

# Adsorption Behavior of Asphalt Models and Asphalts on Siliceous and Calcareous Aggregates

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The adsorption of seven single model species representative of functionalities prevalent in asphalt on siliceous and calcareous aggregates was examined. The seven model species were ranked based on their Langmuir monolayer adsorption amounts as well as their adsorption amounts on one or two grams of aggregates. The aggregates used were gravels, limestones, and greywacke. Benzoic acid showed the greatest affinity for the aggregates tested. In addition, the adsorption and desorption behavior of three asphalts with substantially different chemical compositions was determined on a single siliceous aggregate. Differences observed in their behaviors may be attributed to differences in their chemical compositions. The adsorption and water desorption behavior of an AR-4000 asphalt was also determined on three different aggregates: limestone, gravel, and greywacke. Substantial differences in the amount adsorbed and desorbed as well as the shapes of their adsorption curves were observed. Limestone adsorbed the most asphalt and retained the largest amount of asphalt after desorption by water. Limestone desorbed the most asphalt in the presence of water, and greywacke desorbed the least. The pre-coating of antistripping agent on greywacke resulted in less asphalt desorption by water in comparison with coadsorbing antistripping agent with asphalt or with no antistripping agent being present in the system.

A number of factors affect the interaction of asphalt with aggregate in a road pavement. These factors include the chemistry and composition of the asphalt and aggregate, the surface area and chemistry of the aggregate surface, the specific bonding interactions between the asphalt and aggregate, and the resistivity to moisture of a particular asphalt-aggregate combination. Other factors that influence the interaction involve pavement construction practices, the roughness of the aggregate surface, the propensity of a particular combination toward oxidation of the asphalt as well as the environment of the pavement, both in a localized context at the asphalt-aggregate interface and in a more global sense of heat, cold, and traffic. Although many factors influence the interaction between asphalt and aggregate, the effect of the chemistry and composition of asphalt and aggregate on the affinity of asphalt for adsorbing on a particular aggregate and resistivity of the particular combination to moisture is the focus of this paper.

Previous researchers (1,2) have found that the more polar constituents of asphalt appear to be concentrated at the surface of the aggregate and more sensitive to moisture. Scott (3, p. 19) has stated that oxygen-containing groups present in the asphaltenes of asphalts were preferentially adsorbed

onto the aggregate surfaces. Fritschy and Papirer (4) have shown that asphaltenes, the concentrated polar fraction of the asphalts, adsorbed more onto aggregates than the whole asphalt. Curtis et al. (5,6) have shown that asphaltenes behave similarly to whole asphalt on both sandstone and limestone. The chemistry of the aggregate, particularly the surface chemistry, affects the interaction between asphalt and aggregate. The affinity of a given asphalt for different aggregates may vary considerably depending on the composition and surface activity of the aggregate. The adsorption behavior of asphalts on aggregates is related to the stripping phenomenon only when water is present in the system.

The overall objective was to elucidate chemical interactions that occur at the asphalt-aggregate interface. Three approaches were taken: relative adsorption affinities of model asphalt compounds were determined on aggregates; the adsorption and desorption behavior of asphalt on different aggregates was determined; and the effect of an antistripping (AS) agent on the adsorption and desorption behavior of asphalt was evaluated. Seven compounds representing key functionalities present in asphalt cements were used as models for evaluating physical parameters, for example, monolayer surface coverage, Gibb's free energy of adsorption ( $\Delta G^\circ$ ), and the equilibrium constant ( $K$ ), relating to the adsorptive interactions. The relative adsorption affinities of each of the seven model compounds were determined on five aggregates. This information served as a means of characterizing the chemical reactivity of each aggregate and provided possible explanations for the observed adsorption and desorption behavior of different asphalt-aggregate pairs. The adsorption and desorption behavior of asphalts on both siliceous and calcareous aggregates were determined and compared. The amount of asphalt remaining on each of the aggregates was determined. The effect of an AS agent on the adsorptive and desorptive behavior of an asphalt-aggregate system was also evaluated. Precoating of aggregate surface with AS agent before adsorption investigations as well as coadsorption of AS agent with asphalt onto aggregate surface were examined. The amounts adsorbed by both methods were compared with respect to water sensitivity.

## EXPERIMENT

### Single Component Adsorption

Benzoic acid, indole, phenanthridine, naphthalene, 1-naphthol (all at least 99 percent pure), phenylsulfoxide (97 percent),

9-fluorenone (98 percent), and cyclohexane (at least 99 percent spectrophotometric grade) were supplied by Aldrich Chemical Company. Cyclohexane was dried before being used with activated 4Å molecular sieves. All other compounds were used as received. Aggregates—RC-limestone, RD-limestone, RH-greywacke, RJ-gravel, and RL-gravel—used in the single adsorption study were obtained from the Strategic Highway Research Program (SHRP) Material Reference Library (MRL) at the University of Texas, Austin. Chemical and physical properties of the aggregates were determined by Southwestern Laboratories, Inc., Houston, Texas, and lithologies were provided by the Center for Applied Energy Research, University of Kentucky, Lexington. Aggregates were sized to -40 +80 mesh, washed thoroughly with distilled water, dried at 150°C for 1 week, and stored in a brown bottle. Aggregates were dried for an additional 24 hr before use.

### Procedures

For single component adsorption experiments, standard stock solutions of 100 mg/L of each model compound were prepared in cyclohexane. Exactly 20 mL of the stock solution were pipetted into serum bottles (30 mL capacity) containing varying amounts (1, 2, 3, 4, 6, 8, 10 g) of aggregate. The serum bottles were placed in the controlled temperature (25°C) environment of an orbital shaker (Labline, Fisher Scientific), agitated for 1 hr, and allowed to settle for an additional hour. Powdered aggregate that remained suspended in the solution was removed by filtration through a 0.22 micron MSI teflon membrane (Fisher Scientific). The filtrate was monitored by ultraviolet (UV) spectroscopy, at the wavelength of maximum absorbance of the model compound, to determine the concentration of the model not adsorbed by the aggregate. All experiments were performed at least in duplicate.

### Calculations

Langmuir plots of adsorption data were used for the determination of equilibrium constants, monolayer surface coverages, and Gibb's free energies of adsorption. The Langmuir equation can be stated as follows (7):

$$C/q = C/q_m + 1/bq_m \quad (1)$$

where

- $C$  = equilibrium solution concentration (mg/L),
- $q$  = equilibrium amount adsorbed (mg/g),
- $q_m$  = saturated monolayer amount (mg/g), and
- $b$  = constant related to strength of adsorption (unitless).

