performed under NCHRP Projects 4-8(3) and 4-8(3)/1. NCHRP Project 4-8(3) was conducted at the University of Idaho; part of the work was performed by Battelle-Northwest and the University of Washington under subcontracts with the University of Idaho. NCHRP Project 4-8(3)/1 was coordinated by the University of Idaho; predictive moisture testing and subsequent periodic testing of field cores from pavement test sections were performed by seven highway agencies: Arizona, Colorado, FHWA Region 10 (Western Direct Federal Division), Georgia, Idaho, Montana, and Virginia. The continued cooperation and steadfastness of the materials and research personnel at these agencies has been gratefully appreciated throughout the five-year field evaluation study.

The opinions and findings expressed or implied in this paper are mine. They are not necessarily those of the Transportation Research Board, the National Academy of Sciences, the Federal Highway Administration, the American Association of State Highway and Transportation Officials, or the individual states participating in the National Cooperative Highway Research Program.

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Chemistry of Asphalt-Aggregate Interaction: Relationship with Pavement Moisture-Damage Prediction Test

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Relationships were found between fundamental chemical and physical properties of the asphalt-aggregate bond and moisture-induced damage in asphalt pavement mixtures subjected to the Lottman conditioning procedure in National Cooperative Highway Research Program (NCHRP) Field Evaluation Project 4-8(3)/1. The relative tendency of different chemical functional types in asphalts to be strongly adsorbed on aggregate surfaces and their relative displacement from aggregate surfaces by water were determined. The affinity of the aggregates for pyridine-type nitrogen was also determined. For most asphalt-aggregate mixtures of the Lottman-NCHRP study, resistance to moisture-induced damage appeared to be controlled by a number of interrelated variables. These variables must be considered in concert to rationalize pavement moisture damage. The sensitivity of pavement mixtures to moisture-induced damage was explained by considering fundamental physiochemical properties of the asphalt-aggregate bond.

Premature pavement failure attributed to moisture-induced damage has long been recognized, but solutions to the problem have been far from satisfactory. This type of damage, generally believed related to rupture of the adhesive bond at the asphalt-aggregate interface, is a complex phenomenon involving physical and chemical properties of both the asphalt and the aggregate. Moisture damage is also strongly influenced by pavement-mixture morphology and external environmental factors.

A laboratory test method for predicting moisture-induced damage in asphaltic pavements was developed by Lottman (1) during work sponsored by the National Cooperative Highway Research Program (NCHRP). Phase 2 of this program involved a field evaluation to determine test-method predictability. The field evaluation commenced in 1974 under Lottman's direction with participation by seven state and federal agencies (2, 3) and was completed in 1981.

Our study reported in this paper was conducted by using materials identical to those used in the field-evaluation pavements. Objectives of our study were (a) to determine physiochemical properties of the asphalt-aggregate interaction as related to pavement moisture damage, (b) to correlate these findings with the predictive results of the Lottman test obtained by the participating agencies, and (c) to evaluate potential moisture-damage test methods developed in our own laboratory. The correlation of Lottman test-method results with actual field performance, which requires consideration of construction and environmental factors, is germane to the NCHRP study but is not considered in this paper.

In our study we have used methods developed in our laboratory for qualitatively and quantitatively determining a number of chemical functional group types in asphalts (4,5), their relative tendency to be adsorbed on mineral aggregate surfaces (6-8), and their relative displacement from aggregate surfaces by water (8). The methods are based on selective solvent desorption of asphalt components from aggregate surfaces followed by functional group characterization of the components by using differential infrared spectrometry and selective chemical reactions. These methods provided fundamental data on the chemistry of the asphalt-aggregate interaction by using microcalorimetry (9) and characterization of aggregate surfaces by using a pyridine adsorption-desorption technique (10). Fundamental factors affecting the performance properties of the individual pavement mixtures used in the NCHRP field-evaluation project are discussed.

EXPERIMENTAL

Materials

Asphalts and Aggregates

Seven asphalt cements and aggregate lots, each from the same source used in actual pavement construction, were supplied by the following participating state and federal transportation agencies: Arizona, Colorado, FHWA Region 10 (Oregon), Georgia, Idaho, Montana, and Virginia. The Georgia asphalt was evaluated both with and without 0.25 weight percent antistripping additive. Aggregate types are identified as follows by Lottman (2): Arizona--Santa Cruz River gravels; Colorado--Morrison Creek stone coarse aggregate and Platte River (Littleton) fine aggregate; FHWA Region 10--Pole Creek stockpile and Kalamath County with 14 percent blended sand; Georgia--granite gneiss; Idaho--Salmon River gravels; Montana--bench gravels; and Virginia--granite coarse aggregate plus natural sand. Locations and details of pavement construction have been reported (2). For our study, aggregates were crushed, wet-screened without surfactants to 0.85-0.50 and 0.25-0.18 mm (20-35 and 60-80 mesh size), rinsed with distilled water, and dried at 150°C for 24 h prior to use.

Solvents

Reagent-grade solvents were used. Benzene and pyridine were dried by refluxing for 8 h over calcium hydride before distillation through a Vigreaux column. Peroxide-free tetrahydrofuran (THF) (11,4) was kept dry by storing over 4-A molecular sieves.

Procedures

Asphalt-Coated Aggregates

The asphalts (63 g) and aggregates (1197 g) representing each field mixture were preheated at 150°C for 1 and 24 h, respectively, prior to mixing. The asphalt-aggregate mixtures were held at 150°C for 4.5 h in an oven, slowly cooled to ambient temperature by shutting off the oven, and then stored in the dark at ambient temperature for an additional 62 h before further treatment.

Isolation of Asphalt Fraction Not Strongly Adsorbed on Aggregate

The asphalt-coated aggregate was transferred as a benzene slurry into a separatory funnel containing a glass-wool plug between the main body of the funnel and the stopcock. The bulk of the asphalt was washed from the aggregate by slowly percolating cold benzene through the aggregate bed without agitation until the benzene was colorless. The benzene extract, concentrated by solvent removal in a rotary film evaporator, was filtered through a 0.9- to 1.4-micron fritted glass funnel before final solvent removal at 92°C in a rotary film evaporator at 0.3 kPa (2 Torr). The absence of benzene in the recovered asphalt fraction was established by the absence of an intense benzene infrared absorption band at 670 cm^{-1} in a carbon disulfide solution.

