the importance of both the quantity and gradation of fine material in surface area estimation. The SMA aggregate contained 8.2 percent material passing the 0.075 mm (No. 200) sieve, more than twice the amount of the finer gradations. An inspection of Table 3.2 shows that while the percentage of material passing the 0.075 mm (No. 200) sieve for the SHRP gradation was about the same as that for the finer mixtures, the hydrometer analysis shows it contained smaller particles than the Scandia, Dakota, or Wabasha projects.

Table 3.3. Estimated Aggregate Surface Areas.

<table>
<thead>
<tr>
<th>Test</th>
<th>Scandia</th>
<th>Dakota</th>
<th>Wabasha</th>
<th>Mn/ROAD</th>
<th>SHRP</th>
<th>SMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aggregate Surface Area (Without Minus 0.075 mm, No. 200) m²/kg</td>
<td>3.8</td>
<td>4.2</td>
<td>3.8</td>
<td>4.2</td>
<td>2.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Aggregate Surface Area (With Minus 0.075 mm, No. 200) m²/kg</td>
<td>19.3</td>
<td>18.5</td>
<td>20.2</td>
<td>36.37</td>
<td>26.1</td>
<td>27.0</td>
</tr>
</tbody>
</table>

a: U of M results; tests run with less than ASTM required sample size due to limited amount of material on hand.

Figure 3.3 compares the adsorption results and the surface area for the 0.075 mm (No. 200) and above fraction gradations. As expected, there is a general relationship between the surface area and the results; the amount of adsorption increased as the surface area increased. The lack of better correlations for adsorbed, desorbed, and net adsorption values and the surface area was considered evidence of the differences in the chemical attractions between a given asphalt and aggregate pair. This difference was accentuated when the minus 0.075 mm (No. 200) fraction was included (Figure 3.4). This would appear to indicate that the finer fraction should be included so that asphalt-aggregate interactions are enhanced.
Figure 3.3. Comparison of Adsorption Test Results with the Estimated Aggregate Surface Area (0.075 mm (No. 200) and Above Gradation).

Figure 3.4. Comparison of Adsorption Test Results with the Estimated Aggregate Surface Area (Gradation Including Minus 0.075 mm (No. 200)).
RESULTS AND ANALYSIS

The net adsorption values for the Scandia, Dakota, and Wabasha asphalt-aggregate pairs were all above 0.600 mg/g (Table 3.1). The Mn/ROAD pairs had values greater than 1.00 mg/g while both the SHRP and SMA asphalt-aggregate pairs had values below 0.400 mg/g. Based on the previously suggested limit of 0.700 mg/g below which asphalt-aggregate pairs could have adhesion-related moisture sensitivity problems, the Mn/ROAD materials should not have adhesive related moisture problems. Conclusions about adhesion-related moisture problems with the remaining Minnesota mixtures are questionable as they had results near the selected limit of 0.700 mg/g. Both the SHRP and SMA pairs should be expected to have adhesion-related problems. However, both of the asphalts used with these aggregates were polymer modified which might influence the interpretation of the test results.

As polymers can swell and/or dissolve in compatible solvents, any swelling or dissolution resulting from the interaction between the toluene and the polymer could result in an increase in the size of the polymer. At the short 6 hour net adsorption test time, this could mask a decrease in the asphalt cement concentration by increasing size of the polymer particles. A quick estimate as to whether this could be a problem was made by evaluating the Flory-Huggins interaction parameter, $\chi$:

$$\chi = \frac{V_1}{RT} (\delta_1 - \delta_2)^{1/2}$$

Where:

- $\chi$ = Flory-Huggins interaction parameter, unitless
- $\delta_1$ = solubility parameter for solvent, cal$^{1/2}$/cm$^{1/2}$
- $\delta_2$ = solubility parameter for polymer, cal$^{1/2}$/cm$^{1/2}$
- $R$ = gas constant, 1.98 cal/mole °K
- $T$ = temperature, °K
- $V_1$ = Molar volume of the solvent (106.3 cm$^3$/mole for toluene)
RESULTS AND ANALYSIS