Parfitt and Rochester derived the Langmuir equation to describe adsorption data obtained from dilute solutions, which is given as follows (8):

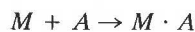
$$c/x = c/x_m + 1/(K - 1)x_m \quad (2)$$

where

- $c$  = mole fraction of solute concentration (unitless),
- $x$  = moles of solute adsorbed per unit mass of adsorbent (moles/g),

$x_m$  = molar monolayer of adsorbed solute per unit weight of adsorbent (moles/g), and

$K$  = equilibrium constant for the interaction of asphalt model  $M$  in cyclohexane with aggregate surface  $A$  to yield the product  $MA$ .



$$K = (MA)/(M)(A) \quad (3)$$

For strongly adsorbing solutes,  $K > 1$ , the Langmuir equation is simplified to the following:

$$c/x = c/x_m + 1/Kx_m \quad (4)$$

$K$  and  $x_m$  can be determined from the slope and intercept of a linear plot of  $c/x$  versus  $c$ . Determination of the equilibrium constant ( $K$ ) allows calculation of the Gibb's free energy of adsorption ( $\Delta G^\circ$  in joules) from the following relation:

$$\Delta G^\circ = -nRT (\ln K) \quad (5)$$

where

- $n$  = number of moles of solute adsorbed (mole),
- $R$  = universal gas constant 8.314 J/K mole, and
- $T$  = absolute temperature in K.

The amount of model compound adsorbed onto aggregate surface is determined from a calibration curve composed of adsorbate solutions with known concentrations for each asphalt model compound at its maximum absorbance wavelength. Beer's law was employed for the determination of solution concentrations before and after the adsorption experiments. Beer's law,  $A = abc$ , is valid for dilute solutions where  $A$  is the absorbance at a given wavelength (unitless),  $a$  the absorptivity (L/mole cm),  $b$  the path length of cell (cm), and  $c$  the concentration (moles/L). The absorbance values obtained in the adsorption experiments were converted to concentrations and the amount of compound adsorbed isothermally onto aggregate was determined from the following:

$$q_i = (C_o - C_i)V/M \quad (6)$$

where

- $q_i$  = amount adsorbed (mg/g aggregate),
- $C_o$  and  $C_i$  = concentrations of adsorbate before contact and after contact with aggregate (mg/L),
- $V$  = volume of adsorbate solution introduced into the system (L), and
- $M$  = mass of aggregate used (g).

### Adsorption and Desorption of Asphalt

The asphalts, AAD-1 (AR-4000), AAM-1 (AC-20), and AAK-1 (AC-30), and aggregates, RC-limestone, RH-greywacke, and RL-gravel, used in this study were obtained from the SHRP MRL. Aggregates were sized to -40 +80 mesh, washed with distilled water, dried at 150°C for 1 week and stored in a brown bottle before use. Chemical and physical properties of the aggregates and asphalts are given in Tables 1 and 2, respectively.

TABLE 1 PHYSICAL AND CHEMICAL PROPERTIES OF AGGREGATES

Property <sup>a,b</sup>	Aggregates				
	RC-limestone	RD-limestone	RH-greywacke	RJ-gravel	RL-gravel
<b>POROSITY</b>					
Avg. Pore Diam. ( $\mu\text{m}$ )	0.0611	0.0111	NA*	0.0151	0.0138
Total Pore Area ( $\text{m}^2/\text{g}$ )	2.548	1.465	NA	1.888	3.027
<b>WATER ABSORPTION</b>					
% Absorption	0.37	0.3	NA	0.7	0.9
<b>BULK SPECIFIC GRAVITY</b>	2.536	2.704	NA	2.625	2.568
<b>ACID INSOLUBLES</b>					
Insoluble Residue %	4.8	18.1	NA	99.2	88.2
<b>WATER INSOLUBLES</b>					
Water solubles %	2.4	1.9	NA	4.1	1.8
pH	9.47	9.12	NA	9.12	9.18
<b>SURFACE AREA (<math>\text{m}^2/\text{g}</math>)<sup>c</sup></b>	1.79	0.43	3.12	0.37	0.93
<b>MAJOR OXIDES</b>					
SiO <sub>2</sub> , %	6.49	16.4	66.0	76.5	63.1
Al <sub>2</sub> O <sub>3</sub> , %	1.23	2.28	10.4	12.2	4.66
Fe <sub>2</sub> O <sub>3</sub> , %	0.78	0.08	12.9	1.09	1.67
MgO, %	2.52	5.29	2.44	0.27	0.32
CaO, %	48.9	39.1	2.35	1.45	14.5
Na <sub>2</sub> O, %	0.24	0.16	2.57	2.91	0.92
K <sub>2</sub> O, %	0.22	1.16	0.99	4.31	1.72
Other, %	< 0.2	< 0.2	< 0.8	< 0.2	< 0.2
Loss of Volatiles, %	40.3	35.0	0.96	0.59	11.2
<b>LITHOLOGY</b>	100% Limestone	53.3% Shaly Limestone 26.8% Limestone 19.7% Arcenaceous Limestone	71.3% Micaceous Sandstone 11.2% Miscellaneous 10.9% Granite 6.6% Chert	47.4% Sandstone 28.4% Granite 23.7% Miscellaneous 0.4% Basalt	59.1% Chert 18.2% Arcenaceous Limestone 11% Granite 5.8% Miscellaneous

\*NA = Not Available

<sup>a</sup> Porosity, water absorption, bulk specific gravity, acid insolubles and water insoluble data were obtained from SHRP A-001.<sup>b</sup> Surface areas and major oxides were obtained from Western Research Institute in SHRP A-003B.<sup>c</sup> Surface area measurements were obtained by N<sub>2</sub> BET by WRI.

Toluene and methylene chloride, Fisher spectranalyzed, were dried with 4Å molecular sieves before use, and polyamine AS agent (M-AS-005-001) obtained from SHRP MRL was used as received. Distilled, deionized water was used in desorption studies.

Adsorption of asphalt from toluene solution onto aggregate was performed using a recirculating system that consisted of a thermo jacketed column containing aggregate through which a solution of toluene and asphalt was circulated repeatedly through a bed of aggregate. The column temperature was maintained at 25°C. Concentration changes of asphalt in solution were monitored after adsorption equilibrium of 7 hr by visible absorbance spectroscopy at 410 nm. Six independent columns that run in parallel, each containing an asphalt solution of specific concentration, were pumped by a microprocessor pump drive. The asphalt concentration of the initial solutions used to develop the isotherm ranged from 0.10 to 0.66 g/L. Desorption of asphalt from aggregate was achieved by introducing ~280 mmolar water after adsorption equilibrium was achieved. The amount of asphalt desorbed was monitored at 410 nm after 2 hr.

