

ASPHALT-AGGREGATE INTERACTIONS AND MECHANISMS FOR WATER STRIPPING

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ABSTRACT

The surface chemical properties of four types of aggregates were measured by electrokinetic and spectroscopic techniques. The isoelectric points of aggregates ranged from 2.3 for granites to 9.3 for limestones. Zeta potential - pH curves were measured for four types of asphalts where the isoelectric points depended on the origin of the crude. Interaction diagrams between several aggregate and asphalt types were constructed and used to predict the extent of aggregate-asphalt adhesion. The contribution of electron donor-acceptor interaction to adhesion will be discussed. The reaction of water soluble ions leaching out from the aggregate surface with the carboxylic acids of asphalts is a major variable affecting adhesion and water stripping in pavements. Surface complexation of aggregate with asphalt species and the dissolution kinetics of such complexes are viewed as an important mechanisms for water stripping.

INTRODUCTION

The strength of the adhesion bond between aggregates and asphalts determines the performance of pavement. For acceptable performance, this adhesion bond must withstand the presence of water for prolonged periods of time. Pavement failure at the aggregate-asphalt interface due to water is termed "water stripping." The donor-acceptor interactions between aggregate and asphalt surfaces determine the extent of their adhesion in pavement. The effect of water on the aggregate-asphalt chemical bonding is expected to influence the water stripping performance.

For solid surfaces such as aggregates, the donor-acceptor surface properties may be divided into proton and electron transfer contributions [1]. Proton transfer surface properties are normally estimated from electrokinetic properties as a function of pH [2]. Electron transfer properties are determined by measuring the zeta potential of the solid particles in nonaqueous liquids of known donor or acceptor properties [2,3].

For asphalts, the proton transfer donor-acceptor surface properties can be determined from electrokinetic measurements of their emulsions as a function of pH. A technique was developed to prepare a stable asphalt emulsion that does not alter the intrinsic surface properties of the asphalt [4]. The electron transfer donor-acceptor properties were measured by FTIR techniques. This was done by measuring the frequency shift of the carbonyl mode in the presence of probe solvents. The above technique was developed for polymer matrices to predict their adhesion properties and performance in composites [5].

In this paper, we describe how the surface chemistry of aggregates and asphalts determines the propensity of interaction - which in turn dictates the extent of their

adhesion. The stability of aggregate-asphalt chemical bonding in the presence of water is discussed on the basis of detailed knowledge of surface chemistry. Mechanisms for water stripping are proposed. The results of this research demonstrate that knowledge of aggregate and asphalt surface properties is needed to construct pavement with better performance and service life.

EXPERIMENTAL PROCEDURES

Materials: Tables I and II summarize the properties of several types of aggregates and asphalts, respectively. The aggregates range from granites to limestones - which cover a wide range of donor-acceptor (acid-base) properties. The asphalts represent the main types and were recommended by the Strategic Highway Research Program (SHRP).

Procedures: The zeta potential of aggregates was measured by the acoustophoresis technique using the Pen Kem System-7000. The nonaqueous zeta potential of aggregate particles was calculated from mobility values measured by the Doppler-shift electrophoresis technique using the Malvern Zetasizer II. Details of the experimental techniques are described elsewhere [2,3]. The zeta potential of aqueous asphalt emulsions was measured by the Doppler-shift electrophoresis technique. The emulsion was stabilized with a peroxide-free nonionic surfactant [4]. The frequency shift of asphalt carbonyl mode due to probe solvents was measured by FTIR using the procedure developed by Fowkes et al [5]. Energy scale conversions were made according to Gutmann [6], Labib and Williams [2] and Fowkes et al [7].

RESULTS AND DISCUSSION:

The results and discussion of this work are presented in several sections. Proton and electron transfer donor -acceptor surface properties of aggregates and asphalts are presented in section I and II. Development of the interaction diagrams of some aggregate-asphalt pairs is given in section III. The last section IV discusses mechanisms of water stripping in pavement.

I. Proton and Electron Transfer Surface Chemistry of Aggregates

1. Proton Transfer Properties of Aggregates and Asphalts: The acid-base properties of aggregates were measured by the electrophoresis technique and expressed as zeta potential - pH curves. Figure 1 shows the electrokinetic properties of the four aggregate types defined in Table I. The isoelectric points ranged from 2.3 for quartz-based granite to 9.3 for calcite-based limestone. Apparently the two limestones RC and RD have different surface compositions, as indicated by their isoelectric points.

An important property of the aggregate surface is its stability towards dissolution in water. Table III summarizes the pH and specific conductivity of various aggregates after several soaking cycles. The results indicate that the surface of aggregates slowly dissolves upon exposure to water and that the pH of the medium near the interface is basic (pH >10.0). This was the case for all aggregate types including the quartz-based RJ. This finding is important to the

understanding of the pH conditions present at the aggregate-asphalt interface under wet conditions.

