

Influence of Aggregate Chemistry on the Adsorption and Desorption of Asphalt

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Asphalt-aggregate interactions were investigated by evaluating the adsorption and desorption of aged and unaged asphalts on four aggregates: limestone, greywacke, gravel, and basalt. The aggregate composition and surface chemistry had a greater effect on the adsorption and desorption characteristics of the asphalt-aggregate pair than the properties of the asphalt did. Adsorption and desorption isotherms were fitted to the Langmuir model and yielded predicted monolayer amounts, equilibrium constants for adsorption, and Gibbs free energy of adsorption. The Gibbs free energies were evaluated in terms of the principles of soil mechanics, which showed that water in the voids can be drawn to the asphalt-aggregate interface at relative humidities of 99 percent or above. Estimates of minimum tensile strength ratios were determined from Gibbs free energies and the extrapolated measured enthalpy values. The presence of water at the interface reduces the Gibbs free energy values between the asphalt and aggregate, thereby reducing the tensile strength and resistance to debonding fracture.

The interaction of asphalt with aggregate is governed by the chemistry and physical properties of the materials. The chemistry and composition of the asphalt determine the types of chemical compounds available for bonding. The surface chemistry and morphology of the aggregate provide the electrostatic and Lewis acid and base active sites available for interaction. When coated on the aggregate surface, asphalt interacts with these active sites through electrostatic and dipole interactions as well as by induced dipole interactions.

Asphalt contacts aggregate under high temperature and well-agitated conditions during the hot-mix process. The asphalt is readily coated on the aggregate because, under these conditions, the asphalt is a flowing liquid and is able to contact the irregular surfaces of the aggregate. As the asphalt-aggregate mix is taken to the road site and compacted, the mix cools, the asphalt hardens, and the mix sets. At this point, the asphalt molecules are no longer fluid. The asphalt is interspersed with a variety of aggregate sizes ranging from over $\frac{1}{2}$ in. to fines. Hence, the asphalt molecules become fixed in an environment that is strongly influenced by the aggregate chemistry. Changes that could occur at this point result from oxidation, stress, and the effects of water.

Specific interaction between asphalt and aggregate in the laboratory can be observed by many different chemical and analytical techniques (1-3). Liquid phase adsorption provides a means of contacting asphalt with aggregate by using the solvent as a dispersing medium instead of the temperature of

the hot-mix process to eliminate associations among asphalt molecules. The solvent tends to dissociate intermolecular bonding in the asphalt and yields molecules free to diffuse and interact with the aggregate at room temperature. Evaluation of model components representative of asphalt in both their adsorptive behavior onto aggregate and their desorptive behavior from aggregate gives information on the types of interactions that occur (4). Using asphalt size or component fractions yields even a better indication of the affinity of these components types (5).

This research investigated the adsorptive and desorptive behavior of three asphalts onto four different aggregates from the Strategic Highway Research Program (SHRP) Materials Reference Library (MRL). The adsorption experiments were performed with unaged asphalts and with the same asphalts aged in a thin-film oven. Adsorption isotherms were prepared after each adsorption experiment. The adsorbed asphalt was then desorbed by a small amount of water introduced into the system, and desorption isotherms were obtained. The amount of asphalt desorbed was subtracted from the amount initially adsorbed, yielding an isotherm of net adsorption—the amount of asphalt remaining on the surface of the aggregate. Each of the isotherms, adsorption and desorption, was treated by the Langmuir model to obtain the Gibbs free energy of adsorption.

The immediate interest in the degree to which an asphalt is adsorbed on and desorbed from the surface of an aggregate is related to questions about stripping aggregates: What are the mechanisms of stripping? Can the likelihood of stripping on a given aggregate and by what mechanism it occurs be anticipated from simple adsorption and desorption measurements made with aged and unaged asphalts on different aggregates? The measurements made on the combinations of three asphalts on four aggregates reported herein lead to some encouraging answers to these questions.

EXPERIMENTAL

Materials

The asphalts obtained from SHRP were three different viscosity grades from three different sources: AAD-1 (AR-4000) from California, AAM-1 (AC-20) from West Texas, and AAK-1 (AC-30) from Venezuela. The asphalts were used as unaged and as aged asphalts after being heated in the thin-film oven for 5 hr at 163°C. The properties of the three unaged asphalts are presented in Table 1. The aggregates represent a wide variety of geologic origin including a limestone (RC), a grey-

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TABLE 1 Chemical and Physical Properties of Asphalts¹

