

Adsorption of Asphalt and Asphalt Functionalities onto Aggregates Precoated with Antistripping Agents

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The adsorption behavior of asphalt and functionalities representative of those present in asphalt on aggregates precoated with antistripping agents was investigated. The amount of adsorption obtained was compared with that of uncoated aggregate. The aggregates used were a high-surface-area synthetic silica and low-surface-area actual siliceous aggregates; Warrior River sand from Alabama; and greywacke from California. The aggregates were precoated with commercial polyamine antistripping agents. The acidic functionalities benzoic acid and phenol demonstrated enhanced adsorption with the antistripping agent precoating, whereas the nonacidic functionalities phenylsulfoxide, benzylbenzoate, benzophenone, quinoline, and pyrene did not. The adsorption of AC-20 asphalt onto precoated silica and Warrior River sand showed decreased adsorption compared to that on the uncoated aggregate. The adsorption of AC-10 on precoated greywacke also showed decreased adsorption compared to uncoated greywacke. The ranking of the AC-20 adsorption on different uncoated aggregates when aggregate surface area was taken into account was Warrior River sand > silica > greywacke. Likewise, AC-20 adsorbed more on precoated Warrior River sand than on precoated silica. Desorption of AC-20 asphalt from precoated silica using distilled water appeared to be less than that from uncoated silica.

Asphalt serves as the binder for aggregates in road pavements. The adhesion of the binder to the aggregate is of utmost importance for achieving and maintaining long-lived, well-performing pavements. Adhesion of the asphalt to the aggregate can be examined in the laboratory using liquid-phase adsorption of asphalt onto different aggregate surfaces. Previous work performed by Plancher et al. (1) and Petersen et al. (2) has indicated the importance of the polar functionalities present in asphalt for providing a binding, strongly adsorbing layer at the interface between asphalt and aggregate. Plancher et al. (1) found that benzoic acid adsorbed most on all of the aggregates used whereas quinoline was preferentially adsorbed with acidic aggregates (quartzite and granite). Phenylsulfoxide, benzophenone, and phenol were favorably adsorbed onto either acidic or basic aggregate (limestone), whereas the other functionalities, benzylbenzoate, 1,2,3,4-dibenzanthracene, and naphthalene, showed little affinity for any of the aggregates. Curtis et al. (3) examined the competitive adsorption of heteroatomic model compounds onto dry and moist silica surfaces. The competitive affinity observed for dry silica was in the order of phenylsulfoxide > quinoline > phenol > benzoic acid, whereas for moist silica the order was phenylsulfoxide > phenol > benzoic acid > quinoline.

Fritschy and Papirer (4) examined the adsorption of asphalt onto different surface area Aerosils that are nonporous pyrogenic silicas. Multilayer adsorption of the asphalt was observed with the most strongly adsorbing fraction appearing to be asphaltenes. Curtis et al. (5) examined the adsorption of asphalt with different degrees of oxidation onto model and actual aggregates. AC-20 achieved a higher level of adsorption on all of the aggregates than did the more highly oxidized asphalts. Moisture on the aggregate surface had different effects on the amount of adsorption, depending on the type of aggregate used.

The stripping or removal of asphalt from the aggregate because of water penetrating between the layer of asphalt and the aggregate surface causes many pavements to fail. Many different antistripping agents have been developed over the years to reduce the stripping propensity of different aggregates; however, many of them are composed of polyamines [for example, Mathews (6), Dybalski (7), Kartashevskii et al. (8), Brown and Swidler (9)]. Mathews (10) reported that using cationic surfactants as antistripping agents promoted adhesion between asphalt and aggregate and effectively reduced water damage. The action of these cationic surfactants is to migrate to the aggregate surface and render the surface lipophilic for facile adsorption of asphalt. Dybalski (11) proposed a method of directly applying antistripping agents to the surface. This method would obviate the possibility that the polyamine antistripping agents would react with acidic components in the asphalt and be rendered inactive. However, the best method for introducing antistripping agents is still in question.

This study investigated the effect of adsorbed antistripping (AS) agents on the chemistry and adsorption behavior of asphalt and asphalt functionalities at the asphalt-aggregate interface. The primary objective was to ascertain the adsorption behavior of asphalt and asphalt functionalities onto synthetic and actual aggregates precoated with AS agents and to compare their adsorptive behavior without AS agents. The asphalts used in this study were an AC-10 and an AC-20. The aggregates used were Warrior River sand; a greywacke; and a high-surface-area, porous silica. The model functionalities representing chemical functionalities present in asphalt selected for this study were carboxylic acids represented by benzoic acid, phenolics by phenol, sulfoxides by phenylsulfoxide, nitrogen bases by quinoline, ketones by benzophenone, esters by benzylbenzoate, and polynuclear aromatics by pyrene. Commercial polyamine antistripping agents were used to precoat the aggregates. Asphalt adsorption was performed from toluene solution using a continuous system,

whereas the asphalt functionalities were adsorbed from cyclohexane solutions using batch adsorption.