The concentration of the asphalt in solution after both adsorption and desorption was obtained using Beer's law. The equations used for calculating these amounts are

$$C/C_o = \text{Abs}/\text{Abs}_o$$

$$AW = V(C_o - C)$$

$$A = VC_o(\text{Abs}_o - \text{Abs})/W\text{Abs}_o$$

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

$$D_w = -V_w C(\text{Abs} - \text{Abs}_w)/W\text{Abs} \quad (7)$$

where

$C_o$  and  $C$  = initial and equilibrated asphalt solution concentrations (g/L),

$\text{Abs}_o$  and  $\text{Abs}$  = absorbances of initial and equilibrated solutions,

$A$  = amount of asphalt adsorbed per gram of aggregate (g/g),

$W$  = mass of aggregate used (g),

$V$  and  $V_w$  = initial and final solution volumes used for desorption (L),

$D_w$  = amount of asphalt desorbed per gram of aggregate (g/g),

$C_w$  = asphalt solution concentration after desorption (g/L), and

$\text{Abs}_w$  = absorbance of the extracted solution.

TABLE 2 PHYSICAL AND CHEMICAL PROPERTIES OF ASPHALTS

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	80.7
Hydrogen, %	10.8	11.2	10.2
Oxygen, %	0.9	0.5	0.8
Nitrogen, %	0.9	0.5	0.8
Sulfur, %	8.6	2.4	6.6
Vanadium, ppm	293	60	1427
Nickel, ppm	145	29	128
Caromatic, %	23.7	24.7	31.9
H <sub>aromatic</sub> , %	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 Groups			
Carboxylic Acids	0.011	0.013	0.000
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	0.027	0.070
Sulfoxides	trace	trace	trace
Pyrroles	0.168	0.110	0.157

### Asphalt and Antistripping Agent Systems

Two different asphalt adsorption experiments using AAD-1 asphalt were performed with AS agent: (a) asphalt from toluene solution was adsorbed onto RH-greywacke precoated with AS agent and (b) asphalt and AS agent were coadsorbed from a 3:1 with toluene/methylene chloride solution onto RH-greywacke. Methylene chloride was required to prevent precipitation of the AS agent. For comparison, AAD-1 asphalt was adsorbed and subsequently desorbed from both toluene and toluene-methylene chloride solution onto uncoated RH-

greywacke. Asphalt remaining on the aggregate surface was determined by subtracting the amount of asphalt desorbed from that originally absorbed.

For the first set of experiments, RH-greywacke was precoated with AS agent from methylene chloride in a batch system that was temperature controlled at 25°C and orbitally agitated at 250 rpm for 1 hr. Initial concentrations of AS agent in methylene chloride of 0.2–5.0 g/L were used to determine the adsorption isotherm; a saturation concentration of 4.3 g/L of AS agent in methylene chloride was selected for precoating the aggregate at a coating level of 7.8 weight per-

cent. RH-greywacke precoated with this AS agent was used for asphalt adsorption experiments from toluene followed by desorption with  $\sim 280$  mmolar water.

Coadsorption of asphalt and AS agent from the 3:1 toluene to methylene chloride solution was conducted at two different concentrations of AS agent: 4.05 g/L (corresponding with the chosen AS concentration for the precoated aggregate) and 0.1025 g/L (corresponding with that used in actual practice). Asphalt, at 0.66 g/L, was added to each of these solutions containing AS agents. As the concentrations of these initial solutions were diluted to perform the adsorption isotherms, the ratio of AS agent to asphalt remained constant.

Although the absorbance spectra of asphalt and AS agent were similar, a significant difference in their molar absorptivities was observed. The ratio of the absorptivity of asphalt to the absorptivity of the AS agent was  $\sim 30$  at 410 nm. Therefore, quantitative determination of adsorbed asphalt was based on a weight ratio of asphalt and AS agent. To determine the amount of asphalt adsorbed and desorbed during the coadsorption experiments, a calibration curve of the ratio of the amount of asphalt adsorbed to the amount of AS agent adsorbed versus the ratio of the initial concentration of AS agent (AS) to asphalt (ASP) was developed. This calibration curve resulted from a series of experimental observations and calculations using Beer's law. For a given solution with an initial concentration ratio of  $(AS)_o/(ASP)_o$ , the total absorbance of both asphalt and AS agent was measured. The absorptivity of the solution was determined by measuring the visible absorbance at 410 nm at different ratios of  $(AS)_o$  to  $(ASP)_o$ . To determine the amount of asphalt adsorbed onto aggregate introduced into the system, the following relationship was used:

$$AMT_{ASP} = AMT_{Tot} \left( \frac{a_{ASP}}{a_{Tot}} \right) \quad (8)$$

where

$AMT_{ASP}$  = amount of asphalt adsorbed onto the aggregate,

$AMT_{Tot}$  = total amount of asphalt and AS agent adsorbed that was obtained experimentally,

$a_{ASP}$  = absorptivity of asphalt at 410 nm obtained experimentally, and

$a_{Tot}$  = absorptivity of the asphalt and AS agent combined at 410 nm and measured as described above.

The amount of AS agent adsorbed ( $AMT_{AS}$ ) was obtained from the difference  $AMT_{Tot} - AMT_{ASP}$ . The quantities for the ratio of the  $AMT_{ASP}$  to  $AMT_{AS}$  were then calculated. Experimental points were generated at varying ratios of  $(AS)_o/(ASP)_o$  and used to produce a curve, Figure 1, of the ratio of amount adsorbed ( $AMT_{ASP}/AMT_{AS}$ ) versus the ratio of concentration of AS agent to concentration of asphalt  $[(AS)_o/(ASP)_o]$  that followed the equation

$$y = 16.6x^{-0.581} \quad (9)$$

where  $y$  is the ratio  $AMT_{ASP}/AMT_{AS}$  and  $x$  is the initial concentration ratio  $(AS)_o/(ASP)_o$ . When a coadsorption exper-

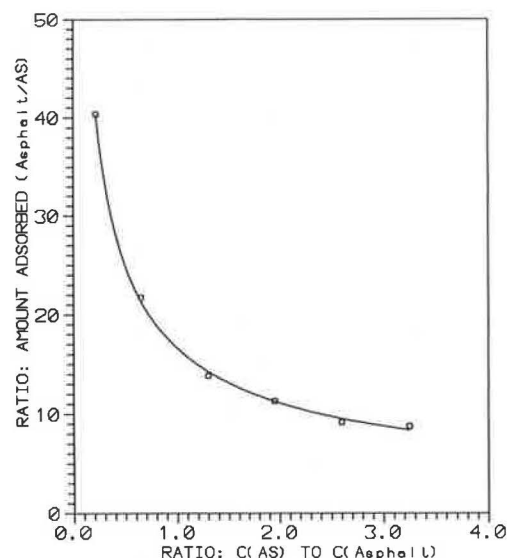


FIGURE 1 Adsorption ratio determination from solution concentration ratio.

iment was performed,  $(AS)_o/(ASP)_o$  was known and the ratio of  $AMT_{ASP}/AMT_{AS}$  was determined from Equation 9. Because the total amount of adsorption was known, the amount of asphalt and AS agent could be determined individually.