The toluene and ethylene methacrylate solubility parameters were estimated at 8.9 and 8.3, respectively resulting in a $\chi$ of approximately 0.15 (10). The critical $\chi$ can be assumed to be 0.5 for solvent-polymer dilute solutions above which little swelling would be expected and below which swelling and/or dissolving of the polymer in the solvent would be likely (11). Since the estimated $\chi$ was substantially lower than the critical value, a substantial interaction of the polymer with the solvent would be expected. Therefore, the net adsorption results for the polymer-modified asphalt-aggregate pairs should be eliminated from any comparisons.

Batch Method

In an effort to improve the net adsorption test results, the batch test method was investigated. The results are shown in Table 3.4. This table shows that results were never consistent, and did not always follow logical trends in test results (i.e., the measured concentration of asphalt cement in solution increased with time). Various methods and times of agitation, and different methods of filtering the solvent were tried, but no reasonable, repeatable numbers could be obtained. Based on these data, this test method was eliminated from the testing program in favor of the column method.
RESULTS AND ANALYSIS

Table 3.4. Adsorption Results Over Time for Batch Test Method
(Consistent Asphalt Cement with Various Aggregates)

<table>
<thead>
<tr>
<th>Test Time</th>
<th>Adsorption mg AC/g Agg.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scandia</td>
</tr>
<tr>
<td>Initial Reading</td>
<td></td>
</tr>
<tr>
<td>Koch, 85/100 Pen</td>
<td>0.951 ± 0.009</td>
</tr>
<tr>
<td>2 Hours</td>
<td>0.926 ± 0.029</td>
</tr>
<tr>
<td>4 Hours</td>
<td>0.897 ± 0.029</td>
</tr>
<tr>
<td>Koch, 120/150 Pen</td>
<td>0.951</td>
</tr>
<tr>
<td>Initial Reading</td>
<td></td>
</tr>
<tr>
<td>2 Hours</td>
<td>0.926 ± 0.029</td>
</tr>
<tr>
<td>4 Hours</td>
<td>0.897 ± 0.029</td>
</tr>
</tbody>
</table>

1: Average of three flasks.

MIXTURES

The moisture sensitivity of the compacted mixtures was evaluated and the test results are shown in Table 3.5. The resilient modulus ratios for four of the six projects were between 60 and 71 percent. The tensile strength ratios were between 62 and 77 for five of the six projects. This indicates that the majority of the mixtures tested exhibited some moisture sensitivity. The Mn/ROAD mixtures showed the most moisture sensitivity of any of the mixtures, with an increase in the moisture sensitivity corresponding to decreasing asphalt cement content (i.e., with increasing numbers of blows used for the mix design). Since this gradation had the greatest estimated surface area of all of the mixtures, this suggests that the moisture sensitivity for these particular mixtures could be more a function of the binder film thickness rather than any true moisture sensitivity of the asphalt-aggregate pair. This is because as the surface area of the
aggregate is increased, there will be a corresponding decrease in the binder film thickness for a given asphalt cement content. Figure 3.5 compares the aggregate surface area with the retained strengths of the mixtures. There is a general trend for increased moisture sensitivity with increasing aggregate surface area which would support this hypothesis. This relationship appears to be stronger for the resilient modulus ratio ($r^2 = 0.56$) than on tensile strength ratio ($r^2 = 0.20$).

The Scandia, Dakota, and Wabasha mixtures all had low resilient modulus and tensile strength values compared to either the Mn/ROAD, SHRP, or SMA mixtures. It is possible that these low initial values could lead to poor performance rather than any chemically-related moisture sensitivity problem. The hypothesis is that there must be a certain terminal strength, above which a pavement will perform well and below which normal traffic and environmental conditions will accelerate pavement distresses. Any mixture subjected to a wet freeze/thaw environment will show some signs of reduced strengths. When the initial values are exceptionally low, it is possible that only a moderate decrease in strength will significantly increase the observed pavement distress.