Asphalt	AAD-1	AAK-1	AAM-1
Grade	AR-4000	AC-30	AC-20
Viscosity			
140°F, poise	1055	3256	1992
275°F, cst	309	562	569
Ductility, cm			
(39.2°F, 1cm/min)	150+	27.8	4.6
Component Analysis, %			
Asphaltenes (n-heptane)	23.0	21.1	3.9
Asphaltenes (isooctane)	3.4	2.8	NA ²
Polar Aromatics	41.3	41.8	50.3
Naphthene Aromatics	25.1	30.0	41.9
Saturates	8.6	5.1	1.9
Elemental Analysis			
C %	81.6	83.7	86.8
H %	10.8	10.2	11.2
O %	0.9	0.8	0.5
N %	0.9	0.7	0.6
S %	6.9	6.4	1.2
V ppm	293	1427	60
Ni ppm	145	128	29
C Aromatic, %	23.7	31.9	24.7
H Aromatic, %	6.8	6.8	6.5
Molecular Wt.	700	860	1300
IEC Separations			
Strong Acid	26.1	18.7	13.7
Strong Base	7.8	8.0	10.4
Weak Acid	7.8	8.6	10.0
Weak Base	5.5	7.5	9.1
Neutral	51.7	52.5	53.4
SEC Fraction, MW			
1	7000	10000	4600
2	2200	1700	1700
3	1200	1000	1100
4	700	650	810
5	470	410	600
6	360	340	480
Infrared Functional Group Analysis			
Carboxylic Acid	0.011	0.013	0.000
Acid Salts	0.000	0.000	0.000
Acid Anhydrides	0.000	0.000	0.000
Quinolines	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

¹Abstracted from SHRP Report on Asphalt Properties.²NA = not available

wacke (RH), a basalt (RK), and a chert gravel (RL). The aggregates were prepared for the adsorption studies by being sized to -40 to 80 mesh, washed with distilled water until all dust was removed, dried at 150°C for 1 week, and stored away from light. Before use, the aggregate was dried again at 150°C for 24 hr, allowed to cool in a desiccator, and then loaded

into the adsorption column. The physical and mineralogical properties of the asphalts are presented in Table 2. Toluene, spectranalyzed from Fisher, was used as the solvent for the adsorption study. The toluene was dried with activated molecular sieves before being used. Distilled and deionized water was used in the desorption studies.

Asphalt Adsorption and Desorption

The adsorption and desorption of asphalt from toluene solution onto aggregate used a recirculating system of a temperature-controlled column and a peristaltic pump. The column contained aggregate through which the toluene solution flowed. The column temperature was maintained at 25°C for the duration of the experiment. Concentration changes of the asphalt were monitored by visible spectroscopy set at 410 nm, where the absorbance of the asphalt solution was measured. The asphalt concentrations of the initial solutions used to develop the adsorption isotherm ranged from 0.10 to 0.70 g/L. Six independent columns were run in parallel, each containing a different initial concentration of asphalt. After 7 hr of adsorption, the concentration of the asphalt in the solution was determined by application of Beer's law:

$$A = abc$$

where

- A = visible absorbance,
- a = absorptivity,
- b = cell path length, and
- c = concentration of asphalt in solution.

Asphalt was desorbed from the aggregate by introducing distilled and deionized water at ~280 mmolar, which equaled about 134 μ L in 27 ml of toluene. After 2 hr, the amount of asphalt desorption leveled out, and the amount of desorption was determined by measuring the amount of asphalt in the toluene solution.

The concentration of asphalt in solution after both adsorption and desorption was obtained using the following equations:

Adsorption:

$$C/C_o = A/A_o$$

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

$$Asp = VC_o(A_o - A)/WA_o$$

Desorption:

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

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

TABLE 2 Physical Properties of Aggregates¹

Sample	RC-Limestone	RH-Greywacke	RK-Basalt	RL-Gravel
SiO ₂	6.49	66.0	50.1	63.1
Al ₂ O ₃	1.23	10.4	13.7	4.66
Fe ₂ O ₃	0.78	12.9	15.0	1.67
MgO	2.52	2.44	6.88	0.32
CaO	48.9	2.35	10.3	14.5
Na ₂ O	0.24	2.57	2.25	0.92
K ₂ O	0.22	0.99	0.62	1.72
TiO ₂	0.03	0.53	1.48	0.09
P ₂ O ₅	<0.05	0.13	0.22	0.05
MnO ₂	<0.02	0.20	0.21	<0.02
LOV	40.3	0.96	-0.36	11.2
	100.71	99.47	100.4	98.23
Surface Area, ² m ² /g	1.78	3.12	17.4	0.93
Pore Volume, cc/g				
> 3000 Å	0.0099	0.0128	0.0079	0.0010
500 - 3000 Å	0.1085	0.0905	0.0289	0.0104
< 500 Å	0.0045	0.0023	0.0031	0.0012
Acid Insolubles, %	7.9	92.1	90.1	85.3
Water Solubles, %	8.1	9.7	7.4	9.3
Lithology, %	100 Limestone	71.3 Micaceous Sandstone 11.2 Misc. 10.9 Granite 6.6 Chert	94.4 Basalt 4.5 Misc. 0.6 Sandstone	59.1 Chert 18.2 Arenaceous Limestone 11 Granite 5.8 Misc.