## RESULTS AND DISCUSSION

### Adsorption of Model Asphalt Compounds onto MRL Aggregates

The adsorption properties of seven model compounds were investigated on five MRL aggregates: RC-limestone, RD-limestone, RH-greywacke, RJ-gravel, and RL-gravel. Each model compound was chosen to represent key asphaltic components that have been reported to be present at the asphalt-aggregate interface (1,2). Benzoic acid was chosen as the model compound to represent carboxylic acids; phenylsulfoxide, to represent sulfoxides; 1-naphthol, phenols; phenanthridine, pyridinics; indole, pyrrolitics; 9-fluorenone, ketones; and naphthalene, aromatic species. All model compounds, because of their respective functionalities, exhibited absorbance characteristics in the same spectral region as asphalt.

Mineralogical characterization of the MRL aggregates used in these studies shows three compositionally different aggregate types (9,10), as shown in Table 1. RJ-gravel and RL-gravel are both mixtures of siliceous gravels consisting of igneous, metamorphic, and sedimentary rocks. RL-gravel contains a small percentage of limestone, thus distinguishing it from RJ-gravel. RC-limestone consists mainly of three major limestone groups: fine-grained crushed limestone, dolomitic limestone, and a significant amount of clay seams. RD-limestone consists of calcareous rocks rich in shale and quartz with small amounts of iron pyrite. The RH-greywacke is a sedimentary rock consisting of a mixture of clay, silt, sand, and rock fragments. These aggregates with different mineralogical, compositional, and acid-base behavior were chosen for testing with the model compounds. The surface areas of



the aggregates ranged in order of magnitude. RH-greywacke had the largest surface area, 3.12 m<sup>2</sup>/g, and RJ-gravel and RD-limestone possessed the least surface areas, 0.37 and 0.43 m<sup>2</sup>/g, respectively. The variety in the aggregate characteristics for the selected aggregates can be observed by comparing the differences in the percentage of water solubles, the percentage of acid insoluble residue, the percentage of volatiles loss, and the percentage of different oxide-containing compounds attributed to the different aggregates. Although the percentage of water solubles was similar (< 5 percent) for all the aggregates—except RH-greywacke, for which these particular physical constants were not determined—the percentage of acid insoluble residue for RL-gravel was more than 15 times greater than for RC-limestone and almost 5 times greater than RD-limestone. The solubility of limestone aggregates in acidic media indicated a strong preference for limestone for interactions with acidic asphalt models. The relatively high percentage of acid insoluble residue given for RL-gravel and RJ-gravel, 88.2 and 99.2 percent, respectively, indicated a lack of preference for acidic asphalt models.

The Langmuir adsorption model was applied to the adsorption data to describe the adsorption behavior of each functionality on each aggregate. Monolayer surface coverages, equilibrium constants, and Gibb's free energies of adsorption for each model compound-aggregate pair were obtained from Langmuir treatment of the adsorption data and are summarized in Table 3. RD-limestone exhibited poor adherence to the Langmuir model for almost all asphalt models with the exception of benzoic acid. RJ-gravel also responded unfavorably to Langmuir treatment for three asphalt models—benzoic acid, indole, and 9-fluorenone—as did RL-gravel with indole. Perhaps this behavior can be attributed to the heterogeneity of these particular aggregates surfaces that might have more than one type of bonding interaction site for these models. Although adsorption occurred for these compounds, and the Langmuir model was applied, not all Langmuir physical constants could be determined for these compounds.

Langmuir monolayer surface coverages ( $\mu\text{mole/g}$  and  $\mu\text{mole/m}^2$ ) for each asphalt model compound on each aggregate are presented in Table 3. Most model compound-

TABLE 3 COMPARISON OF PHYSICAL CONSTANTS DETERMINED FROM LANGMUIR EQUATION FOR SPECIFIC ASPHALT MODELS ADSORBED ON MRL AGGREGATES

Model/Aggregate	Monolayer Amount		Equilibrium Constant (K) $\times 10^{-5}$	Gibb's Free Energy ( $\Delta G^\circ$ ) (KJ/mole)	Correlation Coefficient
	$\mu\text{mole/g}$	$\mu\text{mole/m}^2$			
<b>Benzoic Acid</b>					
RC-limestone	4.65	2.61	3.87	-31.9	0.99
RD-limestone	1.97	4.59	4.09	-32.0	0.99
RH-greywacke	7.38	2.39	1.51	-29.5	0.99
RJ-gravel	2.23	6.02	---	---	0.99
RL-gravel	9.15	9.84	5.92	-32.9	0.99
<b>Phenylsulfoxide</b>					
RC-limestone	3.96	2.23	5.51	-32.8	1.00
RD-limestone	0.667	1.55	---	---	0.89
RH-greywacke	6.35	2.04	6.91	-33.3	1.00
RJ-gravel	8.62	23.27	2.16	-30.4	0.94
RL-gravel	6.33	6.81	2.05	-30.3	0.96
<b>1-Naphthol</b>					
RC-limestone	3.59	2.02	3.50	-31.6	1.00
RD-limestone	0.636	1.48	---	---	0.99
RH-greywacke	4.94	1.58	2.78	-31.1	1.00
RJ-gravel	1.46	3.93	4.44	-32.2	0.99
RL-gravel	3.40	3.65	2.78	-31.1	1.00
<b>Phenanthridine</b>					
RC-limestone	2.86	1.61	6.10	-33.0	1.00
RD-limestone	0.562	1.31	---	---	0.77
RH-greywacke	4.80	1.54	2.07	-30.3	1.00
RJ-gravel	2.53	6.83	1.18	-28.9	0.96
RL-gravel	4.55	4.89	2.86	-31.1	0.99
<b>Indole</b>					
RC-limestone	2.94	1.65	1.61	-29.7	0.93
RD-limestone	0.464	1.08	---	---	0.68
RH-greywacke	4.36	1.40	1.65	-29.8	0.99
RJ-gravel	0.095	0.256	---	---	0.72
RL-gravel	2.02	2.17	---	---	0.93
<b>9-Fluorenone</b>					
RC-limestone	1.70	0.957	17.5	-35.6	0.99
RD-limestone	0.323	0.751	---	---	0.83
RH-greywacke	3.06	0.980	1.84	-30.0	1.00
RJ-gravel	0.619	1.67	---	---	0.87
RL-gravel	3.63	3.90	6.21	-33.0	1.00

— Adsorption isotherm did not conform to Langmuir Equation, yielding a negative intercept that prevented calculation of K and  $\Delta G^\circ$ .

aggregate combinations were in good agreement with the Langmuir model as determined by the correlation coefficients. Correlation coefficients ranging between .68 and 1.00 were considered to be acceptable for the determination of Langmuir surface amounts considering the heterogeneous chemical compositions of actual aggregates that might allow for numerous and varied interactions. The adsorption behavior of indole on RD-limestone was the only asphalt model-aggregate combination that did not adhere to Langmuir monolayer analysis.

