

Net Adsorption of Asphalt on Aggregate To Evaluate Water Sensitivity

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The net adsorption test was developed to evaluate the affinity of asphalt for aggregate and to determine the water sensitivity of a given asphalt-aggregate pair. The development of the test occurred in two steps. First, an initial screening of Strategic Highway Research Program Material Reference Library (MRL) aggregates (both siliceous and calcareous) was performed with three different MRL asphalts. The initial testing used 5 g of -40 to +80 mesh washed aggregates. Second, a scaled-up version of the test was developed that had a sample size of 50 g of minus No. 4 fraction aggregate and used commercially available equipment. The aggregate properties predominated in this test, showing a stronger influence than the asphalt on the initial amount of asphalt adsorbed, the amount of asphalt desorbed by water, and the amount of asphalt remaining, the net adsorption. The aggregate conditions recommended for the test use the minus No. 4 aggregate fraction (unwashed). These conditions yield results most representative of the aggregate used in actual pavement.

The effect of moisture on highway structures has been of concern to the highway community for at least the last 40 years. Extensive studies have been undertaken in both Europe and the United States to help understand the effect of moisture in pavements and to develop methods for determining moisture sensitivity of asphalt-aggregate mixtures prior to construction. As a result, today there exists a substantial industry selling chemicals to prevent moisture damage to pavements. These materials are mainly amine-based organic mixtures and hydrated lime. Current testing practices for assessing the potential for moisture damage in asphalt-aggregate mixtures use variations of the following four basic methods.

The European community primarily uses variations of the rolling bottle test. In this test a large (10 to 15 mm) stone is coated with asphalt and placed in an Erlenmeyer flask. The sample is covered with water, a stirring rod is added to provide tumbling action, and the flask is rotated, usually for a period of 24 hr. The amount of asphalt remaining on the stone after this treatment is evaluated visually.

In the United States, three tests predominate. The first is the boiling water test. In this test an asphalt-aggregate mixture approximating the formulation used in road paving is placed in boiling water, usually for about 10 min. The mix is taken

out of the water and allowed to dry. The amount of asphalt remaining on the aggregate is evaluated visually.

The other two widely used methods in the United States incorporate accelerated conditioning procedures into the test method prior to determining mixture properties such as tensile strength and resilient modulus. These two methods are the Root-Tunnicliff (1) and Lottman (2) procedures. The primary differences in the two methods are the initial saturation levels of the specimens. These methods generate a measurement of mixture properties, rather than requiring visual examination, but there is no general agreement as to the correlation of test results with pavement performance.

The area of moisture damage to pavements was targeted in the original Strategic Highway Research Program (SHRP) planning process as one of six major distress areas for investigation (3). The objective of part of the research was to study the fundamental properties of asphalt-aggregate interactions, including adsorption, absorption, and moisture damage. The research approach was to investigate the fundamental processes of both asphalt adsorption to the aggregate and subsequent deterioration of that adsorption in the presence of water. A relatively fast and simple test has been developed to determine the adsorptive nature and the water sensitivity of a wide range of typical paving quality aggregates. The test was developed to provide a rapid, simple, quantitative measure of the amount of asphalt adhered to aggregate after exposure to water.

TEST PROCEDURE AND METHOD

The test is composed of three parts. First, asphalt is flowed over and adsorbed onto aggregate from a toluene solution using a recirculating column. The adsorption step is allowed to run for 7 hr. Second, a small amount of water is introduced into the toluene solution and the adsorbed asphalt that is sensitive to the presence of water is desorbed from the aggregate. Third, the amount of asphalt remaining on the aggregate after the introduction of water is determined. This amount is termed net adsorption and gives a measure of the affinity of the asphalt for the aggregate. The difference between the amount of asphalt adsorbed before and after desorption by water serves as an indicator of the water sensitivity of the pair.

The test is discussed in two sections. The first part describes the initial experimental work that was performed to screen siliceous and calcareous aggregates. The second part describes

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the scale-up of the test to use both larger quantities and a wider particle size range of aggregate. Washed aggregate samples were used in the first method, while both washed and unwashed aggregates were used in the second. The scaled-up version of the test provided a closer representation of the material actually used in pavement construction.

This test is envisioned as a method to select asphalt-aggregate pairs as road paving materials in terms of the affinity of asphalt for the aggregate and the sensitivity of the pair to water. This test provides a relative measure of water sensitivity within a given set of asphalt-aggregate pairs whose performance in a road pavement and in the net adsorption test is known. This test is applicable in ranking new materials or different combinations of materials by their net adsorption. Their performance could then be predicted within the set of materials typically used for a given state or region.