EXPERIMENTAL

Materials Used

Two commercially available polyamine AS agents (AS1 and AS2) were used as received. The AC-10, labeled in the figures as AAD-1, was produced from California Coastal crude; the AC-20, obtained from Hunt Oil, was produced from 18 percent Maya crude, 65 percent Mississippi-Alabama pipeline crude, and 17 percent Boscan crude. The seven model compounds representing chemical functionalities present in asphalt used were benzoic acid (purity >99 percent), quinoline (>99 percent), phenylsulfoxide (97 percent), phenol (>99 percent), benzophenone (>99 percent), benzylbenzoate (>99 percent), and pyrene (>99 percent), all supplied by Aldrich. The organic solvents used were dichloromethane (>99 percent, spectrophotometric grade, Aldrich) for adsorption of the AS agents, cyclohexane (>99 percent, spectrophotometric grade, Aldrich) for adsorption of the model compounds, and toluene (spectranalyzed grade, Fisher) for adsorption of the asphalts. Distilled water was also used as a desorption solvent for asphalt. The liquid model compounds and the organic solvents were dried before use by adding activated Type 4A molecular sieves, whereas the solid compounds were dried in a vacuum desiccator.

The adsorbents used were Warrior River sand, an aggregate from Alabama; a greywacke, a siliceous aggregate obtained from Kaiser Sand and Gravel, Pleasanton, California; and a silica gel purchased from Alltech Associates, Inc., and manufactured by Davison Chemical Division, W. R. Grace and Company. The aggregate surface areas, obtained using multipoint nitrogen adsorption, are as follows:

Aggregate	Surface Area (m ² /g)
Warrior River sand	0.6
Greywacke	2.5
Silica	294

The aggregates were dried before use at 150°C for 24 hr to remove physisorbed water and volatile organics.

Equipment

The asphalt adsorption experiments were performed using a continuous system described previously [Curtis et al. (3)], consisting of a thermostatted column containing the aggregate and toluene circulating through the system. The column temperature was maintained at 25°C and the change in concentration was monitored by visible spectroscopy. The AS agents and model functionalities were adsorbed from dichloromethane and cyclohexane, respectively, using batch adsorption. Their change in concentration was monitored by ultraviolet (UV) spectroscopy. The adsorption vessels were agitated using a Model 3528CC microprocessor-controlled orbit shaker manufactured by Lab-line Instruments. Adsorption temperature, speed, and agitation time were controlled at 25°C ± 0.65°C, 250 ± 10 rpm, and 60 min, respectively.

Preparation of Precoated Aggregate

Each AS agent was dissolved into dichloromethane to make solutions with initial concentrations ranging from 0.5 to 10 g/L. The insoluble fraction consisting of about 5 percent of the AS agent was removed by vacuum filtering the solution through a Whatman 934 AH glass microfilter. The solution concentration was corrected by subtracting the insoluble fraction from the initial amount of the AS agent introduced. The flasks containing AS agent solution were placed in the orbit shaker for 1 hr to allow equilibration of the solution to 25°C. Then, 2 g of dried aggregate was introduced into 95 mL of AS agent solution, and the solution mixture was stirred for 1 hr, which was sufficient for attaining equilibrium for adsorption. Samples of 5-mL aliquots were taken before and after adsorption by filtering them through 0.22-μm MSI Teflon membrane filters. The weakly adsorbed AS1 fraction on silica was removed by washing the silica three times with 100 mL of pure dichloromethane.

When precoated silica was prepared for the asphalt adsorption studies, only 1 g of silica was introduced to the AS1 solution resulting in a somewhat higher AS1 monolayer amount than with 2 g. When Warrior River sand and greywacke were precoated, 5 g of each material was added to each adsorption flask for precoating with AS1. Neither Warrior River sand nor greywacke was washed with dichloromethane. After precoating, the aggregates were dried for 24 hr at room temperature in a vacuum desiccator.

Adsorption of Model Compounds onto Precoated Silica

Model compounds were each dissolved into cyclohexane to make solutions with various initial concentrations up to 15 g/L. The sample solutions were placed in the orbit shaker for 1 hr to equilibrate at 25°C. Then, 0.5 g of precoated silica was added into 95 mL of model compound solution, and the solution mixture was agitated for 1 hr to attain equilibrium. Samples of 5-mL aliquots were taken before and after adsorption.

Analysis

Samples taken in the adsorption experiments were analyzed by UV-visible spectroscopy using a Model 250 Gilford UV-visible spectrometer. The characteristic wavelengths used for each compound are as follows:

Test Compound	Solvent	Wavelength (nm)
AS1	Dichloromethane	270
AS2	Dichloromethane	270
Quinoline	Cyclohexane	274
Phenylsulfoxide	Cyclohexane	252
Phenol	Cyclohexane	271.5
Benzoic acid	Cyclohexane	274
Benzophenone	Cyclohexane	250
Benzylbenzoate	Cyclohexane	247
Pyrene	Cyclohexane	295
AC-10	Toluene	410
AC-20	Toluene	375

Quantitation was based on Beer's law, $A = abc$, where A , a , b , and c denote UV or visible absorbance, absorptivity (L/g-cm), cell pathlength (1 cm), and solution concentration (g/L), respectively. The calibration curves for the asphalts, AS agents, and model compounds were developed using standard solutions of known concentrations. From the absorbance readings, the solution concentration as well as the amount adsorbed was calculated by using the equations given in the following paragraphs.