For any given aggregate tested with the seven asphalt model compounds (see Table 3), benzoic acid consistently produced the highest relative monolayer coverage ( $\mu\text{mole/g}$ ), with the exception of phenylsulfoxide and phenanthridine on RJ-gravel, which showed larger monolayer amounts. For the five aggregates tested, benzoic acid monolayer surface coverages ranged from 1.97 to 9.15  $\mu\text{mole/g}$  on RD-limestone and RL-gravel, respectively. In general, the lowest monolayer surface coverages ( $\mu\text{mole/g}$ ) were produced by indole and 9-fluorenone adsorption on all aggregates. Correction of the Langmuir asphalt model surface amounts for aggregate areas,  $\mu\text{mole/m}^2$ , produced slightly different results for the relative amounts of asphalt models adsorbed to aggregate surface. Very large surface amounts were observed for benzoic acid on RJ-gravel and RL-gravel at 6.02 and 9.84  $\mu\text{mole/m}^2$ , respectively. The largest of all monolayer surface coverages corrected for aggregate surface area was produced by phenylsulfoxide on RJ-gravel, 23.27  $\mu\text{mole/m}^2$ . Low, less than 1  $\mu\text{mole/m}^2$ , adsorption surface amounts were observed for 9-fluorenone on RC-limestone, RD-limestone, and RH-greywacke in addition to that observed for indole on RJ-gravel. The adsorption of indole on RD-limestone did not fit the Langmuir model; thus, the Langmuir monolayer surface amount was not determined. In general, indole and 9-fluorenone showed the lowest Langmuir monolayer surface coverages,  $\mu\text{mole/m}^2$ , for all aggregates tested. RJ-gravel and RL-gravel showed high Langmuir surface amounts,  $\mu\text{mole/m}^2$ , for all the asphalt models tested with the exception of indole. Although naphthalene, representing aromatic functionality, was tested as an asphalt model on all aggregates, adsorption was observed only on RJ-gravel yielding the smallest amount of surface coverage for any asphalt model-aggregate combination, 0.011  $\mu\text{mole/m}^2$ .

The strength of the interfacial bond between the model functionalities and the aggregate surfaces is represented by the Gibb's free energy values as listed in Table 3. Although all of the Gibb's free energy of adsorption values are similar, the most negative values and, hence, the strongest interfacial bonds were observed for 9-fluorenone on RC-limestone and RL-gravel, phenylsulfoxide on RH-greywacke, and phenanthridine on RC-limestone at  $-35.6$ ,  $-33.0$ ,  $-33.3$ , and  $-33.0$  KJ/mole, respectively. The strengths of interaction between 9-fluorenone and RC-limestone, RL-gravel, and RH-greywacke were relatively strong compared with other model compound-aggregate combinations. Langmuir treatment of benzoic acid on RH-greywacke, indole on RC-limestone and RH-greywacke, and phenanthridine on RJ-gravel produced the least free energy values at less than 30 KJ/mole. The differences in the free energy values of benzoic acid, phenanthridine, and 9-fluorenone on all aggregates may be indicative of variation in bonding sites or heterogeneity of the aggregates.

The equilibrium constants shown on Table 3 can be correlated to the extent of interaction between the model compound and the active sites on the aggregate surface. The equilibrium constant for benzoic acid on RL-gravel of  $5.92 \times 10^5$  as compared to  $1.51 \times 10^5$  for the same functionality on RH-greywacke indicates that benzoic acid interacted more with RL-gravel than RH-greywacke. Thus, for this investigation, each model-aggregate pair that interacted the most, as determined by the magnitude of the equilibrium constants, was as follows: benzoic acid and RL-gravel, phenylsulfoxide and RH-greywacke, 1-naphthol and RJ-gravel, phenanthridine and RC-limestone, indole and RC-limestone or RH-greywacke, and 9-fluorenone and RC-limestone. The largest equilibrium constant,  $17.5 \times 10^5$ , was observed for 9-fluorenone and RC-limestone. The smallest,  $1.18 \times 10^5$ , was observed for phenanthridine and RJ-gravel.

Because some of the adsorption data on the model compound-aggregate pairs showed poor adherence to Langmuir treatment, the relative affinities of the model compounds for each of the aggregates were determined by duplicate adsorption experiments, employing 1 and 2 g of aggregate, for each model compound-aggregate pair. The relative rankings of surface coverage, that is, relative affinities of model compounds for aggregates, are normalized and summarized in Table 4. Benzoic acid showed the greatest affinity for all aggregates ( $\mu\text{mole/m}^2$ ), with the exception of RJ-gravel, and naphthalene showed the least. Phenylsulfoxide was a good adsorber on all the aggregates. Indole usually was a poor adsorber. This method of affinity rankings (Table 4) shows good agreement with similar rankings achieved by Langmuir data ( $\mu\text{mole/m}^2$ ) with the exceptions presented by RD-limestone whereby Langmuir treatment shows 1-naphthol, phenylsulfoxide, and phenanthridine with different relative affinity rankings than those obtained by the empirical method devised for four sample measurements. A reversal in the rankings of benzoic acid and phenanthridine on RJ-gravel is also noted. These anomalies can be attributed to the heterogeneous nature of the aggregate.

#### Adsorption and Desorption Behavior of Asphalts on RH-Greywacke

The adsorption and desorption behavior of three different asphalts—AAD-1, AAM-1, and AAK-1—from toluene solution onto RH-greywacke should indicate the effect of their different chemical properties on the interaction and affinity of the asphalt with a given aggregate. The viscosities of the asphalts (Table 2) corresponded to AC-10, AC-20, and AC-30 for AAD-1, AAM-1, and AAK-1, respectively. AAD-1 and AAK-1 contained asphaltene contents of 23.0 and 21.1 percent, respectively, and AAM-1 possessed a lower asphaltene content of 3.9 percent. AAM-1 contained higher amounts of polar and naphthene aromatics and a lower amount of saturates than did either AAD-1 or AAK-1.