2. Electron Transfer Surface Chemistry of Aggregates: Figure 2 presents the donor-acceptor surface properties of the four types of aggregates. This diagram was constructed from the zeta potential - donicity results of the aggregates in organic solvents, as described by Labib et al [3]. The energy scale used in Figure 2 is based on converting the Gutmann acceptor number to an energy scale using the results of Fowkes et al [7]. The RJ granite exhibited strong acceptor properties while the RD limestone was the strongest donor aggregate. Clay aggregate (RL) has both donor and acceptor surface sites.

II. Proton and Electron Transfer Donor-Acceptor Surface Properties of Asphalts

1. Proton Transfer Properties of Asphalts: Figure 3 presents the zeta potential - pH curves for the four asphalts described in Table II. The measurements were made using an asphalt emulsion stabilized with peroxide-free nonionic surfactant. The asphalts had acid isoelectric points with the exception of non-marine origin AAG which was amphoteric. The results indicate that the surface charge of the asphalts is mainly due to carboxyl functionalities. There is evidence of hydroxyl group contribution to the surface chemistry of asphalts as evidenced by the increase in zeta potential at pH >9.0.

2. Electron Transfer Surface Properties of Asphalts: In the present context, the asphalt was treated as the matrix component of the pavement composite. The electron donor-acceptor properties are determined from the frequency shift of the carbonyl mode of asphalt solutions in probe solvents. The frequency shifts of asphalts carbonyl mode due to chloroform referenced to a cast film and to an asphalt solution in toluene are summarized in Table IV. A higher frequency shift in chloroform indicates stronger base properties of carbonyl functions of asphalts. Data for PMMA and polycarbonate are listed for comparison. It should be noted that the results of Table IV are of oxidized asphalts. We found oxidation to be essential to formation the electron donor groups in asphalts at reasonable concentration.

III. Interaction Diagrams Based on Proton Transfer Surface Properties:

1. Examples of Proton Transfer Interaction Diagrams:

a. Interaction of a Granite Aggregate with Asphalts: Figure 4 is an interaction diagram for quartz-based RJ granite and four asphalt types. The figure shows that the surfaces of the aggregate and asphalt are both negatively charged at pH >3.0. This indicates that under dry conditions (pH 7.0), the propensity of adhesion between asphalt and aggregate is low. At pH 10.0, such as that encountered in the presence of water (Table III), the surfaces of aggregate and asphalt are strongly negative. This is expected to lead to repulsion and therefore water stripping. In actual performance evaluations, RJ was found to be a "stripper" with most asphalt types. The main source of adhesion expected in this case is due to electron transfer donor-acceptor interaction between acceptor sites on the granite and electron donor groups of asphalts.

b. Interaction of a Limestone Aggregate with Asphalts: Figure 5 is an interaction diagram for calcite-based RD limestone and four asphalt types. In this case, the surfaces of asphalt and aggregates have opposite polarities at pH 7.0 (proposed condition for the dry state). The interaction in the presence of water at pH 10.0 is small or zero. In actual performance tests, the RD limestone has been found to be a good performer with respect to water stripping.

Similar interaction diagrams can be constructed with the different aggregate-asphalt pairs. This technique was found to be valuable in predicting the performance of several asphalt -aggregate pairs.

2. Electron Transfer Donor-Acceptor Contribution to Asphalt-Aggregate Adhesion:

The contribution of electron transfer donor-acceptor interaction between aggregates and asphalts is viewed to be essential to their adhesion in some cases. Asphalts, especially after initial oxidation, have been found to contain aprotic electron donor groups such as carbonyl, sulfoxide, ether and lactone. The interaction of these donor groups is likely to take place with aggregate surfaces having acceptor properties. The bonding of asphalts with granite (RJ) and clay (RL) aggregates may be due in major part to the electron donor-acceptor interaction. The oxidation of asphalt surface is essential to the development of the above aprotic donor groups which in turn controls the bonding with aggregates. The donor-acceptor character of aggregates (Figure 2) and the frequency shift data of asphalts (Table IV) provide guidelines for predicting the extent of this contribution to bonding.

IV. Mechanisms of Water Stripping:

Water stripping in asphalt pavement results from the failure of the asphalt-aggregate adhesion bond due to the presence of water. The location of this failure (in the interface region) is crucial to understanding the mechanisms of water stripping. The following is a list of major mechanisms that are expected to lead to water stripping:

1. Weak Adhesion Bond - Lack of Bonding Sites on Aggregate Surface: The adhesion bond may be weak due to the lack of intrinsic chemical interaction between the aggregate and asphalt - as described for the case of granite (RJ) and asphalts. The remaining electron donor-acceptor bonding between aggregate and asphalt can be weakened or even reversed by water. This is a known failure mechanism in other material systems [8].