AS Agent Loading on Silica from Dichloromethane Solution

$$C/C_0 = \text{Abs}/\text{Abs}_0 \quad (1)$$

$$AW = V(C_0 - C) \quad (2)$$

$$DW = VC_D = V(\text{Abs}_D/ab) \quad (3)$$

$$\sigma = A - D \quad (4)$$

where

- C_0 = initial solution concentration (g/L),
- C = equilibrated solution concentration (g/L),
- Abs_0 = UV absorbance of initial solution,
- Abs = UV absorbance of equilibrated solution,
- A = amount adsorbed per gram of silica (g/g silica),
- W = quantity of silica used (g),
- V = solution volume (L),
- D = amount desorbed per gram of silica (g/g silica),
- C_D = solution concentration resulting from washing (g/L),
- Abs_D = UV absorbance of wash solution,
- a = absorptivity of AS agent (L/g-cm),
- σ = amount of AS loading on silica obtained after removing the weakly adsorbed fraction (g/g silica), and
- b = cell pathlength (cm).

Model Compound Adsorption from Cyclohexane Solution

Equations 1 and 2 suffice to describe the adsorption from cyclohexane solution.

Adsorption of Asphalt onto Aggregate

Asphalt solutions were prepared using dry spectroanalyzed toluene. The concentration ranges used were from ~0.4 to 53.5 g/L for silica, 0.02 to ~1.4 g/L for Warrior River sand, and 0.02 to 0.54 g/L for greywacke. The asphalt in toluene solution was introduced to the column and allowed to equilibrate for approximately 5 min. The flow rate of 0.58 mL/sec was then set without aggregate in the column. Aggregate, both precoated and uncoated, consisting of 1 g of silica or 5 g of either Warrior River sand or greywacke, was then added to the column and the experiment begun. The visible absorbance reading was obtained at the wavelengths presented in Table 2 (the last two entries) after each solution had reached equilibrium. The equilibrium time was 8 hr for silica and Warrior River sand and 12 hr for greywacke.

Desorption of AC-20 from Precoated Silica and Uncoated Silica

The desorption experiment was performed by first adsorbing nearly equivalent amounts of AC-20 onto AS1 precoated and uncoated silica. The silica with preadsorbed AC-20 was dried for 48 hr at room temperature in a vacuum desiccator, then placed in 25 or 50 mL of distilled water, and finally agitated for 2 hr at 25°C. The asphalt was extracted from the water phase by toluene. Aliquots (5 mL) of the organic phase were taken for quantitative analysis by visible spectroscopy.

Asphalt Adsorption and Desorption on Aggregate

Adsorption

$$C/C_0 = \text{Abs}/\text{Abs}_0 \quad (5)$$

$$AW_A = V(C_0 - C) \quad (6)$$

$$A = VC_0(\text{Abs}_0 - \text{Abs})/W_A \text{Abs}_0 \quad (7)$$

Desorption

$$D_w W_A = V_w C_w = V_w (\text{Abs}_w/a_w b) \quad (8)$$

$$D_w = V_w (\text{Abs}_w/a_w)/W_A$$

where

- W_A = quantity of aggregate used (g),
- V_w = solution volume used for extraction (L),
- D_w = amount of asphalt desorbed per gram of aggregate (g/g),
- C_w = solution concentration after extraction (g/L),
- Abs_w = absorbance of extracted solution, and
- a_w = absorptivity of asphalt in toluene solution (L/g-cm).

RESULTS AND DISCUSSION

Adsorption Isotherms of AS Agents on Silica

Both AS1 and AS2 were precoated onto silica from a dichloromethane solution. AS1 exhibited a Langmuir-type monolayer adsorption that was characterized by the formation of a plateau at high concentrations, whereas AS2 did not. AS2 had a continuously increasing adsorption with increased concentration. AS2 adsorbed more than AS1 at concentrations below 1 g/L, whereas the reverse was observed between 1 and 8 g/L. At high concentrations (>8 g/L), AS2 again adsorbed more onto the silica than did AS1.

The Langmuir equation having the form

$$C/q = C/q_m + 1/b'q_m$$

where

- C = equilibrium concentration,
- q = amount adsorbed per gram of silica,
- q_m = saturated monolayer amount, and
- b' = a constant, respectively,

was applied to the adsorption isotherms (12). The monolayer amounts obtained for AS1 and AS2 on silica, when 2 g of silica was introduced, were 138 and 139 mg per gram of silica, respectively.