Isolation of Asphalt Fraction Strongly Adsorbed on Aggregate Surface and Displaced by Water

The benzene-washed aggregate particles from the above separation were dried overnight at 30°C and 8-13 kPa (60-100 Torr). The dried aggregate particles were transferred into a glass vessel containing sufficient distilled water to cover the aggregate. Pressure within the vessel was slowly reduced to about 0.8 kPa (5 Torr) over a 1.5-h period and the reduced pressure maintained for an additional half hour after gas bubbles had ceased to appear in the water above the aggregate. After restoration to atmospheric pressure, the vessel was subjected to a 21-h freeze cycle at -10 to -12°C followed by a 24-h heat cycle at 60°C. These exposure conditions were similar to those used by Lottman (1-3) for pavement mixtures. The contents of the glass vessel were transferred to a separatory funnel, and the water was drained from the aggregate. Several bed volumes of benzene (1000 ml total) were slowly percolated through the wet aggregate and combined with the water initially drained from the aggregate. The water was distilled from the combined water-benzene mixture by using the water-benzene azeotrope. The water-displaced asphalt fraction was recovered from the benzene solution by concentration, filtration, and solvent removal as described above for the benzene extract.

Isolation of Asphalt Fraction Strongly Adsorbed on Aggregate Surface and Not Displaced by Water

The aggregate particles separated from the benzene-water mixture described above were washed several times with pyridine followed by an 8-h pyridine extraction in a modified Soxhlet extractor (12). The displaced asphalt components were recovered from the pyridine by concentration, filtration, and solvent removal as described above for the benzene extracts.

Functional Group Analyses

Ketones, carboxylic acids, anhydrides, and 2-quinolone types were quantitatively determined by selective chemical reactions and differential infrared spectrometry as previously described (4,5) except that the sample size was reduced from 0.125 to 0.0312 g for strongly adsorbed and water-displaced fractions. Sulfoxide concentrations were determined from the area of the 1030-cm^{-1} infrared absorption band (12). By using the general differential techniques previously described (4), phenols were determined from the differential spectra of sodium hydroxide-treated asphalt versus untreated asphalt by using the phenol-THF solvent hydrogen-bonding infrared band at 3300 cm^{-1}. Pyrroles, which also absorb at 3300 cm^{-1} in THF, were assigned the balance of the 3300-cm^{-1} band not attributed to phenolics. Apparent integrated absorption intensities (b) used for phenolic OH and pyrrolic NH, not previously reported, were 1.54×10^4 and 1.45×10^4 L mol^{-1} cm^{-2}, respectively. Total nitrogen determinations were made with an Antek Model 720 digital nitrogen detector.

Pyridine-Aggregate Interactions

Aggregates (0.25-0.18 mm, 60-80 mesh) were prepared for analysis by submerging them in pyridine followed by air drying and then by heating the aggregates for two days at 115°C in an air-purged oven. Treated aggregate (0.2500 g) was then placed in an Antek Model 772 microcomputer-controlled pyroreactor coupled to an Antek Model 720 digital nitrogen detector, and the temperature was increased to 900°C at 50°C/min with a 5-min isothermal period at 100°C and 7-min isothermal periods at 150 and 300°C.

Table 1. Selected aggregate properties.

		Aggregate Surface Properties						
			Elements by X-Ray Fluorescence[b]					
Source	Type[a]	Area (m^2/g)	Al	Si	S	K	Ca	Fe
Idaho (no lime)	Salmon River gravels	2.30	M	M	L	L	H	H
FHWA Region 10	Pole Creek stockpile with 14 percent blended sand	1.92	M	M	L	L	H	M
Montana	Bench gravels	0.47	M	M	H	H	M	M
Virginia	Coarse granite	2.61	M	M	M	H	M	M
Colorado	Coarse–Morrison crushed stone; fine–Platte River	1.95	M	M	H	H	M	M
Arizona	Santa Cruz river gravels	3.00	M	M	M	H	M	M
Georgia	Granite gneiss	0.10	M	M	M	H	M	M
Georgia + additive	Granite gneiss	0.10	M	M	M	H	M	M

[a] Lottman (2, 3).
[b] Relative abundance: L = low, M = medium, H = high (abundance levels can be compared for each element among different aggregate systems but not for one element with another of a different type).

Table 2. Selected properties of asphalt-aggregate mixtures.

Source	Lottman's TSR[a] (conditioned/dry)	WST[b] (cycles to failure)	Bonding Energy[c] (mJ/g-min)
Idaho	0.8 (lime)	2 (no lime)	2.8 (no lime)
FHWA Region 10	0.6	5	2.9
Montana	0.6	5	2.1
Virginia	0.4	3-4	4.2
Colorado	0.2	3	0.50
Arizona	0.2	2	1.05
Georgia	0	2	1.7
Georgia + additive	0	2	-

[a] Tensile-strength ratio of laboratory-fabricated pavement specimens (2, 3).
[b] Water-susceptibility test.
[c] Rate of energy release of the asphalt-aggregate interaction after 3 h in a microcalorimeter at 130°C.

Aggregate and Mix Properties

Aggregate surface areas of the 0.85- to 0.50-mm (20- to 35-mesh) fractions were determined by the BET (Brumauer, Emmett, and Teller) method by using krypton as the absorbate. The relative abundance of the aluminum, silicon, sulfur, potassium, calcium, and iron in the aggregates was determined by X-ray fluorescence on pulverized specimens.

Water-susceptibility test (WST) determinations were made on miniature briquets prepared from 0.83- to 0.42-mm (20- to 35-mesh) aggregates as previously reported (13). Briefly, briquets mounted on a stress pedestal and submerged in water were repeatedly subjected to freeze-thaw-warm-water-soak cycling until the briquets failed from crack propagation or fracture.