Table 3.5. Assessment of Moisture Sensitivity for Compacted Samples.

<table>
<thead>
<tr>
<th>Project</th>
<th>Air Voids, %</th>
<th>Resilient Modulus MPa (ksi)</th>
<th>Tensile Strength, kPa (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry 25°C (77°F)</td>
<td>Wet 25°C (77°F)</td>
<td>Ratio, %</td>
</tr>
<tr>
<td>Scandia</td>
<td>4.8</td>
<td>1,497 (217)</td>
<td>1,262 (183)</td>
</tr>
<tr>
<td>Dakota</td>
<td>6.4</td>
<td>1,566 (227)</td>
<td>1,103 (159)</td>
</tr>
<tr>
<td>Wabasha</td>
<td>6.2</td>
<td>1,344 (195)</td>
<td>828 (120)</td>
</tr>
<tr>
<td>Mn/ROAD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35 Blow</td>
<td>2.9</td>
<td>3,357 (487)</td>
<td>1,848 (268)</td>
</tr>
<tr>
<td>50 Blow</td>
<td>3.9</td>
<td>2,909 (422)</td>
<td>1,517 (220)</td>
</tr>
<tr>
<td>75 Blow</td>
<td>2.9</td>
<td>3,674 (546)</td>
<td>1,792 (260)</td>
</tr>
<tr>
<td>SHRP</td>
<td>7.5</td>
<td>2,220 (322)</td>
<td>1,540 (223)</td>
</tr>
<tr>
<td>SMA</td>
<td>6.6</td>
<td>2,014 (292)</td>
<td>1,213 (176)</td>
</tr>
</tbody>
</table>
RESULTS AND ANALYSIS

Figure 3.5. Comparison of the Moisture Sensitivity of Mixtures and the Estimated Aggregate Surface
SUMMARY

Due to the statistically different results obtained for desorption phase of the column net adsorption test and lack of conclusive mixture test results, it was felt that the desorption phase of the net adsorption test did not warrant further investigation or refinements at this time. However, results suggested that this test should be conducted including the minus 0.075 mm (No. 200) aggregate fraction. A solvent-compatible polymer in a modified asphalt should not be used with this test.

Net adsorption results indicated a tendency for the Scandia, Dakota, and Wabasha asphalt-aggregate pairs to have some chemically-related moisture sensitivity. The Mn/ROAD asphalt-aggregate pairs showed very good resistance to moisture damage due to adhesive problems between the asphalt cement and the aggregate surface. No conclusions could be drawn for the SHRP and SMA aggregates because the polymer modified binders probably influenced the test results.

The modified Lotman results indicated that only the Dakota, SHRP, and SMA mixtures met or exceeded the suggested guidelines for 70 percent retained tensile strengths; retained strengths were 85, 77, and 70, respectively. This indicates that the remaining mixtures could be expected to show at least some moisture damage in the field. This moisture damage should be related more to mixture properties such as aggregate surface area, binder film thickness, and low initial strengths rather than chemically-related adhesion problems.
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

CONCLUSIONS

1. The net adsorption test results are dependent upon the surface area of the aggregate as well as the aggregate chemistry.

2. The full aggregate gradation, including the minus 0.075 mm (No. 200) fraction, can be used in the net adsorption test without requiring changes in the test parameters.

3. Caution should be exercised in using polymer-modified asphalt cements in the net adsorption test as solvent-polymer interactions could significantly alter the test results.

4. The batch method did not produce reasonable test results and was eliminated from the testing program.

5. Mixture testing indicated that perceived moisture sensitivity pavement performance problems could be a function of initially low mixture strengths as well as a reduction in binder film thickness due to high aggregate surface areas. It is possible that these problems could be solved in the mix design phase rather than with remedial action for moisture-related problems.