The adsorptions of AS1 on dry and moist silica were also compared as shown in Figure 1. In this case, only 1 g of silica was introduced to the AS1 batch adsorption flask compared to the 2 g in the above experiments. The moisture content of silica was ~4.6 weight-percent moisture, a value that was obtained by placing dry silica in a humidifying chamber containing distilled water. The adsorption behaviors of AS1 on the moist and dry silica were similar although the amount of AS1 adsorbed onto moist silica appeared to be higher than that onto dry silica. The data, when fitted to the Langmuir adsorption model, yielded monolayer values of 265.5 and 217.8 mg per gram of silica with correlation coefficients of 0.991 and 0.981 for moist and dry silica, respectively.

Adsorption of Model Compounds on Precoated Silica

Seven model functionalities were adsorbed onto AS1- and AS2-precoated silica using cyclohexane as the adsorption medium at 25°C. The adsorption of the acidic functionalities benzoic acid and phenol was enhanced when compared to the adsorption on dry silica by the precoating of the AS agents on silica. The adsorption of the compounds representing non-acidic functionalities, such as phenylsulfoxide, quinoline, pyrene, benzylbenzoate, and benzophenone, underwent a large reduction.

Table 1 presents the effect of precoated silica on the adsorption of model functionalities on the basis of the amount adsorbed

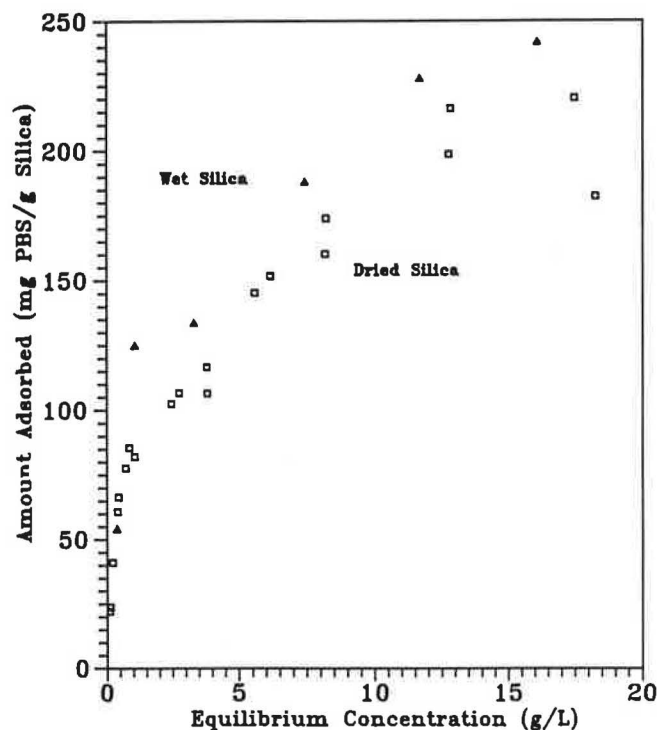


FIGURE 1 Adsorption of antistripping agent onto dried silica and wet silica.

as determined at an equilibrium concentration of 5 g/L and 25°C. The acidic compounds benzoic acid and phenol had enhanced adsorption for the precoated silica ranging from 8 to 57 percent. The largest increase in benzoic acid adsorption of 57 percent was obtained with the 6 to 7 weight-percent AS2-coated silica, whereas the largest increase in phenol adsorption of 25 percent was obtained with the 6 to 7 weight-percent AS1-coated silica. The two acidic functionalities showed different adsorption behaviors; the benzoic acid adsorption was enhanced on the precoated silica over the entire equilibrium concentration range when compared to dry silica whereas phenol was only enhanced at high concentrations.

A proposed mechanism for the interaction of the acidic compounds with the polyamine AS agents is the transfer of a proton from the acidic functionality to the amine group of the AS agent. The acidic molecule is thus negatively charged whereas the amine group has a positive charge by forming a quaternary ammonium ion. As a result, a charge attraction exists between the acidic molecule and the ammonium ion. This acid-base interaction may explain the enhancement by AS agents in the adsorption of acidic compounds benzoic acid and phenol onto the precoated silica. Through hydrogen bonding, benzoic acid and phenol in cyclohexane can also be adsorbed onto the silanols of the silica surface unoccupied by the precoated AS agents.

The other model functionalities underwent more than 80 percent reduction in their adsorption onto the precoated silica when compared to uncoated silica adsorption. Because these AS agents are primarily composed of polyamines as their primary constituents, they do not readily interact with non-acidic functionalities. Amine groups can act as Lewis bases, i.e., as proton acceptors or electron pair providers (13). However, none of the five functionalities has a free proton to release to the Lewis base; therefore, they remain unreactive with the basic AS agents. As a result, the adsorption of these nonacidic functionalities onto the silica surface was inhibited by the preadsorbed AS agents, compared to the uncoated silica.

A second probable mechanism that can be proposed for reduced adsorption of the nonacidic functionalities on the AS1- and AS2-precoated silica is competitive adsorption. The AS agents, which are Lewis bases, may be competing for the same aggregate sites as the nonacidic functionalities that are themselves Lewis bases. The AS agents may occupy the same sites on the uncoated silica surface as would have been occupied by the nonacidic functionalities and, hence, restrict the adsorption of the nonacidic functionalities.