AAD-1 and AAK-1 showed a substantial amount of self-assembly, which is an attraction of asphalt molecules to one another. Although AAM-1 did not show obvious self-assembly, it contained large molecular weight components (11, Pribanic 1990, personal communication). Some of the differences observed among the asphalts were small. The ar-

TABLE 4 RELATIVE AFFINITY RANKINGS OF SURFACE COVERAGE OF MRL AGGREGATES BY MODEL ASPHALT MODELS ( $\mu\text{mole/g} = \mu\text{mole/m}^2$ ,  $\text{mg/g} = \text{mg/m}^2$ )

Asphalt Model (Functionalities)	RC-limestone			RL-gravel			RH-greywacke			RJ-gravel			RD-limestone		
	$\text{mg/m}^2$	$\mu\text{mole/m}^2$		$\text{mg/m}^2$	$\mu\text{mole/m}^2$		$\text{mg/m}^2$	$\mu\text{mole/m}^2$		$\text{mg/m}^2$	$\mu\text{mole/m}^2$		$\text{mg/m}^2$	$\mu\text{mole/m}^2$	
		*	**		*	**		*	**		*	**		*	**
Benzoic Acid (Carboxylic Acids)	2	1	1	1	1	1	2	1	1	3	2	3	1	1	1
Indole (Pyrrolics)	5	4	4	6	6	6	6	5	5	7	7	6	6	5	5
9-Fluorenone (Ketones)	6	6	6	4	4	4	5	6	6	5	5	5	5	6	6
1-Naphthol (Phenolics)	4	3	3	5	5	5	4	3	3	4	4	4	4	4	3
Phenanthridine (Pyridinics)	3	5	5	3	3	3	3	4	4	2	3	2	3	2	4
Phenylsulfoxide (Sulfoxides)	1	2	2	2	2	2	1	2	2	1	1	1	2	3	2
Naphthalene (Aromatics)	—	—	—	—	—	—	—	—	—	6	6	7	—	—	—

— No adsorption occurred

\* Mass basis, average of 4 adsorption experiments using a maximum 2 g of aggregate.

\*\* Ranking determined from Langmuir treatment.

omatic hydrogen content determined by proton nuclear magnetic resonance (NMR) using the calculation of  $H_{\text{aromatic}} / (H_{\text{aromatic}} + H_{\text{aliphatic}})$  yielded aromatic hydrogen contents between 6.5 to ~6.8 percent for the three asphalts (Jennings 1990, personal communication). The aromatic carbon content measured by  $^{13}\text{C}$  NMR and calculated by the equation of  $C_{\text{aromatic}} / (C_{\text{aromatic}} + C_{\text{aliphatic}})$  showed larger differences and ranked AAD-1 at ~23.7 percent, AAM-1 at ~24.7 percent and AAK-1 at 31.9 percent. A substitution index, defined as the ratio of aromatic carbon to aromatic hydrogen, provides an indication of the number of aromatic carbons linked to hydrogens compared with those linked to other types of carbons. The lower the number obtained, the greater the correspondence between the numbers of aromatic carbons and aromatic hydrogens present, and the lesser the substitution. The higher the number obtained, the greater the substitution. AAD-1 showed the least substitution at a ratio value of 2.2; AAM-1 yielded 2.7; the most substituted was AAK-1 at 3.1 (Jennings 1990, personal communication).

The sulfur content of AAD-1 at 8.6 percent was nearly four times that of AAM-1, although the vanadium content of AAK-1 at 1,427 ppm was four times greater than AAD-1 and 20 times greater than AAM-1 (Table 3). When the amount of heteroatoms (O, S, N) present was calculated as the ratio of heteroatoms per asphalt molecule, AAK-1 gave 3.1; AAD-1, 2.65; and AAM-1, 1.8 (Jennings 1990, personal communication).

The chemical composition and characteristics of the asphalts used in this study varied considerably. Experiments were performed adsorbing each of the asphalts from toluene solution onto RH-greywacke to evaluate the effect of their chemistry on adsorption and desorption behavior. After asphalt adsorption onto aggregate, water was added to the system. After adsorption and desorption were completed, the

amount of asphalt present in solution was determined and the amount of asphalt on the aggregate was calculated.

The adsorption and desorption behavior of the three asphalts presented in terms of the amount of asphalt adsorbed per gram of RH-greywacke as a function of the equilibrium concentration of the solution is shown in Figure 2. The points shown are the data points obtained for the different asphalt-aggregate pairs. The solid line represents the best-fit curve obtained by fitting the data points with a polynomial. The shape of the adsorption isotherms was different with AAD-1 showing more adsorption at lower equilibrium concentration

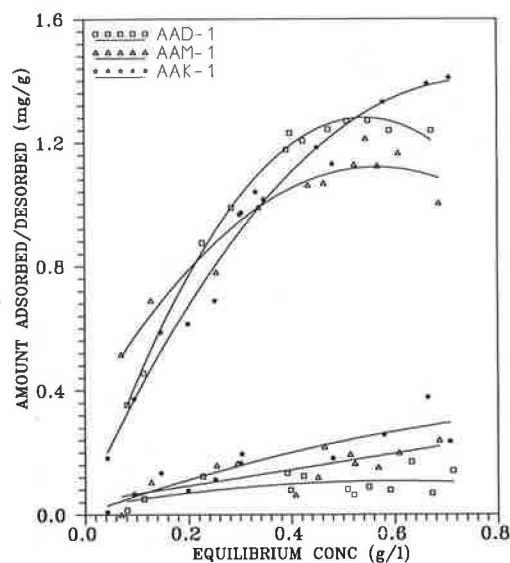


FIGURE 2 Adsorption and desorption of asphalts onto RH-greywacke.



but achieving a lower saturation amount than did AAK-1. AAM-1 showed the least adsorption at all equilibrium concentration levels. AAD-1 and AAM-1 asphalts displayed a maximum in adsorption behavior between 0.5 and 0.7 g/L equilibrium concentration; AAK-1 adsorption appeared to be still rising. At 0.6 g/L equilibrium concentration, the adsorption of the asphalts ranked at  $AAK-1 > AAD-1 > AAM-1$ .

Desorption of the adsorbed asphalt with water resulted in the behavior given in the desorption isotherms presented in Figure 2. Water, introduced at  $\sim 280$  mmolar, was immiscible with toluene. The scatter in the points obtained from the desorption data was larger than that observed from the adsorption data, which was partially caused by the presence of a two-phase system after desorption. AAD-1 lost the least asphalt from the RH-greywacke surface, followed by AAM-1 and then AAK-1. The asphalt was reduced by 9 percent for AAD-1, 20 percent for AAK-1, and 17 percent for AAM-1. The amount of asphalt retained on the aggregate was determined by subtracting the amount desorbed from the amount adsorbed. AAD-1 and AAK-1—with the higher heteroatom contents, metals content, and asphaltenes—retained more asphalt after desorption than did AAM-1, the most hydrocarbonaceous and least polar of the asphalts; however, the differences were not large on RH-greywacke. Other aggregates must be tested to determine the sensitivity of asphalt adsorption behavior to chemical composition.