RECOMMENDATIONS

Before any remedial actions, such as the use of anti-stripping additives, are considered for moisture sensitive mixtures, a thorough evaluation of mix design parameters should be investigated. This should include an evaluation of the binder film thickness based on the aggregate surface area in the mixture as well as an assessment of the initial mixture strength as defined by both resilient modulus and tensile strength.

A larger data base is needed before firm conclusions on the net adsorption test can be reached. Further testing with the materials collected by Mn/DOT for the 9PRS 1016 research program (an investigation of durability, VMA and voids, and absorption) should provide a more state-wide representation of Minnesota materials.
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

While the net adsorption test appears to identify moisture sensitivity related to the loss of adhesion, any observed moisture sensitivity problems could be mix design related. Therefore the inclusion of a test procedure in the mix design process which identifies either moisture sensitive or low strength compacted mixtures would be more beneficial than one which is limited to assessing loss of adhesion. On this basis, Mn/DOT should consider adding the modified Lottman procedures to their mix design testing.
REFERENCES


APPENDIX A

Net Adsorption Test Method
Measurement of Initial Asphalt Adsorption and Desorption in the Presence of Moisture

1. Scope

1.1 This test method describes a procedure for assessing the ability of an asphalt to adhere to the surface of the fine aggregate portion of an asphalt concrete mixture. The strength of the initial adhesion of the asphalt to the aggregate in the presence of moisture can also be assessed.

1.2 This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 Sampling
2.2 Splitting
2.3 Toluene

3. Summary of Test Method

3.1 A solution of asphalt cement and toluene is introduced and circulated in the reaction column. Once the solution temperature has been stabilized, 4 ml of solution is removed and the absorbance is determined with a spectrophotometer. Fifty grams of minus No. 4 aggregate is then added to the column, and the solution is circulated through the aggregate bed for 6.5 hours. At this time a second 4 ml sample of the solution is removed from the column and the absorbance is again determined. The difference in the absorbance readings is used to determine the amount of asphalt that has been removed from the solution due to the chemical attraction of the aggregate for the molecular components of the asphalt cement.

3.2 Immediately after the second solution sample is taken, 1150 μl of water is added to the column. The solution is then circulated through the system for another 2 hours or until
consecutive measurements are consistent. A final 4 ml of solution is taken from the column at the end of this time. The increase in the absorptivity is a measure of the amount of asphalt cement that is displaced by water molecules.

4. Apparatus

4.1 Test Columns-A 4 cm diameter by 15 cm tall chromatography column, with a water jacket, has been adapted for use as the test column in this procedure. This column should conform to dimensions in Figure 1.

4.1.1 Frits-PFE 20 µ filters with mesh supports. These deteriorate over time due to the solvent and will need to be replaced when they will not retain a concave form when inserted in the column end, or when flow in the column is altered.

4.1.2 Hose Connectors— for connecting hosing to column ends should be size 16. Connectors should be equipped with solvent resistant compression fittings and threaded couplers.

4.2 Tubing (for circulating solvent solution)—should be size 16 Viton tubing.

Note 1: Teflon, Versitube, or Viton A have been found to be satisfactorily resistant to toluene.

4.3 Tubing (for circulating constant temperature water in jacket)—may be any suitable hosing that can be firmly attached to the ports on the water jacket.

4.4 Temperature Control Water Bath—The bath should have sufficient capacity to provide a continual supply of constant temperature water to the water jackets of all columns in use. The bath should be capable of maintaining 25°C±1°C (77°F±2°F).

4.5 Pumping System—The pumping system shall consist of a peristaltic pump capable of maintaining a 100 ml/min. flow for each pump cassette in use. The pump should be equipped with one cassette dedicated to circulating water for the water jackets, and one cassette for each column in use.

4.6 Spectrophotometer—Capable of providing a continuous 410 nm wavelength with accuracy of 2 nm, and a precision of not more than 0.5 nm. The photometric precision should not be more than 0.2 percent. The unit shall be capable of receiving standard 10 mm path length cuvettes. This unit should also be capable of measuring absorbance between 0.000 and 1.999.