Asphalt-aggregate interaction energies (bonding energies) were determined by using a sensitive microcalorimeter (9). The interaction energies are reported as the rate of energy release after 3 h of contact between the asphalt and aggregate at 130°C.

RESULTS

Properties of Aggregates

Selected aggregate properties are shown in Table 1. Surface areas ranged from 3.00 m^2/g for the Arizona aggregate to 0.10 m^2/g for the Georgia aggregate. Relative concentrations of selected elements in the mineral surfaces were determined by X-ray fluorescence spectroscopy; however, the chemical structural composition of the mineral was not determined. The Idaho and FHWA Region 10 aggregates were notably different from the remaining aggregates, being lower in minerals containing sulfur and potassium and higher in calcium-containing minerals. Idaho aggregate was highest in iron.

Properties of Asphalt-Aggregate Mixtures

Selected properties of asphalt-aggregate mixtures are shown in Table 2. Values for the Lottman tensile-strength ratios (TSRs) are those obtained by the participating agencies on laboratory-fabricated Marshall specimens before extended aging. TSR is the average tensile strength of a set of specimens after conditioning by vacuum-water saturation, freeze-thaw cycling, and a 24-h warm-water soak at 60°C divided by the average tensile strength of a set of specimens dried in a desiccator to constant weight (1-3). This conditioning procedure was used to predict long-term moisture-induced pavement damage. TSRs for Idaho, FHWA Region 10, and Montana were 0.6 or greater, predicting moisture-resistant mixtures; values for Virginia, Colorado, and Arizona were intermediate; Georgia specimens lost all strength during conditioning.

Results by using the WST developed in our laboratory (13) showed a fair correlation (Table 2) with Lottman's TSR. Our test, which uses a narrow aggregate size range to maximize sensitivity to asphalt bonding properties, subjects a miniature briquet mounted on a stress pedestal under water to repeated freeze-thaw-heat cycling until the briquet fails. A notable exception to the correlation was the Idaho sample (discussed later).

Table 2 also shows the energy of interaction, called bonding energy, of aggregate with asphalt 3 h after mixing as measured with a sensitive microcalorimeter (9). A relationship between the bonding energy and the TSR or cycles to failure in the WST was not apparent.

Analyses of Asphalts and Asphalt Fractions Not Strongly Adsorbed

The concentrations of selected chemical functionality in the original asphalts and in the fractions desorbed from asphalt-coated aggregates with benzene are shown in Table 3. Oxygen-containing functional groups formed by air oxidation, such as ketones (14), carboxylic acids (11), anhydrides (15), and sulfoxides (12,16) were usually found in higher concentrations in the fractions not strongly adsorbed on the aggregate surface than in the original asphalts. This result is attributed to air oxidation during the initial 4.5-h oven aging of the asphalt-aggregate mixtures at 150°C. In some cases, carboxylic acid concentrations are an exception because they are selectively adsorbed on aggregate surfaces (6-8), thus depleting their concentration in the asphalt fraction not strongly adsorbed. As

Table 3. Concentrations of chemical components in original asphalts and their amounts and concentrations in asphalt fraction not strongly adsorbed on aggregate surface.

Source	Percent of Original Asphalt	Concentration (moles/L)							
		Total Nitrogen	Pyrrolic NH	Phenolic OH	Ketones	Carboxylic Acids	Anhydrides	2-Quinolone Types	Sulfoxides
Original Asphalts									
Idaho (no lime)		0.55	0.13	0.06	Trace	0.021	Trace	0.016	0.022
FHWA Region 10		1.07	0.42	0.06	0.03	0.052[a]	Trace	0.029	0.024
Montana		0.46	0.12	0.02	Trace	Trace	Trace	0.025	0.018
Virginia		0.21	0.04	0.02	0.21	0.014	Trace	0.014	0.010
Colorado		0.53	0.093	0.035	Trace	0.0035	0.001	0.023	0.022
Arizona		0.86	0.38	0.10	0.05	0.018	Trace	0.026	0.022
Georgia		0.31	0.05	0.02	0.04	Trace	Trace	0.017	0.036
Georgia + additive		0.35	0.05	0.02	0.024	0.0026	Trace	0.017	0.014
Fraction Not Strongly Adsorbed on Aggregate Surface									
Idaho (no lime)	98.7	0.55	0.14	0.07	0.19	0.005	0.002	0.021	0.28
FHWA Region 10	98.0	1.03	0.46	0.09	0.46	0.037	0.026	0.026	0.18
Montana	99.3	0.46	0.12	0.06	0.25	0.003	0.007	0.014	0.21
Virginia	98.1	0.20	0.05	0.02	0.35	0.014	0.006	0.014	0.18
Colorado	99.1	0.53	0.08	0.08	0.14	0.006	0.005	0.017	0.29
Arizona	98.4	0.82	0.44	0.08	0.46	0.018	0.018	0.024	0.20
Georgia	99.8	0.31	0.05	0.02	0.25	0.006	0.005	0.010	0.23
Georgia + additive	99.9	0.34	0.05	0.07	0.29	0.009	0.007	0.010	0.21

[a] Fifty percent were acid salts.

Table 4. Amounts and concentrations of chemical components in asphalt fraction strongly adsorbed on aggregate surface and their concentration ratios.