¹Abstracted from SHRP Report on Aggregate Properties.²for mesh size -35 +50

where

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

A_o and A = absorbances of initial and equilibrated solutions;

Asp = amount of asphalt adsorbed per gram of aggregate (g/g);

W = mass of aggregate used (g);

V = solution volume used for adsorption;

V_w = solution volume 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

A_w = absorbance of the extracted solution.

Calculations of Experimental Data

The Langmuir model was fitted to the adsorption, desorption, and net adsorption data in order to determine equilibrium constants, monolayer surface coverage, and Gibbs free energy of adsorption. The Langmuir equation used to obtain the monolayer coverage of the asphalt on the aggregate was in the following form (6):

$$C/q = C/q_m + 1/bq_m$$

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 the strength of adsorption (unitless).

Parfitt and Rochester (7) applied the Langmuir equation to the adsorption of dilute solution onto solids as given in the following:

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

where

c = mole fraction of the solute concentration (unitless),

x = moles of solute adsorbed per unit weight of adsorbent (moles/g),

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

K = equilibrium constant for the following adsorption or desorption reaction (unitless).



where

M = asphalt molecule,

A = aggregate, and

$M \cdot A$ = adsorbed asphalt molecule.

For strongly adsorbing solutes, $K \gg 1$, yielding a simplification of the Langmuir equation:

$$c/x = c/x_m + 1/Kx_m$$

K and x_m are determined from the slope and intercept of a linear plot of c/x versus c . The Gibbs free energy of adsorption (ΔG) is then calculated from the following equation:

$$\Delta G = -nRT(\ln K)$$

where

- n = number of moles of solute adsorbed (mole),
- R = universal gas constant (8.3143 J/K-mole), and
- T = temperature in Kelvin.

The units for the Gibbs free energy of adsorption are in Joules [or kilo-Joules (KJ)] per mole of the solute. The Gibbs free energy of adsorption is part of the total energy with which the asphalt is attached to the aggregate surface and carries a negative sign. This is expected, because it acts as the driving potential in the flow of water and water vapor through unsaturated soils, and it also furnishes the energy gradient that attracts water to the interface of the asphalt and aggregate. The potential energy driving water flow is normally expressed as a specific energy (e.g., gm-cm/gm or ft-lb/lb) or feet of head. To convert the Gibbs free energy of the asphalt-aggregate interface (in KJ/mole) into a potential that is specific to water or water vapor, it must be multiplied by the following conversion factors:

$$\Delta G \frac{\text{gm-cm}}{\text{gm}} = \frac{\Delta G \left(\frac{\text{KJ}}{\text{mole}} \right) \times 10.203 \times 10^6 \frac{\text{gm-cm}}{\text{KJ}}}{18.02 \frac{\text{gm}}{\text{mole}} (\text{water}) \times 981}$$

A potential that is specific to a particular asphalt must use the molecular weight in gm/mole of that asphalt.

The total energy that bonds the asphalt to the aggregate surface is that algebraic sum of the enthalpy (ΔH) and the negative of the Gibbs free energy ($-\Delta G$), in accordance with the following thermodynamic relation:

$$T\Delta S = \Delta H - \Delta G$$

where

- T = absolute temperature,
- ΔS = change in entropy,
- ΔH = change in enthalpy, and
- ΔG = change in Gibbs free energy.

Measurements of enthalpy have been made at 140°C by Curtis et al. (8) and recorded in units of mcal per gm, which can be converted into gm-cm/gm by

$$\Delta H \frac{\text{gm-cm}}{\text{gm}} = \Delta H \frac{\text{mcal}}{\text{gm}} \times 4.19 \times 10^{-6} \frac{\text{KJ}}{\text{mcal}} \times 10.203 \times 10^6 \frac{\text{gm-cm}}{\text{KJ}}$$

Because the adsorption tests were made at 25°C and the enthalpy (also called bonding energy) tests were made at 140°C, one measurement had to be converted to the same temperature as the other. The conversion was made approximately by multiplying the enthalpy at 140°C by the ratio of absolute temperature in Kelvin (298/413).

To provide an even more familiar point of reference, the potential "heads" expressed in gm-cm/gm may also be expressed as the pressure (or tensile stress) generated by a column of water by multiplying by 1.422×10^2 psi/cm.

There are two mechanisms of stripping that are suggested by the data and the interpretations presented. In both cases, water is drawn from the air voids through the asphalt surrounding the aggregate and onto the asphalt-aggregate interface, decreasing the size of the Gibbs free energy and diminishing the strength of the bond between the asphalt and the aggregate.