4.7 Cuvettes—Should have a capacity of at least 4.5 ml with a 10 mm (0.4 in.) path
length and suitable optical characteristics for measurements of wavelengths from 375 to 410nm.

4.8 Erlenmeyer Flask (500ml)-with rubber stopper.

4.9 Erlenmeyer Flasks (125ml)-Three flasks are needed for each column in use.

4.10 Ring Stand and Clamps-Stand and clamps should be sufficiently large to hold the column(s), aggregate sample, and solvent without danger of tipping over.

4.11 Graduated Cylinder-glass, 500ml capacity.

4.12 Micro-Pipettes-should be capable of being set to any volume from 1 to 10ml and should be equipped with disposable tips.

4.13 Ring mold (optional)-for introducing the binder into the solvent should be constructed as shown in Figure 2.

4.14 Magnetic Stir-Any small magnetic stir capable of stirring binder in toluene solution.

4.15 Analytical Scale-capable of measuring to within 0.001g.

4.16 Oven-capable of maintaining 135°C±1.3 (275°F±5)

5. Reagents

5.1 Toluene-needs to be UV grade or spectroanalyzed.

6. Aggregate Preparation

6.1 Obtain a 50g sample of the minus No. 4 aggregate stockpile and dry, uncovered, in a 135°C (275°F) for a minimum of 15 hours.

6.2 Remove the sample from the oven at least 15 minutes prior to adding to the column and store in a desiccator until needed. Samples not used within 24 ours of drying should be re-dried. Extreme caution should be used to avoid adding warm aggregate to the toluene solution; toluene has a low flash point.
7. Preparation of Stock Solutions

7.1 The appropriate amount of binder can be added by heating a small sample of the binder in a covered container only until it can be poured. Then fill the ring mold so that the binder rises slightly above the surface of the ring. Cool for a minimum of 30 minutes.

7.1.1 An alternate method of adding the binder is to simply use a sharp knife to "cut" the sample out of a freshly poured but cooled can of binder.

7.2 Place 500ml of toluene in the 50ml Erlenmeyer flask, and suspend the ring mold in the flask by anchoring the cord on the mold with the flask's stopper or drop sample into flask. Place flask with the mold on top of mechanical stir and agitate solution for a minimum of 10 minutes and not more than 30 minutes prior to charging columns.

7.3 At the end of 10 minutes, use the cord attached to the ring mold to remove the mold from the flask. If all of the binder has not been dissolved, return the mold to the flask and continue to agitate the solution. If all visible binder has been dissolved, remove the mold, dry thoroughly, and weigh to the nearest 0.001g. The difference between the two weights is the amount of binder that was added to the toluene.

7.4 If the binder has been dropped into the solvent instead of being added in the mold, stir for a total of 15 minutes to insure that all binder has been dissolved.

7.5 Only binder-toluene solutions prepared within 24 hours of starting the test should be used. Older solutions should be discarded.

8. Test Procedure

8.1 Turn on the spectrophotometer and allow it to warm up per manufacturer's recommendations. Once it has completed its internal calibration sequence, set the wave length to 410nm and set the reference point with toluene according to the manufacturer's directions.

8.2 Next, anchor each column to be used to a suitable stand. The stand should be stable and able to withstand the weight of the column(s), aggregate, and solution without tipping.

8.3 Connect the tubing to the water jacket on the column for circulating the constant temperature water. Start water circulating and stabilize the temperature at 25°C±1 (77°F±3).
8.4 Assemble the column ends, frits, and frit supports. Connect the two column ends with a sufficient length of solvent resistant tubing so that when the ends are inserted into the columns, the tubing can be easily routed through the pump cassette. The ends of the tubing should be secured to the cap with at least two small tie wraps in order to insure that there are no leaks during testing.