Source	Percent of Total Asphalt	Total Nitrogen	Pyrrolic NH	Phenolic OH	Ketones	Carboxylic Acids	Anhydrides	2-Quinolone Types	Sulfoxides	Sum[a]
Concentration of Total Fraction Strongly Adsorbed on Aggregate Surface (moles/L)										
Idaho (no lime)	1.3	0.36	<0.01	<0.01	0.23	0.13	0.07	0.07	0.72	1.5
FHWA Region 10	2.0	0.33	0.07	0.84	0.69	0.45	0.27	0.10	0.31	2.9
Montana	0.72	0.22	0.03	0.20	0.53	0.14	0.12	0.11	0.56	1.5
Virginia	1.9	0.19	<0.01	<0.01	0.35	0.38	0.08	0.05	0.64	1.6
Colorado	0.86	0.10	0.06	0.27	0.26	0.12	0.07	0.10	0.90	1.7
Arizona	1.6	0.42	0.14	0.67	0.36	0.23	0.10	0.06	0.53	2.3
Georgia	0.16	2.39	0.02	0.08	0.29	0.41	0.16	0.10	0.38	3.7
Georgia + additive	0.13	2.78	0.34	0.48	1.8[b]	0.25	0.20	0.09	0.23	5.7
Concentration Ratio[c]										
Idaho (no lime)		0.65	<0.06	<0.15	1.2	26	4	3	2.5	
FHWA Region 10		0.32	0.15	9.3	1.5	12	10	4	1.7	
Montana		0.48	0.25	3.3	1.0	47	17	8	2.7	
Virginia		0.95	<0.2	<0.5	1.0	27	13	4	3.6	
Colorado		0.18	0.75	3.4	1.9	20	14	6	3.1	
Arizona		0.51	0.32	8.4	0.78	13	6	3	2.7	
Georgia		7.7	0.40	4.0	1.2	68	32	10	1.6	
Georgia + additive		8.2	6.8	6.9	6.2[b]	28	29	9	1.1	

[a] Sum of functional groups less pyrrolic NH and 2-quinolone types that contribute to total nitrogen.
[b] Because of the additive, amide and/or ester carbonyl may contribute to this analysis.
[c] Concentration in strongly adsorbed fraction divided by concentration in fraction not strongly adsorbed.

indicated in Table 3, more than 98 percent of the asphalt was recovered from all aggregate mixtures by benzene extraction. Hydrated lime was used in the actual Idaho pavement mixture but was inadvertently omitted in our laboratory studies. Beneficial effects of lime in reducing moisture damage have been reported in both laboratory (13) and field studies (17).

Analyses of Strongly Adsorbed Asphalt Fractions, Their Relative Affinity for Aggregate Surfaces, and Their Relative Displacement by Water

Following extraction of the asphalts from the aggregates with benzene, the aggregates were subjected to a water-saturation freeze-thaw procedure to displace strongly adsorbed water-sensitive components from the aggregate surface; the water-sensitive components were subsequently recovered. Finally, the strongly adsorbed components not displaced by water were recovered from the aggregate surface with refluxing pyridine. Percentages recovered and functional group analyses of the recovered fractions are reported in Tables 4, 5, and 6. Because the entire strongly adsorbed fraction was not isolated as a discrete fraction but as water-displaceable and not-water-displaceable subfractions, data in the upper half of Table 4 were calculated from data obtained on the two subfractions (Tables 5 and 6). The entire strongly adsorbed fraction ranged from 0.13 to 2.0 percent of the total asphalt (Table 4). Amounts of the strongly adsorbed fraction displaceable by water ranged from 1.9 to 9.7 percent (Table 6). The sum of the functional group components of the asphalt found in the strongly adsorbed fraction (Table 4) ranged from 1.5 moles/L for the Idaho and Montana systems to 5.7 moles/L for the Georgia-plus-additive system. Assuming an average molecular

Table 5. Amounts and concentrations of chemical components in strongly adsorbed asphalt fraction that was not displaceable with water.

Source	Percent of Original Asphalt	Concentration (moles/L) Total Nitrogen	Pyrrolic NH	Phenolic OH	Ketones	Carboxylic Acids	Anhydrides	2-Quinolone Types	Sulfoxides
Idaho (no lime)	1.3	0.35	ND[a]	ND	0.23	0.13	0.07	0.07	0.69
FHWA Region 10	1.9	0.32	0.07	0.84	0.70	0.43	0.26	0.10	0.31
Montana	0.71	0.21	0.03	0.20	0.53	0.14	0.12	0.14	0.56
Virginia	1.8	0.19	ND	ND	0.35	0.39	0.08	0.05	0.63
Colorado	0.82	0.10	0.06	0.27	0.26	0.12	0.06	0.10	0.90
Arizona	1.6	0.40	0.14	0.67	0.36	0.24	0.09	0.06	0.50
Georgia	0.14	2.6	0.02	0.08	0.31	0.43	0.17	0.08	0.36
Georgia + additive	0.12	2.9	0.34	0.48	1.8[b]	0.23	0.21	0.07	0.22

[a] Not detected. [b] Includes possible nonketone carboxyl from antistripping additive.

Table 6. Amounts and concentrations of chemical components in strongly adsorbed asphalt fraction that was displaceable with water.

Source	Percent of Total Strongly Adsorbed Asphalt	Concentration (moles/L) Total Nitrogen	Pyrrolic NH	Phenolic OH	Ketones	Carboxylic Acids	Anhydrides	2-Quinolone Types	Sulfoxides
Idaho (no lime)	2.5	0.63	ND	Trace	0.18	0.31	0.27	0.19	1.76
FHWA Region 10	3.0	0.49	ND	ND	0.41	1.12[a]	0.74	Trace	0.46
Montana	1.9	0.54	ND	ND	0.14	0.40	0.34	0.43	2.63
Virginia	3.8	0.21	ND	ND	0.25	0.53	0.22	0.11	0.89
Colorado	3.6	0.10	ND	ND	0.31	0.25	0.41	0.24	0.92
Arizona	2.7	1.21	ND	0.6	0.24	0.60	0.45	0.45	1.60
Georgia	9.7	0.31	ND	ND	0.10	0.22	0.11	0.30	0.61
Georgia + additive	6.3	1.4	ND	Trace	Trace	0.49	0.16	0.32	0.20

Note: ND = not detected.

[a] Plus some insoluble carboxylate salts.

the concentration of a given functional group in the entire strongly adsorbed fraction divided by the corresponding concentration in the fraction not strongly adsorbed. As found earlier (6-8), carboxylic acids and anhydrides have the greatest affinity for aggregate surfaces. Although it seems justified to compare concentration ratios of strongly adsorbed species within a single asphalt-aggregate system, caution should be exercised in comparing concentration ratios from one system to another because concentrations in the initial asphalt, which affect the numerical value of the ratio, vary greatly from one asphalt to another.

weight of 700 and a density of 1 for the strongly adsorbed components, a concentration as low as 1.5 moles/L indicates an average of more than one functional group per molecule, virtually assuring polyfunctionality for many strongly adsorbed molecular species.