2. Naturally Emulsifiable Asphalt Leading to Unstable Adhesion: Due to their composition or balance of constituents, some asphalts are unstable in water and tend to form stable emulsions. This was the case for AAG which was amphoteric in character. This asphalt type is expected to form unstable interface with aggregates in the presence of water. This has been found to cause water stripping [9].

3 Soluble Cations Forming Displaceable Soap at Aggregate-Asphalt Interface: Most aggregates contain a large concentration of soluble ions that are leachable in water (Table III). These ions are known to form soaps (with asphalt carboxylic acids) at asphalt-aggregate interface. These soaps are displaceable and can cause

water stripping. Evidence is present to support better performance of experimental pavements made with thoroughly washed and dried aggregates [9].

4. Aggregates with Weak Boundary Layers: It has been demonstrated by Podoll [10] that the location of failure of some asphalt-aggregate pairs occurs in the aggregate side of the bond. The responsible weak boundary layer may be intrinsic to the aggregate or can be developed by surface complexation/dissolution, as described below.

5. Dissolution of Aggregate-Asphalt Surface Complexes: The exterior surface layers of aggregate may be weakened due to the formation of complexes between the aggregate surface sites and asphalt surface groups. These complexes are known to dissociate and dissolve from the aggregate surface. These concepts are developed by Stumm and are recognized in the literature [11,12].

For different asphalt-aggregate pairs, a combination of mechanisms may explain differences in pavement performance. The results of this work would guide us in selecting proper aggregates and asphalts for various climatic regions and in the design of adhesion promoters and anti-stripping agents, when necessary.

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TABLE I

Composition and Description of Core Aggregates*

Aggregate Properties	RJ Mountain Gravel Conglomerate	RL Gulf Coast Gravel	RC Limestone (McAdams Limestone)	RD Limestone (Genstar Stone Prod.)
X-ray Diffraction- Major Minerals	Quartz, Potassium Cyanide Albite, Sodium Acetate	Quartz, Calcite Albite	Calcite, Dolomite Quartz	Calcite, Dolomite Quartz
Major Oxides, %:				
Silicon Dioxide	63.98	51.27	11.79	14.84
Aluminum Oxide	14.60	5.95	1.955	1.46
Ferric Oxide	4.54	3.77	0.96	0.89
Calcium Oxide	6.09	20.25	35.05	33.71
Magnesium Oxide	1.52	2.49	11.76	11.43
Sulfur Trioxide	0.10	0.15	0.48	0.34
Sodium Oxide	1.67	0.48	0.21	0.08
Potassium Oxide	3.31	1.41	0.51	2.00
Titanium Oxide	0.41	0.88	0.18	0.21
Phosphorus Pentoxide	0.11	0.02	<0.01	<0.01
Manganic Oxide	0.13	0.04	0.03	0.08
Loss on Ignition	3.54	13.29	37.64	34.64

*Source of Data: Southern Laboratories and SHRP Materials Reference Library

TABLE II

ASPHALT ORIGINS AND PROPERTIES

Sample, MRL Code Crude (Origin)	AAA-1 Lloydminster	AAD-1 California	AAD-2 Coastal	AAG-1 California	AAG-2 Valley	AAM-1 West Texas	AAM-2 Intermediate
Component Analysis, %							
Asphaltene, (n-heptene)	18.3	23	21.3	5.8	5.1	3.9	4.0
Asphaltene, (lao-octane)	3.4	3.4		3.3			
Polar Aromatics	37.3	41.3	40.1	51.2	51.0	50.3	50.0
Naphthene Aromatics	31.8	25.1	26.7	32.5	35.3	41.9	41.3
Saturates	10.6	8.6	10.0	8.5	8.8	1.9	3.0
Elemental Analysis							
C, %	84.2	81.8		85.6		86.8	
H, %	10.5	10.8		10.5		11.2	
O, %	0.6	0.9		1.1		0.5	
Nitrogen, %	0.5	0.9	0.9	1.1	1.1	0.6	0.5
Sulfur, %	7.3	8.6	8.3	1.3	2.9	1.2	1.9
Viscosity, Prior to Oxidation	864	1055	600	1882	1056	1892	924
Viscosity, After Oxidation for 140F, poise	1901	3420	1715	3253	1761	3947	1816
Ratio	2.2	3.24	2.86	1.75	1.69	1.98	1.96

TABLE III

pH and Specific conductance ($\mu S cm^{-1}$) of Core Aggregates Slurries* Upon repeated soaking and decanting cycles.