In one mechanism the asphalt is pulled free of the aggregate surface by tensile stresses in the asphalt generated by traffic or environmental stresses. In the other mechanism repeated tensile stresses in the asphalt initiate and propagate a debonding crack along the asphalt-aggregate interface. The critical material property that governs whether such a debonding crack can occur is Γ , the strain energy storage density of the crack surface by which the strain energy released by the growth of the crack is stored on the surface of the newly created crack surface. This quantity can be determined by dividing the Gibbs free energy (gm-cm/gm) by the specific surface area of the aggregate (cm²/gm) as shown by Maquis and Barquins (9).

$$\Gamma \frac{\text{gm-cm}}{\text{cm}^2} = - \frac{\Delta G \frac{\text{gm-cm}}{\text{gm}}}{\text{SSA} \frac{\text{cm}^2}{\text{gm}}}$$

where SSA is the specific surface area of the aggregate.

Experimental Design

The experimental design used in these experiments was a full factorial experiment with three factors: asphalt, aggregate, and aging of asphalt. The response variables observed were adsorption, desorption, and net adsorption. Response variable data were obtained over time, wherein, for example, the amount adsorbed was measured in association with the equilibrium concentration, thus allowing the development of a functional relationship between the two. In most cases, this functional relationship was nonlinear. Correlation coefficients were computed for the fitted equations to provide a measure of how good the relationship was.

RESULTS AND DISCUSSION

Influence of the Aggregates

The adsorption and desorption behavior of unaged and aged asphalt was determined on four MRL aggregates that varied in petrography from limestone, greywacke, gravel, to basalt.

Each of these aggregates had specific chemistries both of the bulk material and surface as described in Table 2 that yielded different adsorption behaviors for each asphalt. The surface areas of the aggregates ranged widely with RK-basalt having the highest at 17.4 m²/g, followed by RH-greywacke at 3.12 m²/g, RC-limestone at 1.78 m²/g, and RL-gravel having the lowest at 0.93 m²/g as measured by nitrogen BET of the -35 to +50 mesh size range. The absorptive nature of these aggregates was also quite different. The porosities as measured by mercury porosimetry showed that RC-limestone was the most porous of the aggregates and that RK-basalt and RL-gravel both had fairly low porosities. Khatri and Kandhal (10) have measured the water and asphalt absorption of these aggregates. RK-basalt showed substantial water absorption but almost no asphalt absorption by the Rice method. RC-limestone, by contrast, has large pores and was highly absorptive of both water and asphalt. RC-limestone is also a very dusty aggregate and formed a muddy solution in the Rice test. RL-gravel has a reputation for being variable in behavior, which is most likely caused by its variability in mineralogy.

When each of the three asphalts was adsorbed on the four aggregates, the differences and specificities in the asphalt-aggregate interactions became apparent. Not only are the amounts of the asphalt adsorbed quite different, ranging from 2.01 mg/g at 0.6 g/L for RC-limestone to 0.74 mg/g at 0.6 g/L for RL-gravel, but the shapes of the isotherms were also quite different. These differences in behavior indicated that the

interactions between the asphalts and aggregate were unique and specific for a given asphalt-aggregate pair.

In this investigation, three different asphalts were used at two different levels of oxidation. The oxidation treatment was relatively mild, using standard thin-film oven test conditions. The adsorption behavior of both sets of asphalts on the four different aggregates was obtained as isotherms covering a range of initial concentrations. The number of data points per isotherm ranged from a low of 6 to a high of 18. After each adsorption experiment was completed, a desorption experiment was performed yielding the amount of asphalt desorbed by water for each adsorption experiment. Isotherms were developed for both adsorption and desorption data. The Langmuir model was then applied to these isotherms. The equilibrium constant, K , and Gibbs free energy of adsorption, ΔG , obtained from these adsorption and desorption isotherms are presented in Table 3. The monolayer amounts predicted from the Langmuir model for both the unaged and aged asphalts for adsorption, desorption, and net adsorption are presented in Table 4.

Adsorption Behavior of Aged versus Unaged Asphalt

A comparison of the unaged and aged adsorption behaviors among the different asphalt-aggregate combinations showed little difference between the two materials. The small changes

TABLE 3 Equilibrium Constants and Gibbs Free Energy of Adsorption from Langmuir Treatment of the Adsorption and Desorption of Asphalt on Aggregate