#### Adsorption and Desorption Behavior of AAD-1 on Three Aggregates

The adsorption behavior of AAD-1 asphalt on three aggregates—RH-greywacke, RC-limestone, and RL-gravel—was determined (Figure 3). The surface areas of these three aggregates as measured by  $N_2$  BET are quite different: RH-greywacke had  $3.12 \text{ m}^2/\text{g}$ ; RC-limestone,  $1.78 \text{ m}^2/\text{g}$ ; and RL-gravel,  $0.93 \text{ m}^2/\text{g}$ . Because of these rather substantial differences, the adsorption and desorption behavior is plotted

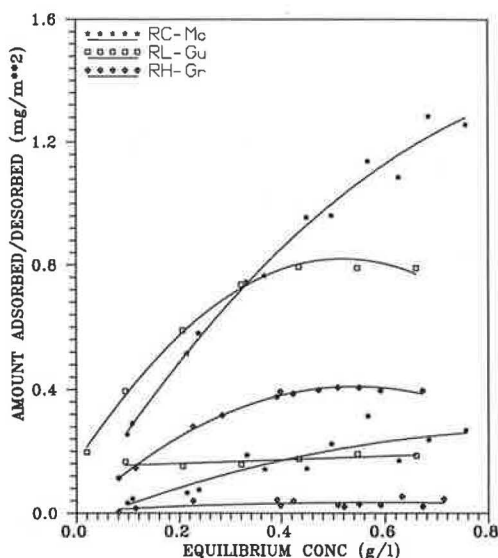


FIGURE 3 Adsorption and desorption of AAD-1 asphalt onto aggregates.

on a basis of mass of asphalt adsorbed per unit surface area of the aggregate ( $\text{mg}/\text{m}^2$ ) rather than per gram. Placing the adsorption on a surface area basis assumes that the BET surface area represents active sites of an aggregate that participate most actively in the adsorption of asphalt. Although this assumption may not be exactly correct, it is likely that the presence of a larger surface area results in a greater number of active sites. This basis changes the ranking of asphalt adsorption when plotted on a mass basis because of the differences in the surface areas among the aggregates.

The shape of the isotherms as well as the amount of asphalt adsorbed was substantially different for the three aggregates (Figure 3). Both RH-greywacke and RL-gravel leveled off and showed definite plateaus at the higher equilibrium concentrations tested. The asphalt adsorption for RL-gravel rose more steeply than that for either RH-greywacke or RC-limestone. When the aggregates are compared on an equivalent surface area or active site basis, AAD-1 had much lower affinity for RH-greywacke than it did for either RC-limestone or RL-gravel. At high-equilibrium concentrations, AAD-1 showed a much higher affinity for RC-limestone than RL-gravel. Because the primary goal was to observe differences among the adsorption behavior of the different asphalt-aggregates, the high concentration levels required to achieve the saturation amount on RC-limestone were not employed.

The desorption of AAD-1 asphalt by water from the three aggregates, also given in Figure 3, showed the different water sensitivities of each asphalt-aggregate combination. AAD-1 desorbed the most from RC-limestone and the least from RH-greywacke; RL-gravel was intermediate. The desorption behavior of AAD-1 varied considerably, depending on the aggregate type. The ranking of the amount of asphalt remaining on the aggregate surfaces after water desorption was the same as that for the initial adsorption; however, the total amount remaining was less. A decrease in the asphalt amount adsorbed was 20 percent for RC-limestone, 22 percent for RL-gravel, and 9 percent for RH-greywacke. Thus, the RL-gravel and RC-limestone showed more than twice the water sensitivity of RH-greywacke.

#### Effect of AS Agent on AAD-1 Adsorption

The effect of AS agent on the adsorption of AAD-1 asphalt on RH-greywacke was examined in two ways: (a) adsorption and desorption experiments with AAD-1 and RH-greywacke precoated with AS-agent, and (b) coadsorption of asphalt and AS agent from solution on RH greywacke. Two different concentrations of AS agent were used, one low and the other high. Toluene was used as the solvent for the first method and a 3:1 toluene-to-methylene-chloride solution was used for the second.

The adsorption behavior of the AAD-1 asphalt in three experiments involving AS agent plus that of AAD-1 asphalt on RH-greywacke, in the absence of AS agent and in toluene, is presented in Figure 4. The amount of AAD-1 adsorbed ranked according to the conditions of no AS agent present, coadsorption with a low concentration of AS agent, adsorption onto precoated RH-greywacke, and coadsorption with a high concentration of AS agent. The amount of AS agent used for adsorbing from solution in the precoated experiment

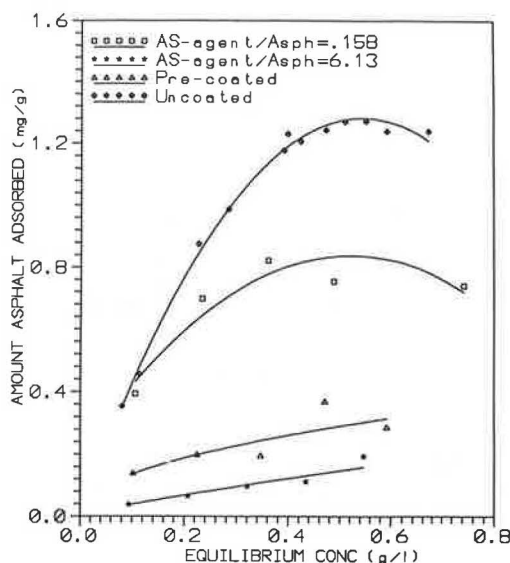


FIGURE 4 Adsorption of AAD-1 asphalt onto RH-greywacke using AS agent.

and in the coadsorption experiment with a high AS agent concentration was equivalent. In all cases in which AS agent was present in the system, the amount of asphalt adsorption decreased. The precoated aggregate was not as detrimental to asphalt adsorption as was the coadsorption with the high concentration of AS agent present. A substantial difference was observed between the AAD-1 adsorption low and high levels of AS agent. Table 5 compares the amount of AAD-1 and AS agent adsorbed at specific equilibrium concentrations of asphalt. AS agent appeared to compete for active sites on the aggregate surface in the coadsorption experiments, thereby limiting the amount of AAD-1 asphalt that was adsorbed.

Precoated RH-greywacke and the high concentration of AS in the coadsorption experiment showed the least amount of asphalt desorbed by water (Figure 5). The asphalt adsorbed individually and the asphalt coadsorbed with a low concentration of AS agent were more readily desorbed by water. AS agent from the high-concentration AS agent coadsorption was removed from the aggregate surface by water more readily than that from the low-concentration AS agent coadsorption. A comparison of the desorption data at six different equilibrium concentrations of asphalt, presented in Table 5, shows a significant solvent effect on asphalt desorption. Approximately 10 percent more asphalt was desorbed by water when methylene chloride was combined with toluene than when toluene was the sole solvent.