EXPERIMENTAL

Materials

Aggregates

Eleven of the SHRP Material Reference Library (MRL) aggregates were evaluated during the initial development of this test procedure. The MRL aggregates included two granites (RA from Georgia and RB from California), three limestones (RC from Kansas, RD from Maryland, and RF from Georgia), three gravels (RE from Illinois, RJ from Wyoming, and RL from Texas), and one each of sandstone (RG from Pennsylvania), basalt (RK from Oregon), and greywacke (RH from California). The chemical and physical properties of each aggregate are presented in Table 1. Eight additional limestones,

TABLE 1 Physical Properties of MRL Aggregates^a

Sample	RA Granite	RB Granite	RC Limestone	RD Limestone	RE Gravel	RF Glacial Gravel	RG Sandstone	RH Greywacke	RJ Gravel	RK Basalt	RL Gravel
SiO ₂	73.4	56.2	6.49	16.4	93.7	15.8	52.8	66.0	76.5	50.1	63.1
Al ₂ O ₃	13.4	19.8	1.23	2.28	1.86	1.89	2.27	10.4	12.2	13.7	4.66
Fe ₂ O ₃	2.24	6.49	0.78	0.80	1.46	1.17	0.72	12.9	1.09	15.0	1.67
MgO	0.49	2.60	2.52	5.29	0.31	16.7	0.35	2.44	0.27	6.88	0.32
CaO	1.24	8.87	48.9	39.1	0.42	25.9	23.78	2.35	1.45	10.3	14.5
Na ₂ O	3.41	3.04	0.24	0.16	0.18	0.41	<0.15	2.57	2.91	2.25	0.92
K ₂ O	4.92	0.44	0.22	1.16	0.23	0.52	0.88	0.99	4.31	0.62	1.72
TiO ₂	0.22	0.51	0.03	0.06	0.09	0.08	0.14	0.53	0.07	1.48	0.09
P ₂ O ₅	<0.05	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	0.13	0.09	0.22	0.05
MnO ₂	0.05	0.12	<0.02	<0.02	<0.02	0.03	0.04	0.20	<0.02	0.21	<0.02
LOI	0.22	1.98	40.3	35.0	0.43	37.4	18.7	0.96	0.59	-0.36	11.2
Total	99.59	100.11	100.71	100.25	98.75	99.95	99.88	99.47	99.48	100.4	98.23
MRL Surface Area, m ² /g	0.19	1.62	2.90	0.72	0.95	1.66	1.99	2.74	1.32	15.73	2.41
Surface Area for -35 to 50 mesh, m ² /g			1.78					3.12		17.4	0.93
Pore Volume, cc/g	0.0045	0.0106	0.0099	0.0013	0.0031	0.0019	0.0170	0.0128	0.0026	0.0079	0.0010
> 3000 Å	0.0100	0.0344	0.1085	0.0301	0.0098	0.0172	0.0482	0.0905	0.0071	0.0289	0.0104
500 - 3000 Å	0.000	0.0017	0.0045	0.003	0.0004	0.0018	0.0018	0.0023	0.0002	0.0031	0.0012
< 500 Å											
Acid Insolubles, %	94.6	87.9	7.9	23.5	96.1	28.2	55.7	92.1	96.2	90.1	85.3
Water Solubles, %	11.7	8.1	8.1	5.1	6.6	5.0	4.9	9.7	6.3	7.4	9.3
Lithology, %	98.4 Granite 1.4 Basalt	100 Granite	100 Limestone	53.3 Shaly Limestone 26.8 Limestone 19.7 Arenaceous Limestone	Misc.	72.6 Limestone 10.8 Misc. 5.9 Greywacke 4.4 Chert 3.7 Gneiss 2.6 Basalt	100 Calcareous Sandstone	71.3 Micaceous Sandstone 11.2 Misc. 10.9 Granite 6.6 Chert	47.4 Sandstone 28.4 Granite 23.7 Misc. 0.4 Basalt	94.4 Basalt 4.5 Misc. 0.6 Sandstone	59.1 Chert 18.2 Arenaceous Limestone 11 Granite 5.8 Misc.

^aData are internal SHRP analyses for MRL aggregates. They are intended for comparison only.

obtained from various states in the eastern United States, were also tested. The limestone sources, their surface areas, and an observation of their stripping problems are presented in Table 2. Since limited quantities of these materials have only recently been added to the SHRP MRL, no further analysis of their properties is available.

Aggregates used in the initial experiments were sieved samples of -40 to +80 mesh. These aggregates were washed with distilled water, dried for 1 week at 150°C, and stored away from light. Before use, the aggregate was dried in an oven for 24 hr at 150°C, placed in a desiccator to cool, and then transferred to the adsorption columns. The aggregate fraction used in the second phase of the test development was the entire minus No. 4 fraction either used as received or washed according to ASTM Method C117. The aggregate was dried overnight at 150°C, then stored in a desiccator.

Binders

Three binders selected from the SHRP MRL were an AR 4000 asphalt approximately equivalent to an AC-10 (AAD-1 from California), an AC-20 (AAM-1 from West Texas), and an AC-30 (AAK-1 from Venezuela). The properties of these asphalts are given in Table 3.

Solvent

The solvent used in this study was toluene, spectranalyzed grade from Fisher Scientific. Toluene was dried prior to use using activated molecular sieves for the initial screening program. In the second phase of the work the drying step was eliminated after no effect of drying was observed. Distilled and deionized water was used in the desorption step of the study.