The relative affinity of functional group types for aggregate surfaces is shown in the lower half of Table 4 as the concentration ratio. This ratio is

The water-displacement ratios (8) shown in Table 7 were calculated from data in Tables 5 and 6. These ratios indicate the relative tendencies for the different functional group types in the strongly adsorbed fraction to be displaced from the aggregate surfaces with water. This ratio is the functional group concentration in the water-displaced fraction divided by the corresponding concentration in the strongly adsorbed fraction not displaced with water. Carboxylic acids, anhydrides, and 2-quinolone types in most systems were the functional types most readily displaced with water. Nitrogen compounds (determined as total nitrogen) and sulfoxides also generally showed significant water displacement. It should be noted that concentration values are not a measure of the amounts of material actually displaced.

Pyridine-Aggregate Interactions

The relative concentration density of adsorption sites on aggregate surfaces that strongly adsorb pyridine (amount divided by surface area) and the thermal desorption characteristics of adsorbed pyridine are shown in Table 8. Pyridine is the lowest-molecular-weight member of a nitrogen type found in petroleum. The data reflect the relative amounts of pyridine nitrogen desorbed from pyridine-treated aggregates as the temperature is slowly raised in the oven of a nitrogen analyzer. No pyridine nitrogen remained on the aggregate above 600°C. Montana aggregate showed the highest pyridine adsorption density and Georgia, the lowest. Most of the pyridine nitrogen desorbed from the aggregates appeared in three desorption temperature ranges with maxima at about 140, 280, and 480°C. The relative amounts desorbed at the different temperature ranges varied with aggregate source.

DISCUSSION OF RESULTS

The adhesive bond between asphalt cements and aggregate surfaces and the effect of moisture on this bond are complex phenomena primarily because of the complex nature and variable composition of materials involved. Consequently, tests to predict the moisture sensitivity of asphalt-aggregate mixtures have been largely empirical. Empirical tests, however, do not provide the fundamental information necessary to optimize the material choices or determine corrective measures when loss of the asphalt-aggregate bond is a potential problem. In this study we have attempted to identify fundamental chemical and physical properties of the asphalt-aggregate bond and show how these properties are affected by moisture.

Table 7. Displacement of strongly adsorbed asphalt components by water treatment.

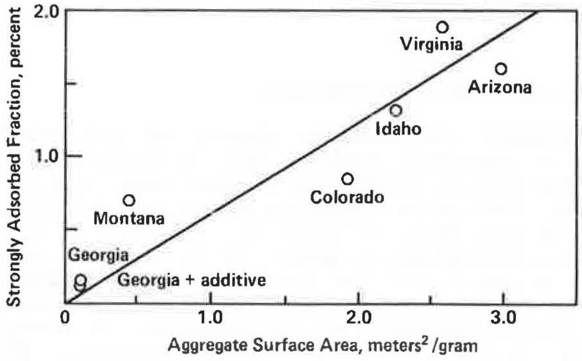
Source	Water-Displacement Ratio[a] Total Nitrogen	Pyrrolic NH	Phenolic OH	Ketones	Carboxylic Acids	Anhydrides	2-Quinolone Types	Sulfoxides
Idaho (no lime)	1.8	ND[b]	ND[b]	0.78	2.4	3.9	2.7	2.6
FHWA Region 10	1.5	Low[c]	Low	0.59	2.6	2.8	<0.1	1.5
Montana	2.8	Low	Low	0.26	2.9	2.8	3.1	4.7
Virginia	1.1	ND[b]	ND[b]	0.71	1.4	2.8	2.2	1.4
Colorado	1.0	Low	Low	1.2	2.1	6.8	2.4	1.0
Arizona	3.0	Low	0.09	0.67	2.5	5.0	7.5	4.4
Georgia	0.12	Low	Low	0.32	0.5	0.6	3.8	1.7
Georgia + additive	0.48	Low	Low	<0.06	2.1	0.8	4.6	0.9

[a] Concentration in fraction displaced by water divided by concentration in fraction not displaced by water.
[b] Not detected in either fraction.
[c] Too small to be measured.

Table 8. Relative surface density of aggregate adsorption sites and their affinity for pyridine as determined by pyridine desorption temperature profile.

Source	Aggregate Surface Area (m^2/g)	Pyridine Nitrogen Desorbed <100°C	100-150°C	150-300°C	300-600°C	Total
Idaho (no lime)	2.30	1.4	14.3	17.2	8.8	41.7
FHWA Region 10	1.92	1.8	9.3	20.2	14.8	46.1
Montana	0.47	3.4	68.3	30.2	30.8	132.7
Virginia	2.61	0.7	8.5	7.0	1.1	17.3
Colorado	1.95	3.1	20.4	12.5	3.8	39.8
Arizona	3.00	1.1	13.9	13.2	5.2	33.4
Georgia	0.10	0	1.0	0.8	0	1.8

Figure 1. Comparison of aggregate surface area and amount of strongly adsorbed asphalt fraction.



Relationships Between Aggregate Surface Area and Adsorption of Asphalt Components

As shown in Table 4, up to 2 percent of the asphalt in the asphalt-aggregate mixtures was so strongly adsorbed on the aggregate surfaces that it was not extractable with benzene. A previous study (8) indicated that aggregates from benzene-extracted mixtures were coated with approximately a monomolecular layer of asphalt molecules, indicating generally a high surface density of active sites. These results are supported by those of the present study (Figure 1) in which a relationship was found between measured aggregate surface area and the amount of strongly adsorbed components. Because all crushed aggregates were screened to a similar particle-size distribution, variations in the measured aggregate surface areas must necessarily relate to variations in aggregate surface characteristics; i.e., higher aggregate surface area indicates more porous or rough surface texture.

The unusually low surface area of the Georgia aggregate is believed related to the high moisture sensitivity of the Georgia pavement mixture. Its low surface area was similar to that of a highly crystalline calcite aggregate characterized previously (8). The low surface areas of both aggregates suggest a smooth, crystalline surface with low voids or surface roughness. This was verified by microscopic examination. From purely mechanical considerations, this should reduce adhesive bond strength. Both the Georgia and the calcite aggregate produced highly moisture-sensitive asphalt-aggregate mixtures.