Adsorption of Asphalt onto Precoated and Uncoated Silica

The adsorption behaviors of AC-20 asphalt onto dry, uncoated silica and onto silica precoated with 8 to 9 percent AS1 agent were compared. The adsorption isotherms developed for these two silicas are shown in Figure 2. The isotherm for the uncoated silica followed the Freundlich model better than the Langmuir model, whereas that for the precoated followed the Langmuir model. However, because the correlation coefficients for the Langmuir model were high for both—0.984 for uncoated and 0.993 for precoated—the Langmuir model was used to obtain the amount of asphalt monolayer coverage for both materials.

TABLE 1 THE EFFECT OF PRECOATED ANTISTRIPPING AGENTS ON SILICA ON THE ADSORPTION OF ASPHALT MODEL FUNCTIONALITIES

Asphalt Functionality	Amount Adsorbed (g/g silica) ¹		
	Uncoated Silica	6 -7 wt% AS1 Coated Silica	6 -7 wt% AS2 Coated Silica
Benzoic Acid (Carboxylic Acid)	0.105	0.140 (33%) ²	0.165 (57%)
Phenol (Phenolic)	0.120	0.150 (25%)	0.130 (8%)
Quinoline (N-Base)	0.145	0.012 (-92%)	0.020 (-86%)
Phenylsulfoxide (Sulfoxide)	0.185	0.034 (-82%)	0.040 (-78%)
Benzophenone (Ketone)	0.095	0.010 (-89%)	NP
Benzylbenzoate (Ester)	0.103	NP ³	0.007 (-93%)
Pyrene (Polynuclear Aromatic)	0.030	0.003 (-90%)	NP

¹ Determined at an equilibrium concentration of 5 g/L and 25°C

² % Change in Adsorption = $[(B-A)/A] \times 100$

where A = Uncoated silica adsorption

B = AS agent coated silica adsorption

³ NP = not performed

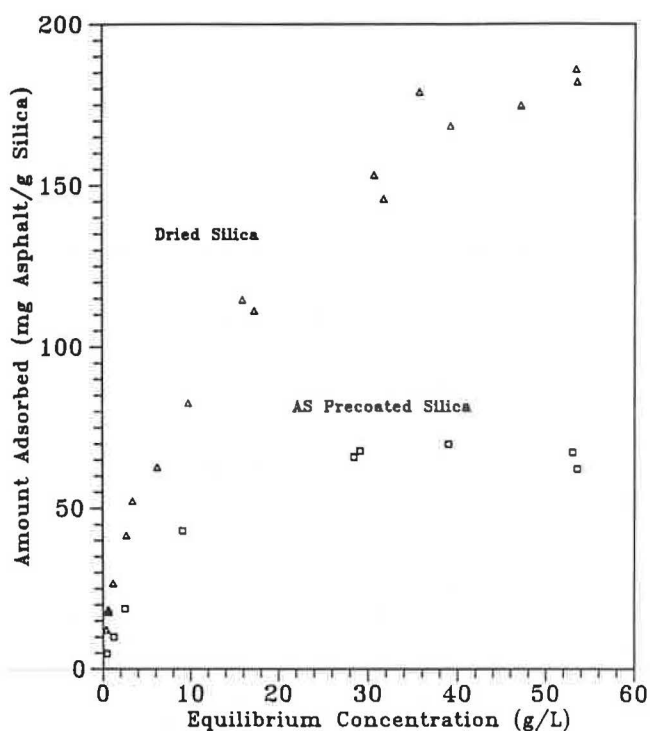


FIGURE 2 Adsorption of asphalt onto dried silica and silica precoated with antistripping agent.

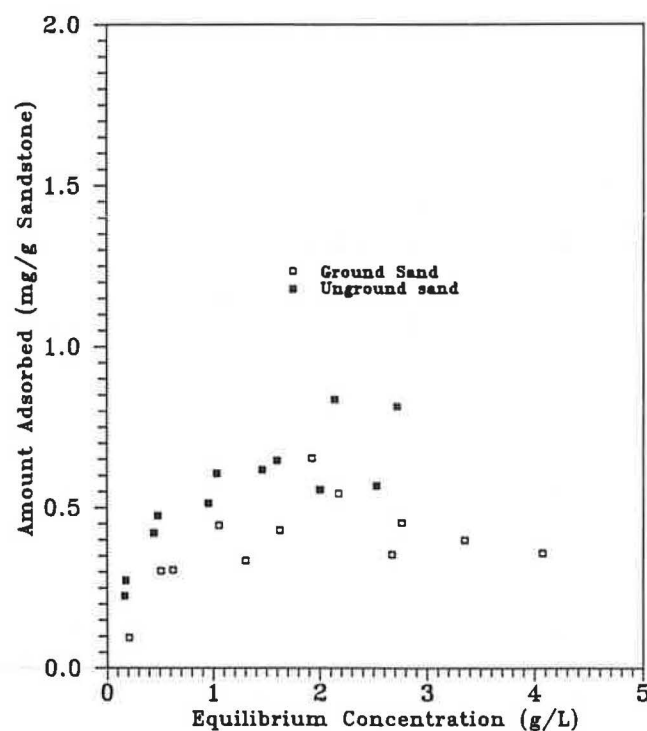


FIGURE 3 Adsorption of antistripping agent onto ground WRS and unground WRS.