Net Adsorption Test

The screening test was performed by adsorbing asphalt from toluene solution onto aggregate using a recirculating system that consisted of a constant-temperature column containing aggregate through which asphalt solution flowed continuously. The column temperature was maintained at 25°C. The time of the adsorption step was 7 hr. The experiment was

begun by charging the asphalt in toluene solution into the column, then adding the aggregate. The initial volume of the solution was 27 ml. As the asphalt in toluene solution flowed over the aggregate, some of the asphalt adsorbed onto the aggregate, reducing the concentration of asphalt in the toluene solution. The initial concentration of asphalt was determined by measuring the visible absorbance at 410 nm using a UV-visible spectrophotometer. The concentration of asphalt after adsorption was determined by measuring the decrease in the visible absorbance of the asphalt at 410 nm after 7 hr of adsorption. The concentration of the asphalt in solution was subsequently determined by using Beer's law:

$$A = abc$$

where

A = absorbance at 410 nm,
 a = absorptivity (L/g cm) of the asphalt at 410 nm,
 b = cell path length (cm), and
 c = concentration (g/L).

The equations for calculating the amount adsorbed are

$$C/C_o = A/A_o$$

$$AspW = V_o(C_o - C)$$

$$Asp = V_o C_o (A_o - A) / WA_o$$

where

C_o and C = concentrations of the asphalt solution before and after adsorption, respectively;
 A_o and A = visible absorbances at 410 nm of the asphalt solution before and after adsorption, respectively;
 V_o = solution volume before adsorption;
 Asp = amount of asphalt adsorbed per gram of aggregate (g/g); and
 W = mass of aggregate used (g).

The desorption step involved introducing 136 $\mu\ell$ of water into ~27 ml of toluene solution and allowing the solution plus water to recirculate over the aggregate bed. After the desorption step was completed (2 hr), the absorbance of the asphalt solution was monitored at 410 nm, and the asphalt concentration was determined using the following equations:

$$D_w W = -V_w (C - C_w)$$

$$D_w = -V_w C (A - A_w) / WA$$

where

C_w = concentration of the asphalt solution after desorption;
 A_w = visible absorbance at 410 nm of the asphalt solution after desorption;
 V_w = toluene solution volume during desorption; and
 D_w = amount of asphalt desorbed per gram of aggregate.

TABLE 2 Limestones Used in Net Adsorption Test

Aggregate Code	Limestone Source	Surface Area, m ² /g*	Aggregate Performance Ranking**
R1	Iowa	1.03	Non-Stripping
R2	Ohio	0.81	Non-Stripping
R3	Florida	2.77	Non-Stripping
R5	Kentucky	1.81	Stripping
R6	Kentucky	2.03	Stripping
R7	Kentucky	5.79	Stripping
R8	Kentucky	6.06	Stripping

* determined by Nitrogen BET Analysis

** opinions of pavement performance were obtained from different state highway officials

TABLE 3 Physical and Chemical Properties of Asphalts^a

PROPERTY	Asphalt Properties		
	AAD-1	AAM-1	AAK-1
	AR4000	AC-20	AC-30
140°F, Viscosity Poise	1055	1992	3256
275°F, cst	309	569	562
Component Analysis			
Asphaltenes, %	23.0	3.9	21.1
Polar Aromatics, %	41.3	50.3	41.8
Naphthene Aromatics, %	25.1	41.9	30.0
Saturates, %	8.6	1.9	5.1
Elemental Analysis			
Carbon, %	81.6	86.8	83.7
Hydrogen, %	10.8	11.2	10.2
Oxygen, %	0.9	0.5	0.8
Nitrogen, %	0.8	0.6	0.7
Sulfur, %	6.9	1.2	6.4
Vanadium, ppm	310	58	1480
Nickel, ppm	145	36	142
C _{aromatic} , %	23.7	24.7	31.9
H _{aromatic} , %	6.8	6.5	6.8
Absorptivity (liters/ gm cm)			
410 nm	3.79	5.74	7.40
375 nm	4.90	8.11	6.57
Functional Group Analysis by IR			
Carboxylic Acids	0.011	0.000	0.013
Acid Salts	0.000	0.000	0.000
Acid Anhydrides	0.000	0.000	0.000
Quinolones	0.024	0.012	0.012
Ketones	trace	trace	trace
Phenols	0.124	0.070	0.027
Sulfoxides	trace	trace	trace
Pyrroles	0.168	0.157	0.110

^a Data are internal SHRP analyses for MRL asphalts. They are intended for comparison only

The net adsorption was obtained by subtracting the amount of asphalt desorbed by water from the amount initially adsorbed, where net adsorption = $A_{sp} - D_w$.

This test procedure used an initial concentration of 0.6 g/L of asphalt in toluene solution. This concentration was chosen on the basis of isotherm data that showed for many aggregates that the adsorption amount was beginning to level out (see companion paper in this Record by Curtis et al.). The asphalt used in the screening study was aged in a thin-film oven for 5 hr at 163°C, TFOT test conditions (ASTM D 1754). The adsorption step ran for 7 hr. The time required is dependent on the equipment used; the time selected should be the time required to reach equilibrium in each step of the experiment. It is not always possible to reach equilibrium in the adsorption step so that sometimes that step is cut short with satisfactory results, but reaching equilibrium is mandatory in the desorption step to achieve satisfactory results.

Duplicate experiments are required for reliability and were performed. Triplicate experiments are suggested if asphalt-aggregate pair shows considerable variability. Several sets of experiments can be run simultaneously using a multiple-head peristaltic pump. The precision of duplicate runs of the experiments performed to date is presented later. Accuracy of the method could not be determined, since there are no standards whose true values are known.