Asphalt-Aggregate Combination	Unaged Asphalt			Aged Asphalt		
	Equilibrium Constant $K \times 10^{-4}$	ΔG , KJ/mole	Correlation Coefficient r	Equilibrium Constant $K \times 10^{-4}$	ΔG , KJ/mole	Correlation Coefficient, r
Adsorption						
AAD-RC	0.5920	-21.5	0.999	0.6146	-21.6	0.965
AAM-RC	0.9568	-22.7	0.999	1.3423	-23.5	0.999
AAK-RC	0.6831	-21.9	0.988	0.7873	-22.2	0.986
AAD-RH	1.836	-24.3	0.978	2.3935	-25.0	0.992
AAM-RH	7.326	-27.8	0.998	2.8502	-25.4	0.957
AAK-RH	1.328	-23.5	0.998	1.5056	-23.8	0.949
AAD-RL	4.539	-26.6	0.997	1.093	-23.0	0.981
AAM-RL	2.130	-24.7	0.982	1.798	-24.3	0.978
AAK-RL	2.125	-24.7	0.994	1.511	-23.8	0.996
AAD-RK	0.8971	-22.7	0.983	0.7530	-22.1	0.999
AAM-RK	0.5453	-21.3	0.998	1.451	-23.7	0.999
AAK-RK	0.5334	-21.3	0.973	0.5342	-21.3	0.942
Desorption						
AAD-RC	2.705	-25.3	0.837	— ¹	—	—
AAM-RC	4.413	-26.5	0.897	0.6592	-21.8	0.938
AAK-RC	—	—	—	1.522	-23.9	0.133
AAD-RH	6.702	-27.5	0.970	2.352	-24.9	0.289
AAM-RH	171.67	-35.6	0.867	5.354	-27.0	1.000
AAK-RH	1.169	-28.7	0.854	13.532	-29.3	0.980
AAD-RL	41.17	-32.0	1.000	4.137	-26.3	0.931
AAM-RL	4.518	-26.6	0.995	16.125	-29.7	0.983
AAK-RL	2.974	-25.5	0.985	3.973	-26.2	0.907
AAD-RK	56.32	-32.8	0.740	0.7633	-22.2	0.066
AAM-RK	—	—	—	18.2372	-30.0	0.991
AAK-RK	—	—	—	4.195	-26.4	0.883

¹Entries designated with a — did not conform to the Langmuir model.

TABLE 4 Monolayer Amounts for Adsorption, Desorption, and Net Adsorption for Four MRL Aggregates and Three Asphalts²

Asphalt/Agg. Combination	Adsorption mg/g	Desorption mg/g	Net Adsorption mg/g	r Adsorption	r Net Adsorption
Unaged					
AAD-RC ²	5.624	1.887	3.737	0.999	0.994
AAM-RC	5.181	2.195	2.986	0.997	0.980
AAK-RC	5.477	0.376	5.101	0.991	0.903
AAD-RH ³	2.137	0.150	1.987	0.978	0.991
AAM-RH	1.439	0.365	1.074	0.999	0.998
AAK-RH	2.560	0.573	1.987	0.995	0.997
AAD-RL	0.853	0.172	0.681	0.989	0.967
AAM-RL	2.073	—	—	0.984	0.911
AAK-RL	1.796	0.294	1.502	0.996	0.953
AAD-RK	3.312	0.390	2.922	0.977	0.995
AAM-RK	6.405	0.304	6.101	0.997	0.893
AAK-RK	5.395	3.001	2.394	0.975	0.988
Aged					
AAD-RC	5.584	2.180	3.404	0.965	0.978
AAM-RC	3.524	0.600	2.924	0.999	0.992
AAK-RC	4.846	1.467	3.379	0.989	0.949
AAD-RH	1.966	0.770	1.196	0.993	0.991
AAM-RH	2.234	0.068	2.166	0.947	0.928
AAK-RH	2.546	0.338	2.208	0.938	0.928
AAD-RL	2.533	0.863	1.670	0.973	0.945
AAM-RL	2.578	— ¹	—	0.979	0.902
AAK-RL	2.654	0.918	1.736	0.997	0.995
AAD-RK	3.969	0.960	3.009	0.998	0.956
AAM-RK	3.340	—	—	0.999	0.900
AAK-RK	4.730	1.382	3.348	0.953	0.961

¹Item designated with a — did not conform to the Langmuir model.²Data taken for 0.1 g/L to 0.7 g/L range.³For range of 0.1 g/L to 0.6 g/L.

in chemistry as reflected by a relatively small increase in viscosity of the asphalt aged in the thin-film oven had little effect on the adsorptive interactions between asphalt and aggregate. The equilibrium constants for the interaction of the asphalts with RC-limestone became somewhat larger with the aged asphalt compared with the unaged asphalt. The ΔG values followed, becoming more negative. The equilibrium constants for the aged asphalts on RL-gravel were always less than those of the unaged asphalts. The ΔG values for the aged asphalts were correspondingly less negative. The interaction of the three asphalts on RH-greywacke and RK-basalt showed variable behavior with the aged asphalt sometimes showing higher or lower equilibrium constants with the aggregate surface than the unaged asphalt. The ΔG values varied accordingly. Much larger changes in the asphalt viscosity (up to 120,000 poise at 60°C) caused by oxidative aging have previously shown substantial changes in adsorption behavior on several substrates (11).