	RJ		RL		RC		RD	
	pH	$\mu S cm^{-1}$						
cycle I 1 hr. soak	9.6	75	9.5	113	9.0	143	9.1	125
cycle II 1 hr. soak	9.4	41	9.4	70	8.1	56	9.2	60
cycle III 1 hr. soak	9.3	37	9.4	61	9.1	46	9.3	49
cycle IV 1 hr. soak	9.5	33	9.6	54	9.1	45	9.5	44
cycle V 12 hrs. soak	9.3	36	9.4	56	9.5	42	9.5	42

* SLURRIES CONSISTED OF 4 GRAMS OF GROUND AGGREGATES IN 25 ML OF WATER.

TABLE IV

SHIFT OF THE CARBONYL MODE, cm^{-1} DUE TO THE LEWIS ACID, CHLOROFORM

Oxidized SHRP Sample	Reference Material <u>Cast Film</u>	Reference Material <u>in Toluene</u>
AAA-1	-1.8	-9.0
AAD-1	-3.0	-8.5
AAG-1	-2.3	-6.4
AAM-1	-3.7	-7.1
PMMA	-2.4	-5.5
PCarb*	-4.5	

PCarb*, poly(carbonate), a reference material for study.

FIGURE 1

Electrophoretic Mobility - pH Curve
for Core Aggregate

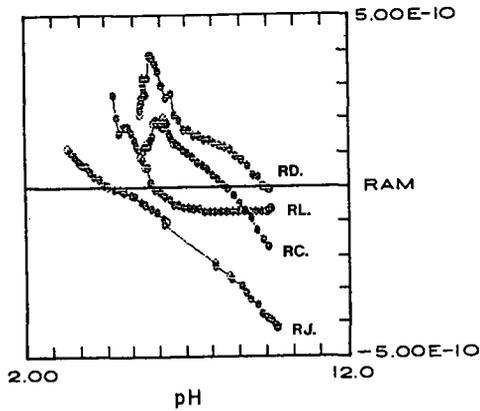


FIGURE 2

The Donor-Acceptor Character of the Four Core Aggregates. They are Arranged Top-to-Bottom According to their Relative Strength, as Judged by the Values of Zeta Potential in Various Liquids of the Donicity Series.

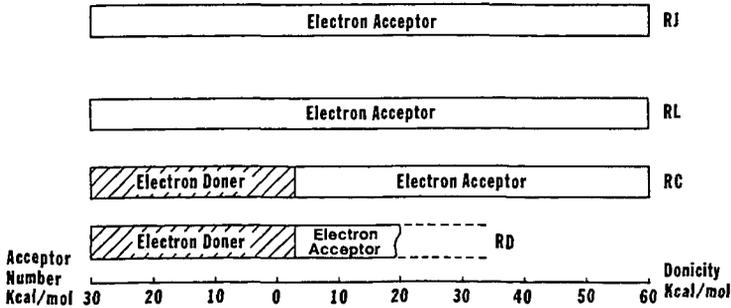


FIGURE 3: ZETA POTENTIAL - pH CURVES FOR AAA-1, AAD-1, AAG-1 AND AAM-1 CORE ASPHALTS.

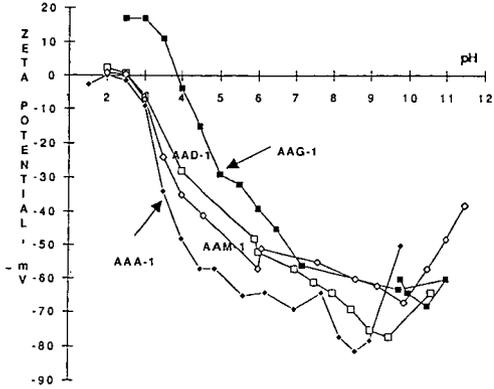


FIGURE 4
INTERACTION DIAGRAMS OF GRANITE AGGREGATE (RJ) WITH SEVERAL ASPHALTS

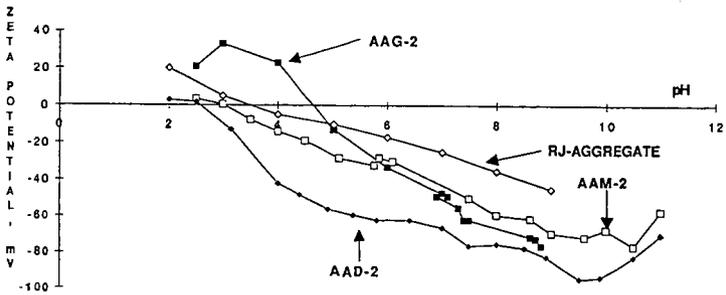


FIGURE 5
INTERACTION DIAGRAMS OF LIMESTONE AGGREGATE
(RD) WITH SEVERAL ASPHALTS