SCALED-UP NET ADSORPTION TEST METHOD

The goals in scaling-up the test developed in the initial phase of this work were as follows:

- Maximize the quantity of aggregate used in the test while minimizing the amount of the solvent.

- Use aggregate gradations as close as practical to those used in producing pavements.
- Keep the relationship between materials quantities the same as in the initial study.
- Adjust the timing of the procedure so that the test can be completed within the typical working day.
- Locate commercially available sources of all equipment.

Since 500 g of the entire minus No. 4 fraction is typically used in conventional laboratory-prepared mixture specimens, it would be desirable to use the same formulation in the net adsorption test. However, this quantity of aggregate would require a minimum of 1.3 L of solvent per test column in order to maintain a constant proportion in material quantities. This quantity of solvent was too large in terms of both cost and requirements for satisfactory recycling or disposal. The resulting compromise between the desirable maximum aggregate quantity and minimum solvent quantity yielded a final aggregate sample size of 50 g. In order to further reduce the amount of solvent used, the volume of solvent was halved compared to quantities used in the initial screening stage of this work, while the concentration of asphalt dissolved in the solvent was doubled. This procedure resulted in no net change in the ratio of asphalt to aggregate.

For the test to best represent actual paving practice, the use of the same gradation as the job mix formula (JMF) was desirable. However, there was concern that the very fine aggregate present in the JMF would become suspended in the solution and result in erroneous spectrophotometer readings. In order to investigate this possibility, both washed and unwashed minus No. 4 fractions were tested.

As discussed previously the volume of solvent was altered in order to reduce the quantity of solvent, which gave rise to the question of how much to increase the water added to the column during the desorption phase of the test. If the volume of water was increased in proportion to the volume of solvent, then 575 $\mu\ell$ of water should be used. If, however, the $\mu\ell$ of water per gram of aggregate was to be kept constant, then 1,150 $\mu\ell$ of water was needed. In order to address this problem, both quantities of water were included in the test matrix.

The time for running the test was reduced to 6.5 hr for the initial adsorption phase; the time of 2 hr was maintained for the desorption phase. With 45 min of preparation time in the morning and 30 min of cleanup, this procedure can now be completed during normal laboratory operating hours.

The goal of equipment changes between the first and second phases of the test development was to make it easier for state highway departments to use this test. The only major change was the substitution of a commercially available jacketed chromatography column for the original hand-blown column. This change had several advantages. First, the unit is commercially available. Second, the column is designed to be disassembled into individual parts, with each component being easily replaceable. Most importantly, the frit which retains the aggregate in the column has a substantially greater surface area and is easily removable for cleaning and replacement.

RESULTS AND DISCUSSION

Initial Net Adsorption Test

The net adsorption test yields data that provide information on the affinity of different asphalt-aggregate pairs under dry and moist conditions. The initial amount of asphalt adsorbed before introduction of water gives an indication of the affinity a particular asphalt has for a given aggregate. The amount of asphalt desorbed is obtained after water is introduced into the system. The net adsorption or the amount of asphalt remaining on the surface of the aggregate after desorption is an indication of the moisture sensitivity of the asphalt-aggregate pair.

Net Adsorption of MRL Siliceous and Calcareous Aggregates

For this study, the 11 MRL aggregates were tested with three different aged asphalts, AAD-1, AAK-1, and AAM-1. Although the asphalts differed substantially in their chemical

TABLE 4 Initial Adsorption and Percent Desorption of Asphalt with MRL Aggregates

Asphalt/ Aggregate	AAD-1		AAK-1		AAM-1	
	Initial Adsorption	Percent Desorption	Initial Adsorption	Percent Desorption	Initial Adsorption	Percent Desorption
RA-granite	0.18 \pm 0.03	61.5	0.25 \pm 0.04	28.7	0.20 \pm 0.18	99.5
RB-granite	0.85 \pm 0.04	19.1	0.89 \pm 0.11	18.1	0.77 \pm 0.03	22.6
RC-limestone	1.9	20	1.7	25	1.4	22
RD-limestone	0.73 \pm 0.06	18.5	0.73 \pm 0.02	18.9	0.77 \pm 0.09	30.4
RE-gravel	0.98 \pm 0.05	29.7	1.01 \pm 0.006	39.0	0.85 \pm 0.02	47.1
RF-glacial gravel	0.90 \pm 0.04	32.2	0.85 \pm 0.06	43.7	0.83 \pm 0.05	47.2
RG-sandstone	0.70 \pm 0.02	17.8	0.60 \pm 0.09	31.0	0.59 \pm 0.02	42.0
RH-greywacke	1.3	25	1.22	23	1.2	24
RJ-gravel	0.31 \pm 0.003	60.3	0.34 \pm 0.06	44.0	0.42 \pm 0.63	50.0
RK-basalt	1.7	17	1.56	19	1.4	17
RL-gravel	1.4	28	1.4	30	1.2	28

composition and characteristics, for a given aggregate the differences in the asphalt initial adsorption behavior were quite small. Based on the amount adsorbed, the asphalts ranked $AAD-1 \geq AAK-1 > AAM-1$ for most aggregates, with $AAD-1$ and $AAK-1$ occasionally changing positions. The initial asphalt adsorption amounts for the 11 MRL aggregates are shown in Table 4.