8.5 Insert one end into the bottom of the column and rest the other end on the top of the column. Finish routing tubing through pump cassette.

8.6 Add 50ml of clean toluene to the column, insert the remaining end into the column, and circulate the toluene through the column for 2 minutes. Stop the pump.

8.7 At the end of this time, remove the hose from the top cap by unscrewing the hose fitting from the cap, and place in a graduated cylinder. The level of the end of the hose should always be kept above the level of solvent in the column. Start the pump and adjust the flow rate to 100ml per minute. It might be necessary to add more solvent if several flow rate measurements are required.

8.8 Once the required flow rate has been obtained, drain the remaining solvent from the column, add 134ml of the solution prepared in Section 7, replace the end cap, and circulate for approximately 2 minutes. Stop the circulation in the column by raising the pump cassette.

8.9 Remove 4ml of solution from the column and place in a 125ml Erlenmeyer flask with an additional 20ml of clean toluene. A micropipette should be used to measure all solutions and solvents placed in the flask. Stopper the flask and gently agitate the solution.

8.10 Unstopper the flask, pipette out 4ml of solution into a clean cuvette. Place the cuvette in the spectrophotometer according to the manufacturer's directions. Record this reading as the initial reading, A₀.

8.11 Add 50g of dried aggregate to the column, replace column end, and press the pump cassette down so the circulation of the solution is resumed. Continue to circulate the solution for 6 hours.

8.12 At the end of this time, stop the circulation by raising the pump cassette, remove the top end cap, and extract 4ml of solution with the micropipette. Discharge the pipette into a 125ml Erlenmeyer flask, add an additional 20ml of clean toluene, stopper, and briefly agitate.

8.13 Unstopped the flask, pipette out 4ml of solution into a clean cuvette. Place the
cuvette in the spectrophotometer according to the manufacturer's directions. Record this reading as the first adsorption reading, $A_i$.

8.14 Use the micropipette with a clean tip to add 1150μl of water to the column, immediately replace the column top, and press pump cassette down so that circulation is resumed. Continue to circulate for 2 hours or until successive measurements don’t change more than 2 percent between readings. Repeat steps 8.12 and 8.13 and record this measurement as the absorbance reading for the amount remaining, $A_r$.

9. Clean Up

9.1 Once the test is completed, unscrew the column top from the tubing and place the tube end in a large flask. Press the pump cassette down so that the solution remaining in the column is pumped into the flask. Dispose of the waste solution in a suitably labeled container for recycling.

9.2 Raise the column on the stand so that a large beaker can be placed below the column while the column bottom is removed. Discard the aggregate into the beaker.

9.3 Unscrew the tubing from the column bottom. Using a blunt wire, push the frit and support out of the column bottom. Rinse all the components in a small container of clean toluene. Repeat the process for the cop column end.

9.4 Wipe in inside of the column clean.

10. Calculations

10.1 Determine the amount of asphalt cement that was initially adsorbed onto the aggregate surface (report to two decimal places):

$$ VC(A_r - A_i) $$

$$ A = 50 \ A_i $$
Where:

\[ \begin{align*}
A &= \text{Initial adsorption, mg/g.} \\
V &= \text{Volume of solution in the column at the time } A_s \text{ is obtained, ml.} \\
C &= \text{Initial concentration of asphalt in solution, g/l.} \\
A_i &= \text{Initial absorbance reading} \\
A_r &= \text{Absorbance reading after 6 hours}
\end{align*} \]

Note 2: If the amount of aggregate used is other than 50g, change the constant, 50 in the above equation to reflect the actual amount used.

10.2 Determine the net adsorption (report to two decimal places):

\[ A_s = \frac{VC(A_i - A_r)}{50A_i} \]

Where:

\[ \begin{align*}
A_s &= \text{Net adsorption, mg/g.} \\
V &= \text{Volume of solution in the column at the time } A_s \text{ is obtained, ml.} \\
C &= \text{Initial concentration of asphalt in solution, g/l.} \\
A_i &= \text{Initial absorbance reading} \\
A_r &= \text{Absorbance reading after water has been added to the column}
\end{align*} \]

Note 2: If the amount of aggregate used is other than 50g, change the constant, 50 in the above equation to reflect the actual amount used.