Data from Table 3 were analyzed using the analysis of variance method. Analyses were run on both equilibrium constant for adsorption data and on the ΔG for adsorption data. For the equilibrium constant data, the statistical analyses showed little difference between the unaged and aged asphalts. No interactions of any significance were detected; only aggregates showed any differences that could be considered significant. The data for the equilibrium constant for unaged and aged asphalts on RH-greywacke clearly exhibited variable behavior,

while the adsorption and desorption on the other aggregates were far more consistent. An analysis of variance of the data in Table 3 clearly indicated that the aggregate effect was statistically most significant, while the asphalt was very weak at best.

By contrast, for a given asphalt-aggregate pair, the desorption behavior of the aged asphalt varied considerably from that of the unaged asphalt. As evidenced by the more variable and frequently lower correlation coefficients, the desorption behavior did not conform as well to the Langmuir treatment. Also, several systems involving RC-limestone and RK-basalt yielded isotherms that did not conform to the Langmuir model. The amount of asphalt desorption from the aggregates was, however, relatively small, so that differences between the unaged and aged asphalt were relatively small. The net adsorption, calculated by subtracting the amount desorbed from the amount adsorbed, yielded similar isotherms for the unaged and aged materials.

The uniqueness of the asphalt-aggregate pair combinations was also evident in the respective monolayer amounts obtained for the adsorption, desorption, and net adsorption with each aggregate grouping. A typical example can be observed with RC-limestone and the three asphalts. For the unaged asphalts fairly consistent monolayer amounts were obtained for adsorption, but the percent desorption ranged from 6.9 percent with AAK-1 to 42.4 percent with AAM-1. As a consequence, the net adsorption ranged rather widely from 2.986

TABLE 5 Adsorption, Desorption, and Net Adsorption Behavior for the MRL Aggregates for Three Asphalts

Aggregate	Adsorption (mg/g)	Desorption (mg/g)	Net Adsorption (mg/g)
Unaged			
RC-limestone	5.427	1.486	3.941
RH-greywacke	1.911	0.318	1.593
RL-gravel	1.574	0.233	1.092
RK-basalt	5.037	1.232	3.806
Aged			
RC-limestone	4.651	1.416	3.236
RH-greywacke	2.249	0.392	1.857
RL-gravel	2.588	0.891	1.703
RK-basalt	4.013	1.171	3.179

mg/g to 5.101 mg/g. In contrast, the aged asphalts showed much more variability in the initial amount of asphalt adsorbed, but the amount desorbed corresponded with the amount adsorbed: the asphalts with high adsorption affinity having high amounts desorbed and, likewise, with the low adsorption affinity having low amounts desorbed. The net adsorption for these aged asphalt/RC-limestone pairs was, therefore, quite similar. The other asphalt-aggregate combinations also showed differences among the asphalt adsorption and desorption within a given aggregate set. RK-basalt showed substantial variability, while RH-greywacke and RL-gravel were more similar in their behavior.

Ranking of Aggregates

When the adsorption, desorption, and net adsorption behaviors of the different unaged and aged asphalts were averaged for each aggregate, the following rankings were obtained (Table 5). For initial adsorption, the aggregates ranked as follows for the adsorption of the unaged asphalts: RC-limestone > RK-basalt > RH-greywacke > RL-gravel. The ranking of the adsorption affinity for the aged asphalts was quite similar, giving RC-limestone > RK-basalt > RL-gravel > RH-greywacke. The desorption rankings for the unaged and aged asphalts were also similar. The ranking for desorption of the unaged asphalts was RC-limestone > RK-basalt > RH-greywacke > RL-gravel. The desorption of the aged followed the same order, except that RL-gravel and RH-greywacke were reversed. The net adsorption ranking for both the unaged and aged asphalts was RC-limestone > RK-basalt > RH-greywacke > RL-gravel.

Attraction of Water to the Aggregate-Asphalt Interface

Water is drawn to the aggregate-asphalt interface by the presence of the negative Gibbs free energy potential of the interface in the same way that water flows in the direction of the negative energy gradient in unsaturated soil. Table 6 presents the Gibbs free energy of the interface in gm-cm/gm, all

of which are in the range -12,000 to -21,000 gm-cm/gm. Table 7 presents the conversion of the Gibbs free energy levels for the adsorption of aged asphalt on the aggregate surface in terms of gm-cm/gm, pF, and the relative humidity corresponding to them. The pF is the \log_{10} of the absolute value of the Gibbs free energy, and the relative humidity (R.H.) is computed using the Kelvin equation:

$$\text{R.H.} = \exp \frac{(\Delta G)m}{RT}$$

where

- ΔG = Gibbs free energy, which is a negative number;
- m = molecular weight of water vapor, 18.02 gm/mole;
- g = constant of proportionality numerically equal to the acceleration due to gravity, 981 cm/sec²;
- R = universal gas constant, 8.314×10^7 ergs/K-mole; and
- T = absolute temperature in Kelvin.