The amounts obtained for initial adsorption ranged from a high of 1.9 mg/g for $AAD-1$ on RC-limestone to a low of 0.18 mg/g on RA-granite; a high of 1.7 mg/g of $AAK-1$ on RC-limestone to a low of 0.25 mg/g on RA-granite; highs of 1.4 mg/g of $AAM-1$ on RC-limestone and RK-basalt to a low of 0.2 mg/g on RA-granite. Hence, each asphalt exhibited high and low levels of adsorption on the same aggregates, but the magnitude of the differences among the aggregates for each asphalt was quite large.

The adsorption behavior of the siliceous aggregates before and after water desorption varied considerably. Two aggregates, RA-granite and RJ-gravel, showed consistently low adsorption and were quite sensitive to water regardless of the asphalt used. Aggregates RB-granite, RE-gravel, and RG-sandstone showed similar behavior in their initial asphalt adsorption for the three asphalts; however, RE-gravel tended to show a higher sensitivity to water and an increased amount of asphalt desorbed compared to the other aggregates. The two siliceous aggregates that gave the largest amounts of asphalt adsorption, regardless of asphalt, were RH-greywacke and RK-basalt. Both of these aggregates also had low sensitivity to water.

The MRL limestones used in this study included RC, a highly absorptive limestone, RD, a nonabsorptive limestone, and RF, a limestone with other types of minerals present. The initial adsorption behavior of the three asphalts was similar on the three limestones and ranked the aggregates $RC > RF > RD$. However, the moisture sensitivities of these limestones seemed somewhat asphalt dependent, with $AAM-1$ showing more sensitivity to water than either $AAD-1$ or $AAK-1$ except for RC-limestone. RF-limestone yielded considerably more desorbed asphalt than did either RC- or RD-limestones.

Even though the amount of adsorption and desorption that occurred varied somewhat from asphalt to asphalt, for a given aggregate the net adsorption, defined as the amount of asphalt remaining on the aggregate, was similar as shown in Figure 1. The net adsorption ranking of the siliceous aggregates for all three asphalts was $RK\text{-basalt} > RH\text{-greywacke} \approx RL\text{-gravel} > RB\text{-granite} > RE\text{-gravel} > RG\text{-sandstone} > RJ\text{-gravel} > RA\text{-granite}$. The net adsorption of the limestone aggregates ranked as $RC > RD \approx RF$.

Relationship Between Net Adsorption Test Results and Aggregate Properties

Stepwise regression analyses were used to estimate the role of aggregate chemistry in the net adsorption test. The test data evaluated were those involving the 11 MRL aggregates used in the initial screening experiments. The variables were the aggregate composition and morphology as measured by X-ray fluorescence, aggregate surface area, and zeta potential. Three regressions were performed, one each for pre-

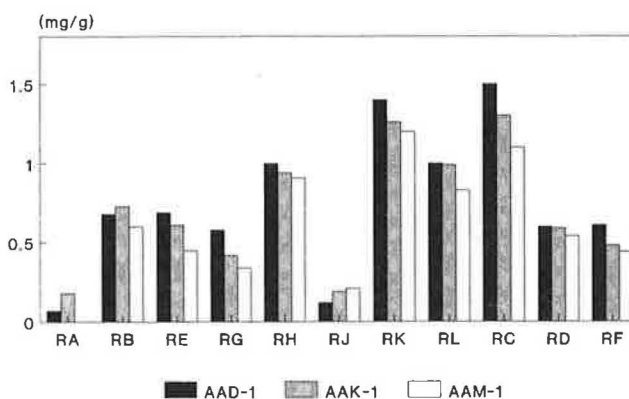


FIGURE 1 Net adsorption of asphalts on MRL aggregates.

dicting initial adsorption, net adsorption, and the difference between the two. The results of these statistical evaluations are presented in Table 5.

The statistical evaluations indicate that the initial adsorption of the binder by the aggregate was a function of potassium oxide and aggregate surface area (by BET analysis). As the potassium oxide content of the aggregate decreased, initial adsorption of asphalt increased. As the surface area increased, the net adsorption increased. The r^2 of the final equation was 0.71, which suggests that the initial adsorption of the binder onto the aggregate surface was influenced by other variables not included in the analysis. The binder properties may also influence the relationship. However, only three binders were used in this study, which did not provide a sufficient data base for further analysis.

The net adsorption, however, was a function of five variables that are listed in decreasing order of impact: the lack of potassium oxide as denoted by the negative sign in the table, surface area, presence of calcium oxide, zeta potential, and presence of sodium oxide. These conclusions pass the test of reasonableness. First, the presence of potassium has been previously identified as being detrimental to adhesion (4). Second, higher surface area provides more active sites per gram of aggregate for interaction between the aggregates and the binder. Third, calcium has long been identified as being beneficial to enhanced adhesion between asphalt and aggregate in the presence of water. Fourth, a more negatively charged aggregate may provide a stronger driving force for the adsorption. The final r^2 of 0.90 indicates that the net adsorption was primarily a function of the aggregate properties, with little influence being contributed by other potential variables such as binder composition.