An important comparison of aggregate adsorption characteristics is provided by the Montana and the Colorado aggregates. Although both had nearly the same amounts of strongly adsorbed asphalt components (Table 4), the Colorado aggregate had four times the surface area (Table 1). This result suggests that the Montana aggregate has either a higher surface density of adsorption sites than the Colorado aggregate or that Colorado aggregate adsorption sites, because of steric hindrance, are not accessible. In any event, the density of asphalt components is much higher on the Montana aggregate than on the Colorado aggregate. Pyridine adsorption and desorption data shown in Table 8 support the high density of surface adsorption sites for the Montana aggregate. Based on the above discussion, one is led to conclude that both chemical and physical properties of the aggregate surfaces play an important role in determining the adhesive properties of the asphalt-aggregate bond.

Relative Affinity of Aggregate Surfaces for Asphalt Components

The varying composition of the strongly adsorbed fraction among asphalt-aggregate systems is demonstrated by the data in Table 4. The functional group types determined are representative of the major polar types initially present in asphalts or formed during pavement preparation and subsequent aging. Although the determinations were made on components recovered from aggregates following a benzene extraction of the asphalt-aggregate mixtures, reasoning suggests that polar components were present in high concentration on the aggregate surfaces prior to the benzene-extraction step. Most asphalts have a large excess of adsorbable species over that needed to saturate the aggregate adsorption sites. High temperatures during pavement-mixture preparation should allow the more polar species to equilibrate with the aggregate surface and displace the more weakly adsorbed or nonpolar components that may have been initially adsorbed. Furthermore, multilayer adsorption (9), which might interfere with the adsorption of polar components at the asphalt-aggregate interface, has not been observed in our laboratory in microcalorimetric studies of nonpolar asphalt fractions. The ability of polar asphalt components formed during oxidative aging to migrate to the aggregate surfaces at pavement mixing temperatures has been demonstrated by inverse gas-liquid chromatography studies (18). In any event, the distribution of strongly adsorbed polar components on aggregate surfaces following benzene extraction serves to characterize the adsorption properties of the aggregate with regard to asphalt components.

The high sum of polar group concentrations in the strongly adsorbed fraction (Table 4) indicates that molecules in this fraction, as previously explained, probably contain more than one functional group and/or that adsorbed molecules are of unusually low molecular weight. Polyfunctionality complicates the determination of adsorption characteristics of adsorbed species, making it difficult to determine the relative contribution to adsorption of different functional groups on the same molecule. This problem can often be partly resolved by knowledge of the chemical properties of the different functional types and general trends observed when comparing similar data on different systems. The high sum of functional group concentrations for the Georgia systems (3.7 and 5.7 moles/L) is attributed largely to the high nitrogen content.

The relative affinity of the aggregate surfaces for the different chemical functional types in each pavement mixture can be judged from the concentration ratios (lower half of Table 4). It becomes apparent, except for the Georgia-plus-additive system, that carboxylic acids are the functional types most strongly adsorbed by all aggregates. The lower value for Georgia-plus-additive than for Georgia alone probably results from competition by the antistripping agent for potential carboxylic acid adsorption sites. The high concentration ratios for carboxylic acids cannot be overemphasized. Carboxylic acids often occur in only trace amounts in asphalts (Table 3) but are usually significant contributors to the strongly adsorbed fraction (Table 4). Phenols, anhydrides, sulfoxides, and 2-quinolone types are also significantly concentrated on the aggregate surface. Notable exceptions are the phenols on the Idaho and Virginia aggregates. These exceptions may be more apparent than real because of possible inability of the solvent to displace phenols from these aggregates; phenols were present in the original asphalt. The relatively low concentration ratios for sulfoxides and ketones do not necessarily reflect correspondingly low contributions to the strongly adsorbed fraction but often result from their relatively high initial concentrations in the asphalts.

Low concentrations of pyrrolic NH in the strongly adsorbed fractions were expected because these types form weak hydrogen bonds (19) and would not be expected to associate strongly with most mineral adsorption sites. The high pyrrolic concentration in the Georgia-plus-additive system probably results from the antistripping additive. Other nitrogen types such as the pyridine type, which have been shown to interact strongly with aggregate surfaces (13,20, and Table 8 of this paper), probably largely account for the strongly adsorbed nitrogen types. The high concentration of nitrogen in many of the original asphalts and/or the low density of nitrogen adsorption sites on the aggregates may in part account for the low total nitrogen concentration ratios. The unusually high concentration attributed to ketones for the Georgia-plus-additive system was indicated from detailed infrared analyses to result largely from amides and/or esters from the antistripping agent that were concentrated on the aggregate surface. The high concentration of ketones in the FHWA Region 10 system is noteworthy since ketones have been shown to resist displacement from the aggregate surfaces by water (8).

X-ray fluorescence analysis (Table 1) showed that Idaho and FHWA Region 10 aggregates were lower in sulfur and potassium and higher in calcium than the other aggregates, suggesting that these aggregates produce more moisture-resistant mixtures for the following reasons. Sulfur-containing inorganic compounds (probably sulfates) and potassium ions often readily associate with water, which could disrupt the asphalt-aggregate bond. Also, aggregate treatment with a hydrated lime slurry (calcium hydroxide) is known to improve moisture resistance of many aggregates, presumably from the interaction of asphalt components with the calcium.

An inescapable conclusion resulting from analyses of the strongly adsorbed fractions is that asphalt-aggregate interaction chemistry is highly complex and variable among different asphalt-aggregate systems and that the interactions are a function of both asphalt and aggregate properties. This conclusion is supported by asphalt-aggregate interaction energies (bonding energies) as measured by microcalorimetry (9); these interactions are highly asphalt- and aggregate-dependent, as illustrated in Table 2. High interaction energies, proposed to result from multilayer adsorption of asphalt components on aggregate surfaces (21), should be related to bond-strength properties. A high interaction energy may not, however, be a necessary condition for resistance to moisture damage in asphalt-aggregate mixtures.