The Langmuir equation was applied in the same form as was stated earlier. The monolayer amount obtained for AC-20 asphalt adsorbed by uncoated silica was 214 mg/g, whereas that for the AS1-precoated silica was 75.7 mg/g. A decrease of nearly 65 percent in the monolayer amount of AC-20 adsorbed was observed with the AS1 precoating of the aggregate.

Adsorption of AS1 on Warrior River Sand and Greywacke

The preparation of the AS1 agent precoating on Warrior River sand and greywacke followed the same procedure as that for silica; however, the actual aggregates were not washed with dichloromethane before being used in the asphalt adsorption experiments. As shown in Figure 3, adsorption of AS agent onto Warrior River sand followed the Langmuir model. A coating of 0.012 weight-percent AS1 was obtained.

The Warrior River sand used in this experiment, as well as that for asphalt adsorption, was sieved material of the quarry mixture consisting of particles between -40 and +80 mesh. Some material ground from larger sizes from -40 to +80 mesh was also used for the adsorption of AS1, as is also shown in Figure 3. The adsorption behavior for these two sands was different even though they were both obtained from the same material and had the same particle size range. The monolayer amounts obtained for AS1 adsorption on the unground and ground sand were 0.789 and 0.423 mg/g, respectively, indicating that the unground sand adsorption was about 86 percent greater than the ground sand. Hence, the grinding of the sand sufficiently affected the aggregate surface chemistry and properties to reduce the adsorption of the AS1 agent.

In contrast to the adsorption behavior of Warrior River sand, the adsorption of AS1 on greywacke followed a Freundlich isotherm behavior rather than the Langmuir model. The Freundlich model is represented by the equation

$$\ln q = \ln K + (1/n) \ln C$$

where q and C denote the amount adsorbed per unit weight of adsorbent and the equilibrium adsorbate concentration, respectively, K and n being constants. The Freundlich model generally represents a heterogeneous surface and physisorption, whereas the Langmuir model generally represents a homogeneous surface and chemisorption. The fact that different models were followed indicates a difference in the interaction between the AS1 agent and the surface of the two aggregates. The greywacke was precoated with approximately 0.04 weight-percent AS1 agent, more than three times the amount adsorbed on Warrior River sand. The larger adsorption of AS1 agent by greywacke followed the same trend as the surface areas because greywacke had four times as much surface area as Warrior River sand.

Adsorption of AC-20 on Warrior River Sand

AC-20 asphalt was adsorbed on both dry and AS1 precoated Warrior River sand. An adsorption versus time study indicated that within 8 hr adsorption on both the precoated and uncoated Warrior River sand reached equilibrium. The adsorption isotherms of both uncoated and precoated Warrior

River sand shown in Figure 4 had Langmuir behavior characterized by formation of a plateau at high concentrations. The monolayer amounts obtained were 0.251 and 0.982 mg of asphalt per gram of uncoated sand. The amount of asphalt adsorbed on the AS1-precoated sand was about four times less than that adsorbed onto uncoated sand. Hence, the types and number of functionalities adsorbing on the precoated Warrior River sand were much less than those on the uncoated sand.

Adsorption of AC-10 and AC-20 onto Greywacke

An adsorption-versus-time experiment for the adsorption of AC-10 on greywacke indicated that 8 hr was required to achieve a saturated equilibrium amount for the precoated greywacke and 12 hr for the uncoated greywacke. The adsorption isotherms performed using both precoated and uncoated greywacke exhibited Langmuir adsorption behavior yielding monolayer amounts of 0.4 and 1.0 mg/g, respectively (Figure 5). The decrease in adsorption caused by aggregate precoating was 60 percent. AC-20 asphalt was also adsorbed onto the uncoated greywacke and followed a similar behavior to that of AC-10. The AC-20 asphalt adsorbed a slightly higher monolayer amount of 1.17 mg/g.

Comparisons of Different Asphalt-Aggregate Systems

A comparison of the monolayer amounts obtained from the different asphalt-aggregate combinations is presented in Table 2. Each aggregate, whether synthetic or actual, yielded asphalt monolayer amounts for the AS1-precoated aggregates that