The difference between the two measurements was moderately dependent on the lack of potassium oxide. However, the r^2 was only 0.34, and the stepwise regression was not improved with the addition of any of the other variables.

Net Adsorption of Various Limestones

Additional limestone samples were obtained by SHRP and used in the net adsorption test. The sources and surface areas of the limestones are given in Table 2. The initial adsorption behavior of $AAD-1$ and $AAK-1$ on the seven limestones was

TABLE 5 Results of Stepwise Regression Analysis

Variable	Step				
	1	2	3	4	5
Initial Adsorption					
K ₂ O	-0.241 ^a -5.70 ^b	-0.205 -5.82			
Surface Area		0.046 4.04			
Regression Constant <i>r</i> ²	0.322 0.54	0.258 0.71			
Net Adsorption					
K ₂ O	-0.200 -5.10	-0.0164 -5.26	-0.135 -4.25	-0.186 -7.01	-0.251 -7.31
Surface Area		0.045 4.52	0.049 5.18	0.158 6.27	0.132 5.35
CaO			0.006 2.27	0.017 5.41	0.020 6.55
Zeta Potential ^c				-0.038 -4.52	-0.033 -4.18
NaO					0.111 2.63
Regression Constant <i>r</i> ²	0.300 0.48	0.230 0.71	0.213 0.75	0.161 0.87	0.145 0.90
Difference Between Initial and Net Adsorption					
K ₂ O	-0.041 -3.79				
Regression Constant <i>r</i> ²	0.300 0.34				

a: the regression coefficient

b: t-ratio

c: zeta potential is typically negative, the negative coefficient means the more negative the zeta potential the greater the adsorption

very similar as presented in Table 6, while that of AAM-1 was somewhat less. The initial amount of AAD-1 adsorbed ranged from a high of 1.8 mg/g on R8 to a low of 0.56 mg/g on R2; AAK-1 ranged from a high of 1.7 mg/g on R7 to a low of 0.64 mg/g on R2; while AAM-1 ranged from a high of 1.4 mg/g on R7 to a low of 0.58 mg/g on R2. The range in the adsorption amounts was not as great on the limestones as it was on the MRL aggregate, although a considerable vari-

ation in the amount adsorbed was observed for a given asphalt over the seven limestones.

The desorption behavior of the three asphalts on the limestones also varied. Their desorption behavior ranged from being similar for the three asphalts for R1, R5, R6, R7 and R8 to being very different for R2 and R3. In the latter two cases, AAM-1 asphalt desorbed considerably more than did either AAD-1 or AAK-1. The specificity of the interaction

TABLE 6 Initial Adsorption and Percent Desorption of Asphalt with Various Limestones

Asphalt/ Limestone	AAD-1		AAK-1		AAM-1	
	Initial Adsorption	Percent Desorption	Initial Adsorption	Percent Desorption	Initial Adsorption	Percent Desorption
R1	1.06±0.04	32.3	1.08±0.05	32.0	0.95±0.01	33.8
R2	0.56±0.01	35.0	0.64±0.05	30.0	0.58±0.03	66.4
R3	1.31±0.08	15.0	1.23±0.07	12.8	0.97±0.04	41.6
R5	0.92±0.01	21.0	0.90±0.02	33.6	0.75±0.02	33.2
R6	1.23±0.04	31.2	1.27±0.02	19.9	1.01±0.07	34.0
R7	1.73±0.05	16.7	1.75±0.04	24.7	1.37±0.01	24.3
R8	1.79±0.03	42.4	1.51±0.11	37.7	1.35±0.01	42.6

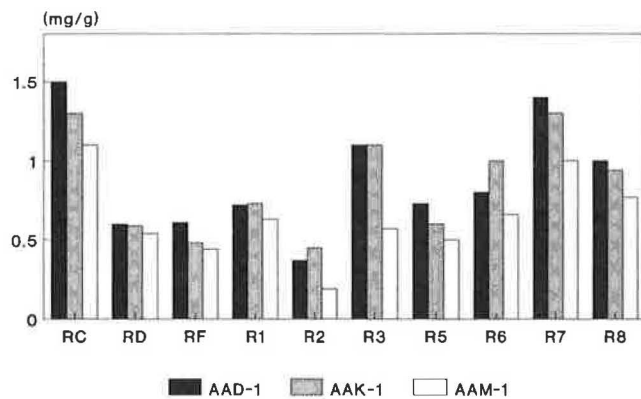


FIGURE 2 Net adsorption of asphalts on various limestones.

between asphalt and limestone became apparent with limestones such as R3, where AAD-1 and AAK-1 showed very little sensitivity to water at 15 and 13 percent desorption, respectively, while the AAM-1/R3 pair yielded a very high desorption of 42 percent.

The net adsorption for the limestones is given in Figure 2. The net adsorption ranking of the limestones for all three asphalts was $R7 > R3 \geq R8 > R6 > R1 > R5 > R2$. The averaged net adsorption ranged from a high of 1.27 mg/g on R7 to a low of 0.34 mg/g on R2.