Water Displacement of Asphalt Components from Aggregate Surfaces

The ability of water to displace strongly adsorbed components from aggregate surfaces should significantly affect the sensitivity of asphalt-aggregate mixtures to moisture damage. Fundamental studies in our laboratory (8) have shown that the water desorption characteristics of the strongly adsorbed fraction are dependent both in quantity and quality on individual mixture characteristics. The systems of the present study were no exception. The Montana aggregate had the highest density of pyridine adsorption sites (Table 8) and the least amount of the strongly adsorbed fraction displaced by water (1.9 percent, Table 6). The Georgia aggregate, on the other hand, had the lowest density of pyridine adsorption sites and the highest amount of strongly adsorbed fraction (9.7 percent) displaced by water. Based on these facts alone, moisture-damage resistance should be high for the Montana system and low for the Georgia system. Colorado aggregate, with nearly the same amount of strongly adsorbed fraction as Montana aggregate, showed twice the quantity of water-displaced material; thus, based on this consideration, the Montana system would be rated superior to the Colorado system.

The relative tendency for the various chemical functional groups to be displaced by water, as indicated by the water-displacement ratio, is shown in Table 7. These ratios should be considered together with the relative amounts of strongly adsorbed fraction displaced by water in assessing moisture-damage potential of pavement mixtures. In general, those functional types most highly concentrated in the strongly adsorbed fraction, with the exception of phenols, were most readily water-displaced. This result is consistent with previous work (8). Thus, high concentrations of these groups on aggregate surfaces may contribute to the moisture sensitivity of mixtures. Carboxylic acids, anhydrides, and 2-quinolones showed the highest displacement ratio, probably because these functional group types and the aggregate surfaces both have a high affinity for water via hydrogen bonding. Sulfoxides, major components of the strongly adsorbed phase, were generally selectively displaced by water, as was total nitrogen. Many nitrogen types may be present; those types more readily displaced by water are probably weakly adsorbed or sterically hindered. The low water-displacement ratio of pyrrolic nitrogen together with low original adsorption (Table 4) suggest that the pyrroles in the strongly adsorbed fraction may exist in polyfunctional molecules and are not adsorbed via the pyrrolic functional group alone. The high resistance of ketones and phenolics to water displacement together with their relatively high concentrations in the strongly adsorbed fraction suggest that they should contribute to increased moisture-damage resistance.

Interactions of Pyridine with Aggregate Surfaces--Model Studies

Pyridine treatment of a moisture-sensitive aggregate (13) and the addition to petroleum asphalt of pyridine-type weak bases from shale oil (20) significantly improved the resistance of corresponding asphalt-aggregate mixtures to moisture damage in the water-susceptibility test. Asphalts prepared from shale oil residues also produced water-resistant pavement mixtures (22). Because pyridine-type functionality may exist in petroleum asphalts and strongly adsorb on aggregate surfaces, the stability of pyridine-aggregate bonds was investigated. Preliminary studies of the pyridine aggregate bond have been reported (10).

Data in Table 8 show that even at temperatures above 300°C, significant amounts of pyridine (boiling point, 115°C) remained strongly adsorbed to the aggregates; strong chemisorption is indicated. A high aggregate surface density for adsorbed pyridine resistant to desorption at the higher temperature ranges suggests that resistance to moisture should be enhanced when the aggregate is used with asphalt that has a high availability of unhindered pyridine-type nitrogen. Montana aggregate showed the highest surface density of adsorbed pyridine at the higher temperatures. FHWA Region 10 aggregate also showed a relatively high adsorption density at high temperatures. Georgia aggregate had almost no affinity for pyridine and the small amount that was adsorbed was desorbed below 150°C.

The Colorado and the Arizona aggregates (Table 8) showed a greater affinity for pyridine than the Virginia aggregate. Colorado and Arizona asphalts also had higher total nitrogen contents than the Virginia asphalt (Table 3). However, the amount of strongly adsorbed nitrogen was lower for the Colorado system than for any other system (Table 4), and nitrogen compounds displaced by water were greatest for the Arizona system. These data indicate that the nitrogen compounds in the Colorado and the Arizona asphalts are less effective than those in the Virginia asphalt in forming strong, pyridine-type bonds with the aggregate and thus are less effective in reducing mixture sensitivity to moisture damage. Differences in nitrogen types and/or steric hindrance of the nitrogen atom partly explain these results.

Rationalization of Fundamental Asphalt-Aggregate Interaction Data with Moisture-Induced Damage Observed in Laboratory Pavement Mixtures

It is apparent from the data presented that pavement sensitivity to moisture damage is probably a function of many interrelated variables. Thus, no one factor may be identifiable as the cause of moisture-induced failure except where a factor may dominate. Therefore, the various factors involved must be considered in concert to make a judgment of their net effect. In this section, significant data are summarized for the individual systems and related to moisture-induced damage in the laboratory-prepared pavement mixtures of the Lottman-NCHRP study. The systems are discussed in increasing order of sensitivity of moisture-induced damage.

Idaho

The high TSR (0.8) for the Idaho mixture is predictive of high moisture resistance. The high concentration of nitrogen compounds in the strongly adsorbed fraction should promote moisture resistance. The potential for stable, high-quality aggregate bonds with nitrogen compounds is suggested by the significant proportion of pyridine-aggregate bonds that are stable at high temperatures. The moderately low carboxylic acid, anhydride, and 2-quinolone-type concentrations in the strongly adsorbed fraction together with their moderate water-displacement ratios should promote moisture resistance, as might also the high calcium and low potassium contents of the aggregate. Although lime was used in the Idaho pavement, it was omitted in our studies; this omission may in part be responsible for the failure of our miniature briquet specimen in the water-susceptibility test after two cycles. In the absence of lime, adsorption data suggest a system with moisture resistance somewhere between that of the Montana and that of the Virginia systems.