10.3 Determine the percentage of difference between the amount initially adsorbed and the net adsorption:

\[ P_o = \left(\frac{(A - A_s)}{A}\right) \times 100 \]

Where:

\[ P_o = \text{percent difference, } \% \]
10. Report

10.1 The report shall contain the following:

10.1.1 Initial absorbance readings at 410 nm.
10.1.2 Absorbance readings at 410 nm after 6 hours.
10.1.3 Absorbance readings at 410 nm after the injection of water into the system and reading stabilize.
10.1.4 Initial absorption, mg/g.
10.1.5 Net adsorption, mg/g.
10.1.6 Percent difference, %
Figure A-1. Description and Assembly of Column.

A - 9
Figure A-2. Schematic of Mold for Preparing Asphalt Cement Sample.
APPENDIX B

Batch Method Net Adsorption Procedures
Preparation of Stock Solution:

1) Use a sharp knife to "cut" a 0.6 g sample out of a freshly poured, but cooled can of asphalt cement.
2) Place 500 ml of toluene in a 500 ml Erlenmeyer flask.
3) Drop sample of asphalt cement into the toluene. Place a stopper on the flask and put the flask on top of a mechanical stir. Stir for a minimum of 15 minutes to ensure that all of the asphalt cement has been dissolved.

Test Procedure:

1) Turn on the spectrophotometer and allow it to warm up per manufacturer's recommendations. Once it has completed its internal calibration sequence, set the wavelength to 410 nm and set the reference point with toluene (4 ml) according to the manufacturer's instructions.
2) Place 134 ml of the prepared solution into a 300 ml flask. Extract 1 ml of solution and place it into a flask containing 5 ml of clean toluene. Briefly agitate and extract 4 ml of the sample and place it into a clean cuvette. Place the cuvette in the spectrophotometer according to the manufacturer's directions. Record the reading.
3) Deposit 50 g of aggregate into the 300 ml flask containing the initial solution. Use a funnel to deposit the aggregate and brush the inside of the funnel when finished to ensure that all the aggregate is now in the solution. Cover the flask with a stopper.
4) Place flask into casing on platform. (The flask fits loosely so it may be necessary to stabilize the flask with a small piece of wood or rubber—a small rubber stopper will work as well as a small wad of paper towels.) Allow the solution to agitate for one hour at a speed of 250 rpm.
APPENDIX B

5) After agitation, allow sample to settle for one hour. Then take a sample:
   Place a gooch crucible on top of a vacuum flask. Place an appropriate filter at
   the bottom of the gooch crucible (i.e. 0.2 μm Super-200 Membrane filters).
   Extract 4 ml of the solution. Turn on the vacuum and slowly begin pouring the
   4 ml extraction into the vacuum flask. Once the filtration is complete, take a 1
   ml sample of the filtered solution and place it into a flask containing 5 ml of
   clean toluene. Briefly agitate and extract 4 ml of the sample and place it into a
   clean cuvette. Place the cuvette into the spectrophotometer according to the
   manufacturer’s directions. Record the reading.

6) Replace the flask with solution and aggregate into the casing on the platform and agitate
   again for 10 minutes at a speed of 250 rpm.

7) Let solution settle for one hour and 50 minutes.

8) Following sampling procedure given in step 5, extract another sample and place it into
   the spectrophotometer and obtain a second reading.

Clean up:

1) Dispose of the waste solution in a suitably labeled container for recycling. Place waste
   aggregate in a pan and place pan in a fume hood to allow waste toluene to evaporate off.

2) Clean all glassware using clean toluene and place glassware in a fume hood to allow
   excess toluene to evaporate off.