Comparison of Initial and Scaled-Up Net Adsorption Test Methods

To compare the results between the initial net adsorption test and that of the scaled-up version, scaled-up experiments were

TABLE 7 Comparison of Net Adsorption Results from Scaled-Up (575 $\mu\ell$ water) Test to Initial Screening Test

Measurement		Scaled-Up		Initial
		575 $\mu\ell$ water 50 g Aggregate		136 $\mu\ell$ water 5 g Aggregate
		—No. 8	—No. 8 to No. 200	—No. 40 to No. 80
		Unwashed	Washed	Washed
AAD and RK-basalt				
AA	mg/g	1.98 \pm 0.10	1.46 \pm 0.13	1.68
AD	mg/g	0.25 \pm 0.06	0.63 \pm 0.17	0.28
Net	mg/g	1.74 \pm 0.14	0.83 \pm 0.19	1.39
D	%	12.8 \pm 3.6	43.3 \pm 11.4	17
AAD and RB-granite				
AA	mg/g	1.26 \pm 0.09	0.97 \pm 0.18	0.85
AD	mg/g	0.17 \pm 0.19	0.03 \pm 0.02	0.17
Net	mg/g	1.09 \pm 0.17	0.94 \pm 0.19	0.68
D	%	13.5 \pm 13.8	6.1 \pm 5.15	19
AAK and RK-basalt				
AA	mg/g	0.93 \pm 0.12	0.63 \pm 0.20	1.56
AD	mg/g	0.16 \pm 0.24	0.13 \pm 0.07	0.30
Net	mg/g	0.78 \pm 0.12	0.13 \pm 0.07	1.26
D	%	15.1 \pm 24.4	20.2 \pm 6.9	20
AAK and RB-granite				
AA	mg/g	1.21 \pm 0.15	0.83 \pm 0.10	0.89
AD	mg/g	0.08 \pm 0.12	−0.03 \pm 0.065	0.16
Net	mg/g	1.13 \pm 0.09	0.87 \pm 0.10	0.73
D	%	5.8 \pm 9.1	−4.03 \pm 8.56	18
AAM and RK-basalt				
AA	mg/g	1.38 \pm 0.11	0.82 \pm 0.015	1.43
AD	mg/g	0.15 \pm 0.08	0.03 \pm 0.0	0.24
Net	mg/g	1.23 \pm 0.15	0.79 \pm 0.15	1.19
D	%	11.0 \pm 6.0	3.5 \pm 0.0	17
AAM and RB-granite				
AA	mg/g	1.09 \pm 0.06	0.80 \pm 0.04	0.77
AD	mg/g	−0.08 \pm 0.096	0.16 \pm 0.16	0.17
Net	mg/g	1.17 \pm 0.04	0.67 \pm 0.19	0.60
D	%	−7.7 \pm 9.01	20.5	23

AA = Amount Adsorbed
AD = Amount Desorbed

Net = Net Adsorption
D = Desorption

performed with three aggregate sources (RC-limestone, RJ-gravel, and RL-gravel) and three binders (AAD-1, AAK-1, and AAM-1). For all of the combinations the scaled-up method showed higher initial adsorption than did the initial method. One possible explanation for this consistent increase was that the flow rate in the scaled-up version was nearly three times faster than that of the initial method. The increased flow rate would allow the asphalt more opportunity to contact the aggregate, since the method involved recirculation of the solvent.

Likewise, the net adsorption values were correspondingly higher for the scaled-up test than for the initial test. However, although the absolute values for the net adsorption were quite different, the resulting rankings of the asphalt-aggregate pairs were nearly identical.

Calculation of the percent difference between the amount of binder initially adsorbed and the amount lost because of water was much less for the scaled-up version than for the

initial test. The time on the desorption step in the initial test represented an equilibrium value, while on the scaled-up version it did not. Thus, in order to achieve reproducible and representative desorption values, either the amount of water used or the test time for the desorption phase should be increased.

Impact of Graded Aggregates on Scaled-Up Test Method

The text matrix used to evaluate the scaled-up test setup and procedures involved asphalts, AAK and AAM, used in conjunction with the aggregates, RB-granite and RK-basalt. Table 7 presents the net adsorption test data from a first sampling of aggregates and using 575 μl of water in the desorption step while Table 8 presents data from a second sampling of aggregate and using 1,150 μl of water in the desorption step.

TABLE 8 Comparison of Net Adsorption Results from Scaled-Up (1,150 μl water) Test to Initial Screening Test

Measurement		Scaled-Up		Initial
		1150 μl water 50 g Aggregates		136 μl water 5 g Aggregate
		—No. 8	—No. 8 to No. 200	—No. 40 to No. 80
		Unwashed	Washed	Washed
AAD and RK-basalt				
AA	mg/g	1.4 \pm 0.09	1.45 \pm 0.15	1.68
AD	mg/g	−0.45 \pm 0.13	0.30 \pm 0.01	0.28
Net	mg/g	1.86 \pm 0.16	1.14 \pm 0.14	1.39
D	%	−31.4 \pm 7.27	20.9 \pm 1.88	17
AAD and RB-granite				
AA	mg/g	1.62 \pm 0.029	1.46 \pm 0.005	0.85
AD	mg/g	0.05 \pm 0.11	0.064 \pm 0.002	0.17
Net	mg/g	1.57 \pm 0.08	1.39 \pm 0.003	0.68
D	%	3.2 \pm 6.8	4.4 \pm 0.141	19
AAK and RK-basalt				
AA	mg/g	1.99	1.25 \pm 0.14	1.56
AD	mg/g	0.05 \pm 0.006	0.04 \pm 0.21	0.30
Net	mg/g	1.94 \pm 0.03	1.18 \pm 0.15	1.26
D	%	2.72 \pm 0.36	3.4 \pm 1.47	20