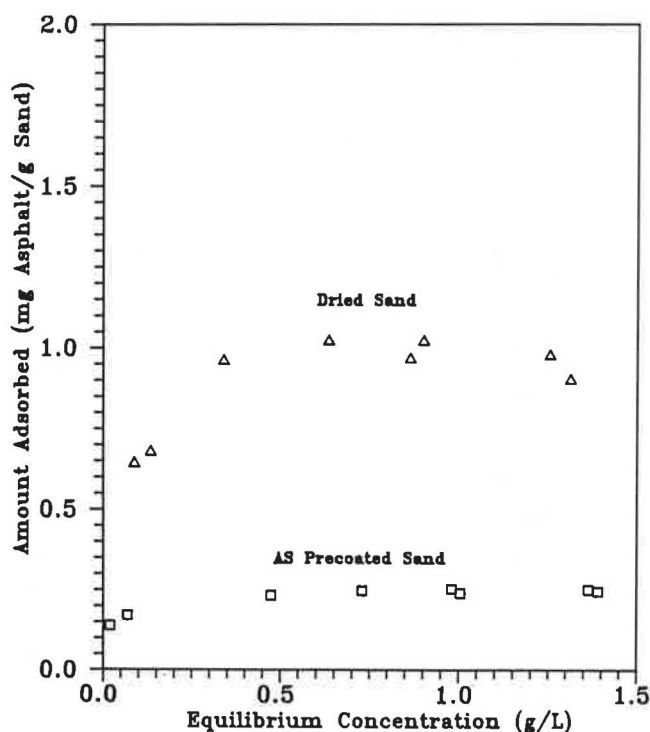


FIGURE 4 Adsorption of asphalt onto dried WRS and AS1-precoated WRS.

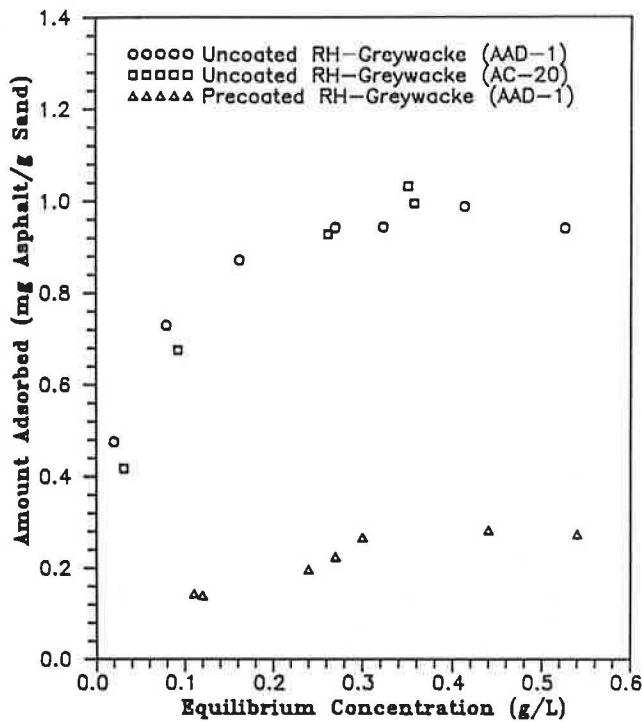


FIGURE 5 Adsorption of AAD-1 and AC-20 asphalts onto uncoated RH-greywacke and precoated RH-greywacke.

were one-fourth to one-third of those for uncoated aggregate. Thus, the uncoated aggregate adsorbed a greater quantity of asphalt than the precoated aggregate regardless of the type of siliceous aggregate used. The model functionality study indicated that only acidic functionalities were promoted by the precoating of siliceous aggregates with polyamines. All of the other functionalities tested were inhibited. Hence, the adsorbing species from the AC-10 and AC-20 asphalts used appeared to be composed of substantial quantities of compounds that were not acidic and, hence, did not adsorb on the precoated aggregates.

Because these siliceous aggregates possessed substantially different surface areas, comparison on the basis of surface area allows direct comparison of the amount adsorbed among the different aggregates. The adsorption of AC-10 and AC-20 asphalts on the basis of surface area is shown in Figure 6. The adsorption behavior of the two asphalts was nearly equivalent on greywacke. By contrast, on the basis of surface area the AC-20 adsorbed much more on Warrior River sand.

The same types of comparisons can be made from the data presented in Table 2. The adsorption behavior of the three uncoated aggregates on the basis of surface area for AC-20 ranked as Warrior River sand > silica > greywacke. The precoated Warrior River sand also adsorbed more AC-20 than did precoated silica on the basis of surface area. These results suggest that the aggregate had a substantial effect on the adsorption of the AC-20 asphalt. For uncoated greywacke, AC-10 adsorption was slightly less than AC-20, suggesting that asphalt type and composition had a small effect on adsorption behavior. The more influential factors on asphalt adsorption were aggregate type and surface properties as changed by precoating with AS1 agents.

Desorption Behavior of AC-20 Asphalt

AC-20 asphalt was adsorbed at an equivalent amount on both AS1-precoated and uncoated silicas. Desorption with distilled water resulted in removing 0.7 to 1.9 percent of the preadsorbed asphalt from uncoated silica and 0.4 to 0.9 percent from precoated silica. These results were obtained when 25 mL of distilled water was used for desorption; however, when 50 mL of distilled water was used, the amount of asphalt desorbed from uncoated silica for two samples ranged from 8.4 to 9.0 percent, whereas that from AS1-precoated silica ranged from 0.39 to 0.46 percent. These results indicated that the precoating of silica with AS1 agents rendered the asphalt surface less susceptible to desorption by water. Although the adsorption of asphalt was reduced by the precoating of aggregate with AS agents, asphalt retention in the presence of water was increased.