TABLE 6 Aggregate-Asphalt Interface Gibbs Free Energy of Water Vapor

Aggregate	Asphalt	Asphalt-Aggregate Interface Gibbs Free Energy of Water Vapor, gm-cm/gm			
		Adsorption		Desorption	
		Unaged	Aged	Unaged	Aged
RC	AAD	-12,409	-12,467	-14,602	— ¹
	AAM	-13,102	-13,564	-15,295	-12,582
	AAK	-12,640	-12,813	—	-13,794
RH	AAD	-14,025	-14,429	-15,872	-14,372
	AAM	-16,045	-14,660	-20,547	-15,584
	AAK	-13,563	-13,737	-13,678	-16,911
RL	AAD	-15,352	-13,275	-18,469	-15,180
	AAM	-14,256	-14,025	-15,353	-17,142
	AAK	-14,256	-13,737	-14,718	-15,122
RK	AAD	-13,102	-12,755	-18,931	-12,813
	AAM	-12,293	-13,679	—	-17,315
	AAK	-12,293	-12,294	—	-15,237

¹Item designated with a - did not conform to the Langmuir model

TABLE 7 Aged Adsorption Gibbs Free Energy of Water Vapor on the Asphalt-Aggregate Interface

Aggregate	Asphalt	Aged Adsorption Gibbs Free Energy of Water Vapor		
		gm-cm gm	pF	Relative Humidity %
RC	AAD	-12,467	4.10	99.1
	AAM	-13,564	4.13	99.0
	AAK	-12,813	4.11	99.1
RH	AAD	-14,429	4.16	99.0
	AAM	-14,660	4.17	99.0
	AAK	-13,737	4.14	99.0
RL	AAD	-13,275	4.12	99.1
	AAM	-14,025	4.15	99.0
	AAK	-13,737	4.14	99.0
RK	AAD	-12,755	4.11	99.1
	AAM	-13,679	4.14	99.0
	AAK	-12,294	4.09	99.1

$$pF = \log_{10} |\Delta G|$$

$$\text{Relative Humidity} = e^{-\frac{|\Delta G| m}{RT}}$$

$m = 18.02 \text{ gm/mole of water}$
 $g = 981 \text{ cm/sec}^2$
 $R = 8.314 \times 10^7 \text{ ergs/K-mole}$
 $T = K, 273^\circ + ^\circ C$

Table 8 gives some benchmark Gibbs free energy states of water vapor in unsaturated soils for comparison with the potentials of the asphalt-aggregate interface. This table demonstrates that the interface will draw water vapor toward the interface when the relative humidity of the water vapor is above 99 percent (pF 4.15). The interface cannot draw water away from soil at the wilting point, for example. Water at a higher level of relative humidity will continue to be drawn toward the interface to reduce the Gibbs free energy of the interface until the water and interface are at equal levels. Potentially, the Gibbs free energy can be reduced to zero. This has implications for the total bonding energy with which asphalt is bound to the asphalt-aggregate interface.

Table 9 shows the enthalpy (ΔH) of the asphalt-aggregate interface as measured by Curtis et al. (8, p. 107). The measurements were made with a calorimeter at 140°C, and they have been converted approximately to the corresponding enthalpy at 25°C by multiplying by the ratio of the absolute temperatures. The algebraic sum of enthalpy (ΔH) and Gibbs

TABLE 8 Some Familiar Comparison States of Water Vapor

Water State	Gibbs Free Energy gm-cm gm	Gibbs Free Energy pF	Relative Humidity at 20°C %
Saturated Soil of Pavement	-100	2.0	99.993
Air Entry into Soil	-1000	3.0	99.927
Plant Wilting Point	-3.2 x 10 ⁴	4.5	97.7
Tensile Strength of Water	-2 x 10 ⁵	5.3	86.5
Air Dry	-10 ⁶	6.0	48.4
Oven Dry	-10 ⁷	7.0	0.07

TABLE 9 Total Bonding Energy of the Asphalt-Aggregate Interface

Aggregate	Asphalt	ΔH Bonding Energy* Enthalpy	ΔH Bonding Energy* Enthalpy (Approximate)	ΔG Gibbs Free Energy (Aged Adsorption)	$\Delta H - \Delta G$ = T ΔS	Minimum Tensile Strength Ratio ¹
		m-cal gm	psi	psi	psi	$\frac{\Delta H}{T \Delta S}$
		(140°C)	(25°C)	(25°C)	(25°C)	
RC	AAD	157	68.9	-177.3	246.2	0.28
	AAM	247	108.4	-192.9	301.3	0.36
	AAK	—	—	-182.2	—	—
RH	AAD	429	188.3	-205.2	393.5	0.48
	AAM	276	121.0	-208.5	329.5	0.37
	AA	—	—	-195.4	—	—
RL	AAD	152	66.7	-188.8	255.5	0.27
	AAM	314	137.8	-199.5	337.3	0.41
	AAK	314	137.8	-195.4	333.2	0.41
RK	AAD	500	219.4	-181.4	400.8	0.55
	AAM	570	250.1	-194.6	444.7	0.56
	AAK	425	186.5	-174.9	361.4	0.52