AAK and RB-granite				
AA	mg/g	1.68 \pm 0.11	1.40 \pm 0.05	0.89
AD	mg/g	0.22 \pm 0.20	0.07 \pm 0.11	0.16
Net	mg/g	1.45 \pm 0.13	1.32 \pm 0.085	0.73
D	%	13.0 \pm 11.0	6.1 \pm 7.5	18
AAM and RK-basalt				
AA	mg/g	1.29	1.03 \pm 0.11	1.43
AD	mg/g	−0.24	0.03 \pm 0.02	0.24
Net	mg/g	1.53	1.00 \pm 0.11	1.19
D	%	−18.6	1.6 \pm 0.05	17
AAM and RB-granite				
AA	mg/g	0.84 \pm 0.20	0.83 \pm 0.04	0.77
AD	mg/g	−0.05 \pm 0.03	−0.10 \pm 0.01	0.17
Net	mg/g	0.88 \pm 0.16	0.93 \pm 0.05	0.60
D	%	−5.6 \pm 5.9	\pm 12.5 \pm 1.9	23

AA = Amount Adsorbed
AD = Amount Desorbed

Net = Net Adsorption
D = Desorption

Ideally, the net adsorption should have decreased as the water increased. However, this did not happen. The second set initially had a higher amount of binder adsorbed and continued to have a higher amount of binder remaining on the aggregate surface. Also, the washed aggregate continued to be more consistent than the unwashed aggregate.

A comparison of the net adsorption test results obtained for the initial screening test and for the scaled-up version is presented in Tables 7 and 8. The initial screening data used 5 g of aggregates that were washed, sieved to between -No. 40 and +No. 80, and had an initial adsorption test time of 7 hr. The scaled-up data were for 50 g of aggregate consisting of the entire minus No. 4 fraction. For ease of comparison only, the same screening data were compared to both washed and unwashed data from the scaled-up test.

The initial adsorption results for the RB-granite with the three binders were fairly consistent with the washed aggregates used later for desorption with 575 μl of water. The impact of the material sampling variability became evident between the two sets of scaled-up data. The data for the RK-basalt were somewhat more variable than the RB-granite; the degree of variability was dependent on binder and whether the aggregate was washed.

The net adsorption amounts achieved for the scaled-up test tended to be equal to or greater than those for the initial screening for RB-granite. The variability in the RK-basalt was substantially reduced when washed RK-basalt and 1,150 μl of water were used during desorption. These data indicate that increased water quantity should help reduce the testing variability for the desorption phase.

The difference between the initial and net adsorption for the initial screening study versus the scaled-up test is highly variable. The difference is attributed to the wide range of test method and materials changes represented by the scaled-up data. Because the unwashed materials represent the most realistic JMF materials, and the use of 1,150 μl of water during the desorption phase appeared to give the consistent data, these test conditions were adopted. However, the reliability of this method should be checked against mixture test results such as tensile strength ratios before any conclusions are reached.

The standard deviations associated with measuring the amount of binder initially adsorbed for washed versus unwashed aggregates were compared. All of the standard deviations were less than 0.2 mg of binder per gram of aggregate. Neither dependence upon aggregate source nor an apparent bias of the variability caused by washed or unwashed aggregates was evident. Using this information, the precision of this first measurement can be estimated at a standard deviation of 0.13 mg/g for either washed or unwashed aggregates. Estimates of precision were obtained using the equations presented in ASTM C670 and C802.

The standard deviations associated with determining the net adsorption were also evaluated. Again, all standard deviations were below 0.2 mg/g. The precision is estimated at 0.14 mg/g for either washed or unwashed aggregates.

The standard deviations associated with the difference between the amount of binder initially adsorbed and the net adsorption were examined. The standard deviations for tests

using the unwashed aggregates were significantly larger than those for the washed aggregates, a fact that was not evident when only the individual adsorption values were used. Estimates of precision are 0.13 and 0.08 for the unwashed and washed aggregate, respectively.

Conclusions

The net adsorption test offers an effective means of evaluating the affinity and water sensitivity of an asphalt-aggregate pair. Although the actual performance of the SHRP aggregates is not known, the perceived performance and the results of the net adsorption test seem to agree quite well, particularly with the siliceous materials.

Since the net adsorption test gives a relative measure of the affinity that an asphalt has for an aggregate and the sensitivity of the asphalt-aggregate pair to water, this test can best be used as a screening test for materials. Highway departments could develop libraries of net adsorption results from a set of materials, asphalts, and aggregates with known performance on the road. The new materials or new combinations of materials could be tested, compared to the known set, and their performance predicted. For the net adsorption test to represent most accurately the aggregates used in road paving, the recommended sample is a minus No. 4 fraction of unwashed aggregate.

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