TABLE 2 COMPARISON OF MONOLAYER AMOUNTS OBTAINED FROM DIFFERENT ASPHALT AND AGGREGATE COMBINATIONS

Aggregate	Asphalt	Pretreatment	Monolayer (mg/g)	Monolayer (mg/m ²)	% Difference from Uncoated Aggregate ¹
Silica	Hunt AC-20	Uncoated	213.9 ± 9.24	0.73 ± 0.03	NA ²
Warrior River Sand	Hunt AC-20	Uncoated	0.98 ± 0.04	1.63 ± 0.07	NA
Greywacke	Hunt AC-20	Uncoated	1.17 ± 0.04	0.47 ± 0.02	NA
Greywacke	AC-10 (AAD-1)	Uncoated	1.01 ± 0.02	0.40 ± 0.01	NA
Silica	Hunt AC-20	Precoated	75.7 ± 3.48	0.26 ± 0.01	-64.6
Warrior River Sand	Hunt AC-20	Precoated	0.25 ± 0.01	0.42 ± 0.01	-74.5
Greywacke	AC-10 (AAD-1)	Precoated	0.39 ± 0.20	0.16 ± 0.08	-61.4

¹ % Difference = [(B-A)/A] × 100

where A = Monolayer of Uncoated Aggregate
B = Monolayer of Precoated Aggregate

² NA = Not Applicable

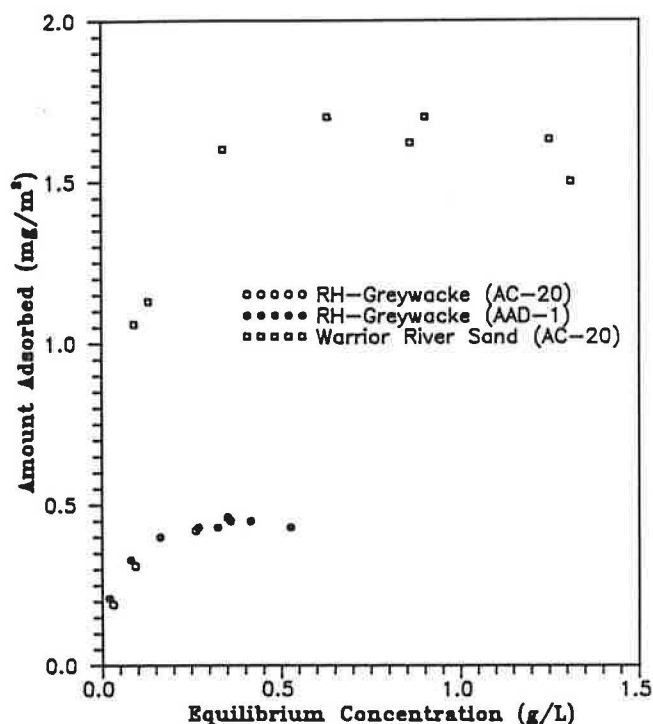


FIGURE 6 Adsorption of AC-20 and AAD-1 asphalts onto Warrior River sand and RH-greywacke on the basis of surface area.

SUMMARY AND CONCLUSIONS

The adsorption behavior of asphalt and asphalt functionalities was substantially affected by precoating the aggregate surface with AS agents. Acidic functionalities increased in adsorption on the precoated silica compared to the uncoated silica whereas the nonacidic functionalities decreased. This behavior may be explained by acid-base interactions between the acidic functionalities and the Lewis base AS agents and by repulsion between the AS agents and the nonacidic functionalities that are also Lewis bases. Another possible explanation for the decreased adsorption of the nonacidic functionalities is that the preadsorbed AS agents were occupying sites on the aggregate that would have been otherwise occupied by the nonacidic functionalities. The nonacidic functionalities were unable to replace the preadsorbed AS agents and, hence, showed minimal adsorption. These results indicate that if aggregate was precoated with AS agents or if the surface of the aggregate became coated with the AS agent because of migration of the AS agent to the aggregate surface, then the aggregate surface chemistry changed substantially. This change directly affected the adsorption behavior of different asphalt functionalities and the character of the asphalt-aggregate bond.

Substantial reductions in the asphalt adsorption onto aggregates precoated with AS agents were also observed. Because the amount of asphalt adsorbed decreased for the precoated aggregate compared to the uncoated, the functionalities involved at the uncoated interface most likely were composed of nonacidic as well as acidic functionalities. The presence of some asphalt adsorption indicated that some of the bonding functionalities were acidic or at least were able to replace the AS agents on adsorption sites on the aggregate surface.

Insights were gained into the chemistry occurring at the asphalt-aggregate interface when AS agents are present. The AS agent changed the chemistry at the interface. Less asphalt was adsorbed with precoated aggregate but less asphalt was desorbed also. Recommendations for actual practice must await further research investigating the asphalt-aggregate bond and its link to performance.

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