The AS agent in the asphalt-aggregate system, regardless of whether it was precoated or coadsorbed, affected the amount of asphalt adsorption on the aggregate. The more AS agent present, the greater the effect. If the total amount of asphalt adsorbed is the most important factor in bonding asphalt to aggregate, then AS agent interferes with that phenomenon. If the AS agent promotes stronger bonding through a lesser quantity of asphalt, then the AS agent may be beneficial to the longevity and water resistivity of the system. The ranking of the amount of asphalt remaining on RH-greywacke after water desorption was the same as it was for the initial adsorption. The effectiveness of the AS agent for retaining as-

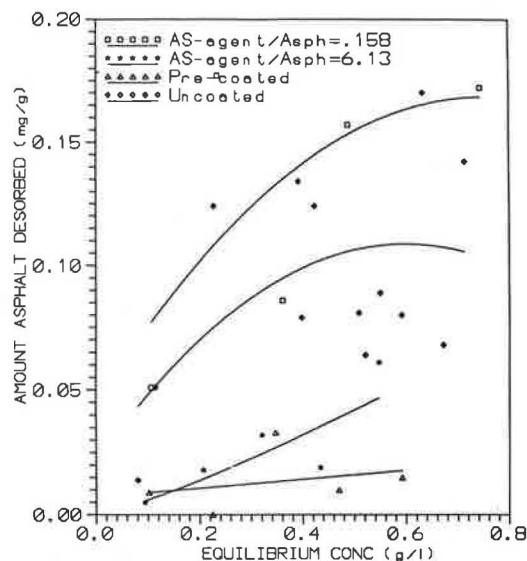


FIGURE 5 Desorption of AAD-1 asphalt from RH-greywacke using AS agent.

phalt in the presence of water ranked according to the following order: precoated aggregate at 6.5 percent desorption > low concentration of AS agent at ~20 percent desorption > high concentration of AS agent at ~30 percent.

## SUMMARY AND CONCLUSIONS

The adsorption and desorption behavior of asphalts varied according to their chemical compositions as evidenced by their different isotherm shapes and adsorption amounts on RH-greywacke. Different chemical functional groups representative of heteroatomic-containing groups in asphalt showed different affinities and adsorption amounts. Benzoic acid and phenylsulfide had the highest adsorption affinity, followed by such species as phenanthridine, fluorenone, and naphthol. Low affinity was shown by the least polar species, indole and naphthalene. Different aggregates showed varied adsorption amounts for the same asphalt, indicating that aggregate-asphalt pairs have unique interactions between the active sites on the surface of the aggregate and the composition of the asphalt. A similar behavior was observed between the asphaltic models and five aggregates. Some aggregates adsorbed considerably more material than others, whereas some aggregates had more affinity for particular polar functional groups than others. Introduction of AS agent into the system reduced the amount of asphalt adsorbed. Precoating of the aggregate surface by AS agent decreased both the adsorption and desorption of asphalt.

## RECOMMENDATIONS

Characterization of the aggregates by evaluating the adsorption behavior of models that represent specific functionalities provides a good measure of the reactivity of different aggregate surfaces. This reactivity measure may be applicable to asphalt systems and provide a predictive means for matching

TABLE 5 ASPHALT AND AS AGENT ADSORPTION AND DESORPTION BEHAVIOR  
ON RH-GREYWACKE

	Concentration of Asphalt (g/L)					
	0.1	0.2	0.3	0.4	0.5	0.6
<b>Adsorption (mg/g)</b>						
<b>Asphalt</b>						
No AS (Toluene)	0.426	0.769	1.024	1.192	1.273	1.266
No AS (MeCl <sub>2</sub> + Tol)	0.418	0.714	0.940	1.095	1.180	1.195
Low AS	0.420	0.595	0.723	0.804	0.837	0.823
High AS	0.038	0.068	0.096	0.122	0.148	0.172
Precoated	0.129	0.173	0.205	0.232	0.255	0.275
<b>AS Agent</b>						
Low AS	0.007	0.010	0.012	0.013	0.013	0.013
High AS	0.006	0.012	0.016	0.021	0.025	0.029
<b>Desorption (mg/g)</b>						
<b>Asphalt</b>						
No AS (Toluene)	0.048	0.070	0.087	0.102	0.106	0.109
No AS (MeCl <sub>2</sub> + Tol)	0.027	0.084	0.135	0.180	0.220	0.254
Low AS	0.075	0.102	0.124	0.141	0.154	0.163
High AS	0.005	0.015	0.025	0.035	0.045	0.055
Precoated	0.009	0.011	0.013	0.014	0.016	0.018
<b>AS Agent</b>						
Low AS	0.002	0.001	0.002	0.003	0.003	0.003
High AS	0.001	0.002	0.004	0.006	0.007	0.009
<b>Remainder (mg/g)</b>						
<b>Asphalt</b>						
No AS (Toluene)	0.378	0.699	0.937	1.090	1.167	1.157
No AS (MeCl <sub>2</sub> + Tol)	0.391	0.630	0.805	0.915	0.960	0.941
Low AS	0.345	0.493	0.599	0.663	0.683	0.660
High AS	0.033	0.053	0.071	0.087	0.103	0.117
Precoated	0.120	0.162	0.192	0.218	0.239	0.257
<b>AS Agent</b>						
Low AS	0.005	0.009	0.010	0.010	0.010	0.010
High AS	0.005	0.010	0.012	0.015	0.018	0.020
<b>% Desorbed</b>						
<b>Asphalt</b>						
No AS (Toluene)	11.3	9.1	8.5	8.6	8.3	8.6
No AS (MeCl <sub>2</sub> + Tol)	6.5	11.8	14.4	16.4	18.6	21.3
Low AS	17.9	17.1	17.2	17.5	18.4	19.8
High AS	13.2	22.1	26.0	28.7	30.4	32.0
Precoated	7.0	6.4	6.3	6.0	6.3	6.5
<b>AS Agent</b>						
Low AS	28.6	10.0	16.7	23.1	23.1	23.1
High AS	16.7	16.7	25.0	28.6	28.0	31.0

asphalt with aggregate. Determining the adsorption and desorption behavior of asphalt on aggregate provides a direct means of evaluating the interaction between the asphalt-aggregate pairs. These methods lay the groundwork for a simple laboratory test evaluating specific asphalt-aggregate interactions. More experiments are under way to evaluate the applicability of these tests to a wide variety of asphalt-aggregate systems.

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