¹Controlled by adhesion.

free energy (ΔG), which is a negative number, is the product, $T\Delta S$ (i.e., the absolute temperature times the entropy). All three quantities, ΔH , ΔG , and $T\Delta S$ are converted into the equivalent tensile stress in psi. This gives an estimate of the tensile stress in the asphalt that is required to pull the asphalt free of the asphalt-aggregate interface.

If water at zero Gibbs free energy is attracted to the interface, it can reduce that component of the tensile strength to zero, leaving only the enthalpy to maintain the bond. The ratio of $\Delta H/T\Delta S$ gives an estimate of the minimum tensile strength ratio (TSR) that can be observed with each asphalt-aggregate combination. In Table 9, known stripping aggregates, RC-limestone and RL-gravel, have an estimated minimum TSR of around 0.41 and less. It is interesting to note that these correspond to a minimum tensile strength, the en-

TABLE 10 Surface Strain Energy Storage Density for the Asphalt-Aggregate Interface

Aggregate	Asphalt	SSA Specific Surface Area ¹ (m ² /gm)	ΔG Gibbs Free Energy of Asphalt Aggregate ² gm-cm/gm	Γ Surface Strain Energy Storage Density gm-cm/cm ²
				x10 ²
RC	AAD	1.78	-321	1.80
	AAM	1.78	-188	1.06
	AAK	1.78	-268	1.51
RH	AAD	3.12	-371	1.19
	AAM	3.12	-203	0.65
	AAK	3.12	-288	0.92
RL	AAD	0.93	-342	3.68
	AAM	0.93	-194	2.09
	AAK	0.93	-288	3.10
RK	AAD	17.4	-328	0.19
	AAM	17.4	-190	0.11
	AAK	17.4	-258	0.15

¹Measured by the B.E.T. Method

²Aged Adsorption ΔG

thalpy, ΔH , which is lower than currently measured truck tire pressures that frequently reach 150 psi.

An alternative way that asphalt may become debonded from an aggregate surface is by the propagation of a debonding crack along the interface due to repeated tensile stresses in the asphalt. The critical material property is the amount of released strain energy that can be stored on the surface of the debonded crack. The crack surface strain energy storage density, Γ , is found by dividing the Gibbs free energy by the specific surface area as given in Table 10 (9). This table suggests that RK-basalt, having a large specific surface area, is highly susceptible to this kind of debonding fracture.

CONCLUSIONS

Asphalt-aggregate adsorption and desorption studies show specificity in the interactions between asphalt and aggregate. The amount of a particular asphalt adsorbed or desorbed on aggregate was dependent upon the aggregate bulk and surface chemistry and morphology. The amounts adsorbed and desorbed varied considerably over a range of four aggregates. Likewise, the composition of the asphalt and its degree of aging affected the interaction with aggregate. The influence of the aggregate on adsorption and desorption was much greater than that of the asphalt. Fitting these behaviors to the Langmuir model yielded equilibrium constants and Gibbs free energy values of adsorption that can be related to concepts used in unsaturated soil mechanics. Evaluation of the Gibbs free energy in terms of those units typically used in soil mechanics yielded the following conclusions:

- Water in the voids in asphaltic concrete can be drawn toward the asphalt-aggregate interface by the negative Gibbs free energy potential of that interface as long as the water is in a potential state that is less negative than the interface. This effect will occur for all water vapor at a relative humidity greater than 99 percent or for liquid water in equilibrium with water vapor.
- Accurate measurements of enthalpy, ΔH , as it varies with temperature can give reasonable estimates of the minimum tensile strength of the asphalt-aggregate interface, which is useful in estimating the potential of an aggregate for stripping. Estimates of the enthalpy are presented at 25°C, but what is really needed is a way of measuring it at that temperature.
- The role of Gibbs free energy of the asphalt-aggregate interface is to increase its tensile strength and resistance to debonding fracture. As water is drawn by diffusion through the asphalt and to the interfaces, it reduces the size of the Gibbs free energy and thus the tensile strength and the resistance to debonding fracture. Thus, Gibbs free energy represents the safety factor that an asphalt-aggregate interface has against stripping. Air voids in an AC mix that are filled

with water or at a relative humidity greater than 99 percent will eventually reduce this factor of safety.

• A chemical means of identifying the asphalt-aggregate combinations that are likely to strip has been developed, and the measured data suggest two related mechanisms for stripping: tensile adhesive fracture and debonding fracture caused by repeated tensile stresses in the asphalt binder.

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