FHWA Region 10

A number of factors that should promote pavement moisture-damage resistance are prominent with this system. These include the highest concentration of ketones and phenolics in the strongly adsorbed fraction of any system studied; these types are resistant to water displacement. Strongly adsorbed nitrogen is moderately high. The high concentration of nitrogen in the original asphalt should promote adsorption of nitrogen types most strongly adsorbed. An abundance of high-quality adsorption sites for nitrogen is shown by the resistance to displacement of more than 75 percent of the pyridine from pyridine-treated aggregate at temperatures above 150°C--more than for any other aggregate. The high carboxylic acid concentration in the strongly adsorbed fraction, which could promote moisture sensitivity, is apparently more than offset by the many positive factors cited above to produce a moisture-resistant pavement mixture, as indicated by the TSR of 0.6.

Montana

A number of prominent features of the Montana system (TSR = 0.6) also suggest moisture resistance. Probably the most dominant feature is the unusually high surface density of aggregate adsorption sites for both pyridine and the strongly adsorbed fraction. The aggregate also showed a high percentage of pyridine adsorption sites with high thermal stability. The Montana system also had the lowest percentage of the strongly adsorbed phase displaceable by water. Finally, the concentration of potentially moisture-sensitive carboxylic acids and anhydrides was relatively low in the strongly adsorbed fraction.

Virginia

With a TSR of 0.4, the Virginia system should have intermediate resistance to moisture-induced damage. Our data support this prediction with a balanced array of factors suggesting both increased and decreased moisture resistance. Moisture resistance should be increased by the low acid and anhydride concentrations in the strongly adsorbed fraction and by their low water-displacement ratios. Offsetting these factors is the low amount of nitrogen in the strongly adsorbed fraction. Although the water-displacement ratio for nitrogen was low (increases moisture resistance), this factor was offset by a low pyridine surface density of adsorption sites. The amount of strongly adsorbed fraction and the aggregate surface area were high, which promoted water resistance. However, bond quality may be poor, as suggested by the relatively high displacement of the strongly adsorbed fraction by water.

Colorado

The low TSR of 0.2 for the Colorado mixture predicts a system with a significant potential for moisture-induced damage; a number of factors support this prediction. The ratio of aggregate surface area to the amount of strongly adsorbed fraction was high--four times greater than that for the Montana system--indicating reduced reactivity of the aggregate surface for asphalt components. In addition, the nitrogen content of the strongly adsorbed fraction was lower than that for any system, even though nitrogen content of the asphalt was moderately high, indicating a low interaction of nitrogen compounds with the aggregate. Because of the moderate interaction of the Colorado aggregate with pyridine nitrogen, these data suggest that the nitrogen compounds in the Colorado asphalt, for either chemical or physical reasons, are relatively unreactive with the aggregate. Thus, both asphalt and aggregate possess properties that could contribute to moisture sensitivity.

Arizona

Like the Colorado system, the TSR of 0.2 for the Arizona system indicates sensitivity to moisture damage. The potential benefits of high aggregate surface area and high nitrogen content of both the asphalt and the strongly adsorbed fraction appear to be more than offset by the ability of water to displace polar functional groups from the aggregate surface. The amount of nitrogen compounds in the strongly adsorbed fraction and their corresponding water-displacement ratio were higher for the Arizona system than for any other system. Further, concentrations and water-displacement ratios for carboxylic acids, anhydrides, 2-quinolones, and sulfoxides were also high. In addition, the Arizona system was the only system showing significant amounts of phenolics displaced by water. In summary, this system's moisture sensitivity seemed to result largely from the combined effect of water disruption of a wide variety of chemical functional groups forming the asphalt-aggregate bond.

Georgia and Georgia-Plus-Additive

The high moisture sensitivity of the Georgia systems, as predicted by a TSR of zero, was supported by our fundamental studies. The extremely low aggregate surface area suggests a smooth, crystalline surface with poor mechanical bonding properties. The strongly adsorbed fraction was several times more sensitive to water displacement than that of any other system. The aggregate surface showed almost no affinity for pyridine, which suggests a surface unable to form moisture-resistant bonds. Although the nitrogen-containing antistripping agent added to the one Georgia system was found concentrated at the aggregate surface and did displace some carboxylic acids from the strongly adsorbed fraction, the poor bonding properties of the Georgia aggregate may have rendered the additive relatively ineffective in preventing moisture damage.

SUMMARY

Relationships were found between fundamental chemical and physical properties of the asphalt-aggregate bond and moisture-induced damage in laboratory-prepared pavement mixtures that were subjected to accelerated conditioning by using the Lottman procedure. For most mixtures of the Lottman-NCHRP study, resistance or susceptibility to moisture-induced damage appeared to be controlled by a number of interrelated variables. These variables must be considered in concert to rationalize pavement moisture damage with fundamental bond properties. The moisture sensitivity of the pavement mixtures in the Lottman-NCHRP study, as predicted by the TSR ratios, was explained by considering fundamental properties of the asphalt-aggregate bond.

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Silane Pretreatment of Mineral Aggregate to Prevent Stripping in Flexible Pavements

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Debonding of asphalt from mineral aggregates (stripping) was termed a problem as far back as 1938, yet it continues to plague the paving industry today. Commercial antistrip additives are available, but their long-term effects are not well understood. A silane coupling agent was compared with a well-known commercially available liquid antistrip agent (amine) in the immersion-compression and double-punch debonding tests on two Arizona mineral aggregate sources. The silane was used as a mineral aggregate pretreatment, whereas the amine was added to the asphalt. The results of this research are encouraging and indicate that the silane generally performed as well as the liquid antistrip agent or better. Further testing is recommended along with construction of experimental projects to evaluate field performance.

An asphalt concrete pavement is inherently dependent on the cohesive and adhesive characteristics of the binder to hold it together. As a result, the bond between the asphalt binder and the mineral aggregate is of special importance. It is critical that a good bond be developed during construction and maintained for the life of the pavement. Any degree of loss of the asphalt-aggregate bond will result in a corresponding loss of pavement performance in one manner or another. The strength of an asphalt concrete mixture is a result of the cohesive resistance of the binder, the adhesive bond between the binder and the aggregate, the aggregate interlock, and the frictional resistance between aggregate particles.

Several methods have been used to limit the possibility of stripping. Some of the more common methods are as follows: