

TOPIC 2

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Historically, six contributing mechanisms to moisture damage have been identified: detachment, displacement, spontaneous emulsification, pore pressure–induced damage, hydraulic scour, and the effects of the environment on the aggregate–asphalt system. However, it is apparent that moisture damage is usually not limited to one mechanism but is the result of a combination of processes. It has become necessary to seek a more fundamental understanding of the moisture damage process by carefully considering the micromechanisms that influence the adhesive interface between aggregate and asphalt and the cohesive strength and durability of the mastic. Factors that influence the adhesive bonds in asphalt mixtures and the cohesive strength of the mastic in the presence of water are presented and discussed as a fundamental approach to calculating adhesive bond strength in asphalt mixtures in the presence of water on the basis of surface free energy measurements. The adhesive bond that determines the durability of asphalt mixtures in the presence of water is described in this paper to be based on a nonuniform distribution of charges in the asphalt and on the aggregate surface. The polar compounds in the asphalt that react with the aggregate polar sites determine the strength and durability of the adhesive bond. Several processes are presented that affect this bond. The effect of aggregate mineralogy, surface properties, and the pH at the water–aggregate interface is discussed.

BACKGROUND

Description of Moisture Damage

Moisture damage can be defined as the loss of strength and durability in asphalt mixtures due to the effects of moisture. Moisture damage can occur because of a loss of bond between the asphalt cement or the mastic (asphalt cement plus the mineral filler—74 μm and smaller aggregate) and the fine and coarse aggregate. Moisture damage also occurs because moisture permeates and weakens the mastic, making it more susceptible to moisture during cyclic loading.

The literature (Taylor and Khosla 1983; Kiggundu and Roberts 1988; Terrel and Al-Swailmi 1994) refers to at least five different mechanics of stripping: detachment, displacement, spontaneous emulsification, pore pressure, and hydraulic scour. Kiggundu and Roberts (1988) suggest additional mechanisms that may well play a part in moisture damage. These include pH instability and the effects of the environment or climate on asphalt–aggregate material systems.

Detachment

Detachment is the separation of an asphalt film from an aggregate surface by a thin film of water without an obvious break in the film (Majidzadeh and Brovold 1968). Theories that explain adhesive bond energy provide the rationale to understand detachment. Several factors are involved in detachment. First of all, it is necessary to develop a good bond between the asphalt and the aggregate. Such a bond is initially dependent on the ability of the asphalt to wet the aggregate. Wettability of aggregate increases as surface tension or free surface energy of adhesion decreases (Majidzadeh and Brovold 1968). According to Majidzadeh and Brovold (1968), if a three-phase interface consisting of aggregate, asphalt, and water exists, water reduces the free energy of the system more than asphalt to form a thermodynamically stable condition of minimum surface energy. Surface energy measurements at Texas A&M University have established that when the free energy at the asphalt–aggregate interface is calculated in the presence of water, energy is released, meaning that the aggregate surface has a strong preference for water over asphalt. The negative values of free energy in Column 5 of Table 1 establish that this is true for each of four asphalt–aggregate combinations listed in Table 1. The more negative the value, the stronger is the preference for detachment of asphalt from aggregate in the presence of water. The thermodynamic basis for these calculations is presented by Cheng et al. (2002).

Work at the Road Research Laboratory in 1962 suggests that most asphalts have relatively low polar activity and that the bond that develops between the aggregate and asphalt is chiefly due to relatively weak dispersion forces. Water molecules are, on the other hand, highly polar and can replace the asphalt at the asphalt–aggregate interface. Recent work at Texas A&M University by Cheng et al. (2002) has established this to be the case and will be discussed later. Texas A&M researchers have developed a methodology to measure component surface energies and to calculate adhesive bond strengths from these measurements (Cheng et al. 2002).

Displacement

Displacement differs from detachment because it involves displacement of asphalt at the aggregate surface through a break in the asphalt film (Tarrer and Wagh 1991; Fromm 1974). The source of the break or disruption may be incomplete coating of the aggregate surface, film rupture at sharp aggregate corners or edges, pinholes originating in the asphalt film because of aggregate coatings, and so forth. Scott (1978) states that chemical reaction theory can be used to

TABLE 1 Comparison of Free Energy of Adhesion (ergs/gm) and Rate of Damage Under Repeated Load Triaxial Testing (After Cheng et al. 2002)

Mix	Cycles to Accelerated Damage	Loss of Contact Area (Debonding), %	Free Energy of Adhesion (Dry)	Free Energy of Adhesion (Wet)
AAD + Texas Limestone	275	34	141	-67
AAM + Texas Limestone	550	27	205	-31
AAD + Georgia Granite	250	35	150	-48
AAM + Georgia Granite	455	26	199	-30

explain stripping as a detachment mechanism. Some authors describe film rupture as a separate mechanism of moisture damage, but it can be incorporated as part of the displacement mechanism. The process of displacement can proceed through changes in the pH of the water at the aggregate surface that enters through the point of disruption. These changes alter the type of polar groups adsorbed, leading to the buildup of opposing, negatively charged, electrical double layers on the aggregate and asphalt surfaces. The drive to reach equilibrium attracts more water and leads to physical separation of the asphalt from the aggregate (Scott 1978; Tarrer and Wagh 1991).

Spontaneous Emulsification

Spontaneous emulsification is an inverted emulsion of water droplets in asphalt cement. Fromm (1974) demonstrated how an emulsion forms and that once the emulsion formation penetrates the substrata, the adhesive bond is broken. Some research indicates that the formation of such emulsions is further aggravated by the presence of emulsifiers such as clays and asphalt additives (Asphalt Institute 1981; Fromm 1974; Scott 1978). Fromm (1974) observed that spontaneous emulsification occurs when asphalt films are immersed in water and that the rate of emulsification depends on the nature of the asphalt and the presence of additives. However, commercial amine-based asphalt additives, which are organic amine compounds, are chemically different from cationic asphalt emulsifiers, and they cannot function as an emulsifier in their amine form to make normal oil in water–asphalt emulsions. The cationic emulsifier solutions are obtained by reacting amines such as fatty amines with dilute hydrochloric or acetic acid to produce an amine salt (Morgan and Mulder 1995). Furthermore, organic amines, which are basic nitrogen compounds, bond strongly to aggregates in the presence of water (Robertson 2000). Kiggundu (1986) demonstrated how the rate of emulsification is dependent on the nature and viscosity of asphalt, with an AC-5 emulsifying in distilled water much faster than an AC-10. He also demonstrated that the process is reversible upon drying.

Pore Pressure

Pore pressure development in water that is entrapped can lead to distress. Stresses imparted to the entrapped water from repeated traffic load applications will worsen the damage as the continued buildup in pore pressure disrupts the asphalt film from the aggregate surface or can cause the growth of microcracks in the asphalt mastic. Bhairampally et al. (2000) used a tertiary damage model developed by Tseng and Lytton (1987) to demonstrate that well-designed asphalt mixtures tend to “strain harden” on repeated loading. This “strain hardening” is of course not classical strain hardening that occurs when metals are cold-worked to develop interactive dislocations to prevent slip but is the “locking” of the aggregate matrix caused by densification during repeated loading. On the other hand, some mixtures exhibit microcracking in the mastic under heavy repeated loading. This results in progressive cohesive or adhesive failure, or both, and is evident in a plot of accumulated permanent strain versus number of load cycles as the rate of damage dramatically increases as the microcracking progresses. The rate of this accelerated or tertiary damage is exacerbated in the presence of water as the pore pressure developed in the microcrack voids increases the rate of crack growth and damage through the development of higher pressures at the crack tip and through a weakening of the mastic and of the adhesive bond between the mastic and the aggregate.

Terrel and Al-Swailmi (1994) described the concept of pessimum air voids, which is the range of air void contents within which most asphalt mixtures are typically compacted (between

about 8% and 10%). Above this level the air voids become interconnected and moisture can flow out under a stress gradient developed by traffic loading. Below this value the air voids are disconnected and are relatively impermeable and thus do not become saturated with water. In the pessimum range, water can enter the voids but cannot escape freely and is, thus, subjected to pore pressure buildup upon repeated loading.

Hydraulic Scour

Hydraulic scour occurs at the pavement surface. Here stripping results from the action of tires on a saturated surface. Water is sucked under the tire into the pavement by the tire action. Osmosis and pullback have been suggested as possible mechanisms of scour (Fromm 1974). Osmosis occurs in the presence of salts or salt solutions in aggregate pores and creates an osmotic pressure gradient that actually sucks water through the asphalt film. Researchers are mixed on support of this process. Mack (1964) supports it, while Thelen (1958) feels it is too slow to be valid. However, several factors support the potential occurrence of this mechanism, including the fact that some asphalts are treated with caustics during manufacture, some aggregates possess salts (compositionally), and asphalt films are permeable. In fact, Cheng et al. (2002) have demonstrated that the diffusion of water vapor through asphalt cement itself is considerable and that asphalt mastics can hold a rather surprisingly large amount of water. Table 2 compares the water vapor diffusion rates and the amount of water that can be accommodated by two compositionally very different asphalts (AAD-1 and AAM-1). They also showed that the amount of water held by these asphalts is related to the level of moisture damage that occurs in the mixtures using these asphalts.

pH Instability

Scott (1978) and Yoon (1987) demonstrated that asphalt–aggregate adhesion is strongly influenced by the pH of the contact water. Kennedy et al. (1984) investigated the effect of various sources of water on the level of damage that occurred in a boiling test. Fehsendfeld and Kriech (undated) observed that the pH of contact water affects the value of the contact angle and the wetting characteristics at the aggregate–asphalt interface region. Scott (1978) observed that the value of interfacial tension between asphalt and glass peaked at intermediate pH values, up to about 9, and then dropped as pH increased. Yoon (1987) found that the pH of contact water increased with duration of contact and was aggregate-specific and that the values stabilized after about 5 to 10 minutes of boiling. Yoon determined that the coating retention in boiling tests

TABLE 2 Effect of Moisture-Holding Potential of Asphalt on Moisture Damage in Triaxial Testing (After Cheng et al. 2002)

Parameter	Binder		Ratio, AAD-1/AAM-1
	AAD-1	AAM-1	
Diffusivity, m^2/s	0.0008	0.0029	
Water-holding potential, W_{100} , parts per 100,000	153	114	1.34
Percent debonding of binder from aggregate	34 (AAD/limestone)	27 (AAM/limestone)	1.26
	35 (AAD/granite)	26 (AAM/granite)	1.35

decreased as pH increased. Kiggundu and Roberts (1988) point out that these results indicate that stabilization of the pH sensitivity at the asphalt–aggregate interface can minimize the potential for bond breakage; provide strong, durable bonds; and reduce stripping.

Tarrer (1996) concluded that (a) the bond between asphalt and aggregate depends on surface chemical activity, (b) water at the aggregate surface (in the field) is at a high pH, (c) some liquids used as antistrippers require a long curing period (in excess of about 3 hours) to achieve resistance to loss of bond at higher pH levels, and (d) it is possible to achieve a strong chemical bond between aggregate and asphalt cement that is resistant to pH shifts and a high pH environment. This strong chemical bond can be achieved by the formation of insoluble organic salts (such as calcium-based salts), which form rapidly and are not affected by high pH levels or pH shifts.

Although pH shifts affect chemical bonds, it is important to keep the magnitude of the pH shifts in proper perspective. Normally pHs as high as 9 or 10 will not dislodge amines from the acidic surfaces of aggregates, nor will they affect hydrated lime. Values of pH greater than 10 are not normally developed in asphalt mixtures unless a caustic such as lime is added. However, pHs below about 4 can dislodge amines from an aggregate surface and can dissolve lime depending on the type of acid used; these low pHs are not found in hot-mix asphalt.

Environmental Effects on the Aggregate–Asphalt System

Terrel and Shute (1989) report that factors such as temperature, air, and water have a profound effect on the durability of asphalt concrete mixtures. In mild climates where good-quality aggregates and good-quality asphalt cements are available, the major contribution to deterioration is traffic loading and the resulting distress manifestations. Premature failure may result when poor materials and traffic are coupled with severe weather. Terrel and Al-Swailmi (1994) identify a number of environmental factors of concern: water from precipitation of groundwater sources, temperature fluctuations (including freeze–thaw conditions), and aging of the asphalt. They identify traffic and construction techniques, which are external to the environment, as important factors. Factors considered by Terrel and Shute to influence water sensitivity in asphalt mixtures are given in Table 3.

Adhesion Theories

Terrel and Shute (1989) describe four theories that are often used to explain the adhesion between asphalt and aggregate: (a) chemical reaction, (b) surface energy, (c) molecular orientation, and (d) mechanical adhesion. Most likely a combination of mechanisms occurs synergistically to produce adhesion, and no one theory describes adhesion. Terrel and Shute explain that the four theories are affected by the following factors: surface tension of the asphalt cement and aggregate, chemical composition of the asphalt and aggregate, asphalt viscosity, surface texture of the aggregate, aggregate porosity, aggregate cleanliness, and aggregate moisture content and temperature at the time of mixing with asphalt cement.

Chemical Reaction

Chemical reaction is based on the premise that acidic and basic components of both asphalt and aggregate react to form water-insoluble compounds that resist stripping. Rice (1958) suggests the possibility of selective chemical reactions between aggregate and asphalt species. Jeon et al. (1988) described chemisorption of asphalt functionalities on aggregate surfaces and quantified the amount of coverage using a Langmuir model. Thelen (1958) had previously proposed that a

TABLE 3 Factors Influencing Response of Mixtures to Water Sensitivity (After Terrel and Shute 1989)

Variable	Factor
Existing condition	Compaction method
	Voids
	Permeability
	Environment
	Time
	Water content
Materials	Asphalt
	Aggregate
	Modifiers or additives
Conditioning	Curing
	Dry versus wet
	Soaking
	Vacuum saturation
	Freeze–thaw
	Repeated loading
	Drying
Other	Traffic
	Environmental
	Age

bond formed by chemical sorption might be necessary in order to minimize stripping potential in asphalt–aggregate mixtures.

Robertson (2000) states that overall polarity or separation of charge within the organic molecules promotes attraction of polar asphalt components to the also polar aggregates. He explains that while neither asphalt nor aggregate has a net charge, components of both form nonuniform charge distributions and behave as if they have charges that attract the opposite charge of the other material. As established by Curtis et al. (1992), this is confounded by the fact that aggregates vary substantially in charge distribution and this charge distribution is affected by the environment. Robertson (2000) goes on to explain the types of reactions that might occur between the polar aggregate surface and asphalt cement. He states that, at a molecular level, basic nitrogen compounds (pyridines) adhere tenaciously to aggregate surfaces. He also describes carboxylic acids in asphalt cement. While they are quite polar and adhere strongly to dry aggregate, they tend to be removed easily from aggregate in the presence of water; but this varies with the type of acid. Plancher et al. (1977) explain that monovalent cation salts, such as sodium and potassium salts of carboxylic acids in asphalt, can be easily removed from the aggregate surface because they are essentially surfactants or soaps, which debond under the “scrubbing” action of traffic in the presence of water. On the other hand, Robertson (2000) indicates that divalent or doubly charged salts of acids (such as calcium salts from hydrated lime) are much more resistant to the action of water. This is also discussed by Scott (1978), Plancher et al. (1977), and Petersen et al. (1987). Robertson (2000) describes very recent observations at Western Research Institute (Williams et al. 1998) that indicate that aged asphalts may be much more prone to moisture damage than unaged asphalts. In some but not all asphalts, a very strongly acidic material appears with oxidation. Robertson (2000) indicates that if asphalt acids are converted to sodium salts (as can happen with some aggregates), a detergent will be formed.

However, calcium salts of detergents are far less moisture sensitive or are deactivated with lime. Robertson (2000) concludes by warning the user to ensure that the acids in asphalts are neither free nor in the form of monovalent salts.

Surface Energy and Molecular Orientation

From a simplistic viewpoint, surface energy may be described in terms of the relative wettability of aggregate surfaces by water or asphalt. Water is a better wetting agent than asphalt due to lower viscosity and a lower surface tension. However, the concept of using surface energy to calculate the cohesive strength of the asphalt mastic and the adhesive bond energy between aggregate and the asphalt cement or between aggregate and the mastic is a much more complex subject that is worthy of a more detailed discussion. This is presented in the section entitled “Nature of Asphalt–Aggregate Interaction.”

Molecular orientation is coupled with surface energy because both are a part of a theory that considers structuring of asphalt molecules at the asphalt–aggregate interface and assumes that adhesion between asphalt and aggregate is facilitated by a surface energy reduction at the aggregate surface as asphalt is adsorbed to the surface (Hubbard 1938; Rice 1958; Sanderson 1952). Kiggundu and Roberts (1988) describe molecular orientation and surface energy as synergistic processes. They also mention the observations of researchers regarding surface phenomena. For example, Yoon (1987) and Tarrer (1996) described how aggregates that impart a relatively high pH to contact water or that have a relatively high zeta potential have a high stripping or debonding potential. Scott (1978) stated, “If water penetrates the asphalt film to the mineral aggregate surface under conditions where micro droplets form, the pH reached may be sufficient to ionize and dissociate adsorbed water molecules.”

Mechanical Adhesion

This physical form of adhesion relies on physical aggregate properties, including surface texture, porosity or absorption, surface coatings, surface area, and particle size (Terrel and Al-Swailmi 1994). The philosophy is rather simple—to produce an aggregate surface capable of maximizing the surface area and texture to facilitate a strong physical bond that can synergistically improve the nature of the chemical bond between the asphalt and aggregate even in the presence of water. Aggregate properties that affect adhesion will be discussed in more detail later.

Cohesion Theories

Cohesion develops in the mastic and is influenced by the rheology of the filled binder. As will be discussed in more detail subsequently, Kim et al. (2002) describe how the resistance of a mastic to microcrack development is strongly influenced by the dispersion of mineral filler. Thus, the cohesive strength of the mastic is controlled not by the asphalt cement alone, but by the combination and interaction of the asphalt cement and the mineral filler. Terrel and Al-Swailmi indicate that water can affect cohesion in several ways, including weakening of the mastic due to moisture saturation and void swelling or expansion. Cohesion properties would logically influence the properties in the mastic beyond the region where interfacial properties dominate. A classic reminder of this is the work of Schmidt and Graf (1972), who show that an asphalt mixture will lose about 50 percent of its modulus upon saturation. The loss may continue with time, but upon drying, the modulus can be completely recovered. This is shown graphically in Figure 1.

Cheng et al. (2002) describe the severe weakening of asphalt mixtures when they are subjected to moisture conditioning. Figure 2 illustrates the strength loss in a repeated load triaxial test when subjected to 85% saturation. Cheng et al. (2002) indicate that this strength loss is predictable when one compares the wet adhesive bond strength between the asphalt and the aggregate with the much higher dry adhesive bond strength. But Cheng et al. (2002) go on to demonstrate that the rate of damage in various mixtures is also related to the diffusion of water into the asphalt mastic, and that the asphalts that hold the greatest amount of water accumulate damage at a faster rate.

Combining Theories

Kiggundu and Roberts (1988) attempted to combine some of the theories discussed above. They realized that no single theory properly explains moisture damage. They tabulated the primary and secondary contribution relationships in Table 4. This table attempts to relate theories that explain loss of adhesion to stripping mechanisms. For example, the mechanism of pH instability is, according to Kiggundu and Roberts, explained by both chemical reaction theory and physical and chemical components of interfacial energy theory. Detachment, as a second example, is believed by Kiggundu and Roberts to be explained by physical and chemical aspects of interfacial energy theory as well as physical aspects of mechanical interlock theory. The physical aspects are manifested, according to Kiggundu and Roberts, by surface energy, while the chemical aspects are contributed by the effect of polarity of the molecules present at the common boundary. Even with this attempt to simplify the interaction of different theories and mechanisms, the interactive complexity of the processes becomes clearly evident. For example, surface bond is not solely a physical process because surface bond is dictated by the chemical nature of bonding at the asphalt and aggregate surface as well as by the presence of broken bonds or incomplete coordination of atoms due to broken bonds resulting in an increase in free energy.

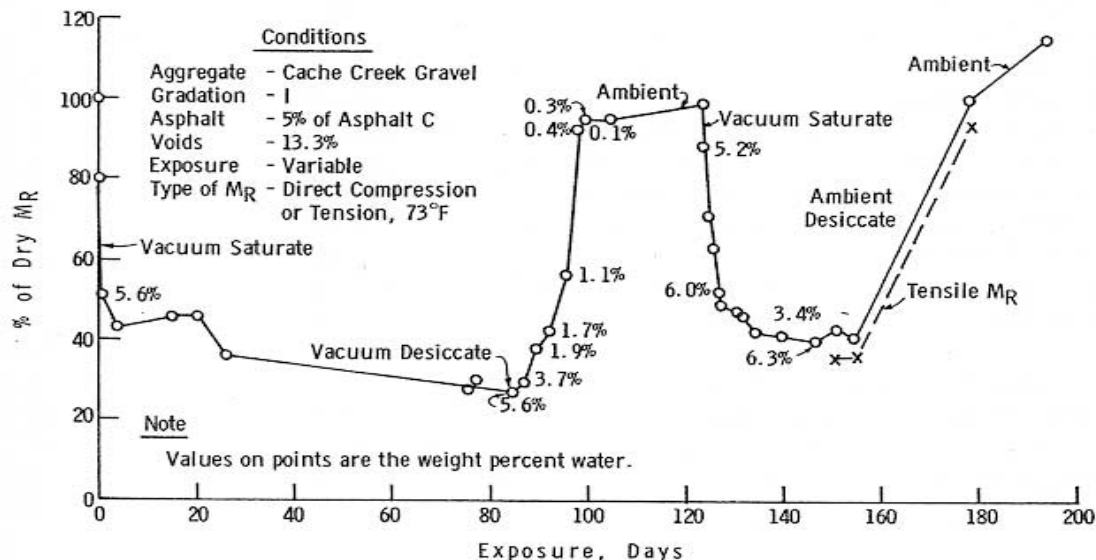


FIGURE 1 Effect of moisture on resilient modulus is reversible. (After Schmidt and Graf 1972.)

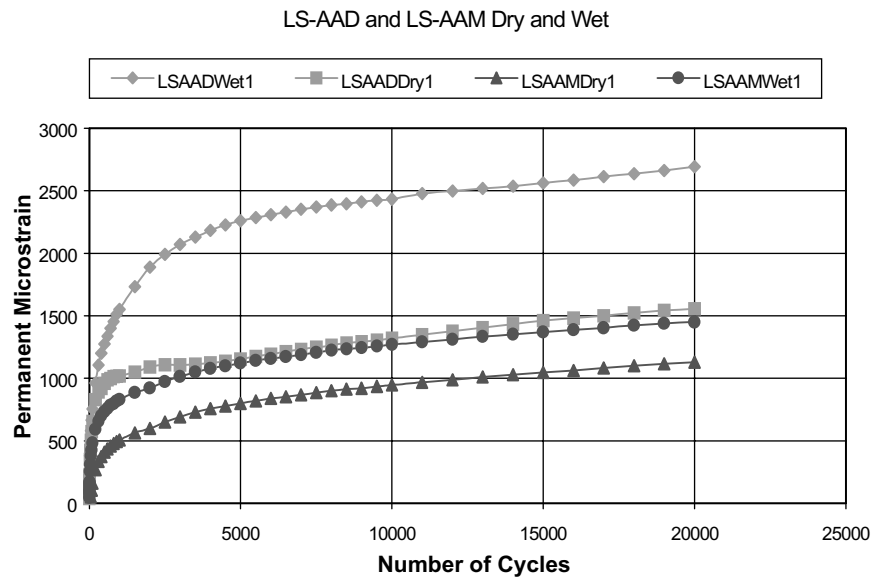


FIGURE 2 Repeated load permanent deformation experiments for AAD-limestone and AAM-limestone in the dry and wet conditions. (After Cheng et al. 2002.)

TABLE 4 Proposed Relationships Between Theories of Adhesive Bond Loss and Stripping Mechanisms (After Kiggundu and Roberts 1988)

		THEORY								
		Mechanical Interlock			Chemical Reaction			Interfacial Energy		
Proposed Operating Mode		P	C	P-C	P	C	P-C	P	C	P-C
Stripping Mechanism	Detachment	S						S	W	
	Displacement					S		S		
	Spontaneous Emulsification				S	W				
	Film Rupture	S								
	Pore Pressure	S								
	Hydraulic Scouring	S								
	pH Instability					S				S

P = Physical

C = Chemical

P-C = Physical – Chemical

S = Primary Contributor

W = Secondary Contributor

NATURE OF ASPHALT–AGGREGATE INTERACTION

Adhesive Failure Versus Cohesive Failure

Damage in asphalt mixtures can occur within the mastic (cohesive fracture) or at the aggregate–mastic interface (adhesive fracture or failure). Whether or not a cohesive or adhesive failure occurs depends on the nature of the mastic and the relative thickness of the mastic around the coarse and fine aggregate. Lytton (personal communication, 2002) used micromechanics to assess the “thickness” of the asphalt film at which adhesive failure gives way to cohesive failure. Figure 3 is a plot of the cohesive and adhesive bond strength determined from cohesive and adhesive surface energies versus thickness of the asphalt binder or mastic. The theory essentially states that asphalt mixtures with thin asphalt films fail in tension by adhesive bond rupture, while those with thicker asphalt films (or mastic films) fail because of damage within the mastic (cohesive failure) as opposed to interfacial debonding. The thickness that differentiates these two types of failure is dependent on the rheology of the asphalt (or mastic), the amount of damage the asphalt or mastic can withstand prior to failure, the rate of loading, and the temperature at the time of testing.

Consider an example. According to Figure 3, when asphalt or mastic coatings are thin, adhesive strength controls performance. In this stage, the adhesive bond strength in the presence of water determines mixture strength and is the critical condition. On the other hand, when asphalt or mastic coatings are relatively thick, thicker than the transition point of Figure 3, cohesive properties limit or control damage resistance. Therefore, in this situation, the impact of moisture intrusion into the mixture may be the key to assessing moisture damage of the mixture. In this case it may be more important to consider the impact of how much moisture the mastic holds and the impact on rheology of this infused water (Table 1) than to consider adhesive bond strength in the presence of water.

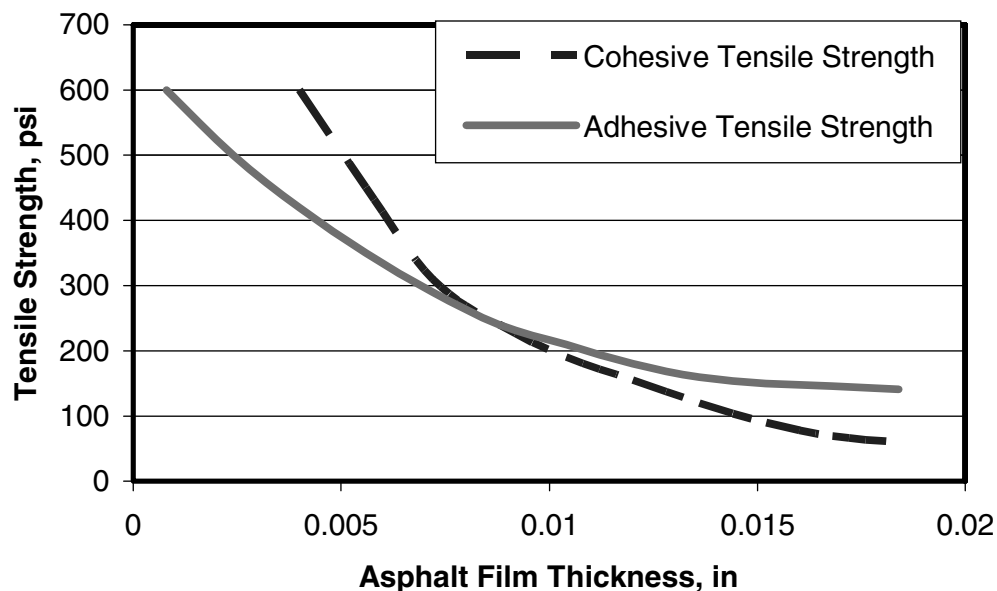


FIGURE 3 Adhesive versus cohesive bond failure based on asphalt film thickness.

Realistically, it is necessary to consider both adhesive bond and cohesive strength properties of the mixtures as mastic coatings range from relatively thin to relatively thick throughout the mixture. Mixture strength then becomes a question of the statistical distribution of conditions where adhesion or cohesion strengths control. Thus the effects of moisture on adhesive bond strength and cohesive mastic strength are perhaps equally important.

Kim et al. (2002) used dynamic mechanical analysis (DMA) testing to evaluate the rate of damage in asphalt binders and mastics. DMA subjects a cylindrical asphalt mastic to cyclic, torsional loading until failure occurs. Failure is due to the development and propagation of microcracks, which begin at the outer circumference of the cylindrical sample. Kim et al. (2002) demonstrated that the rate of damage and the amount of damage various mastics can accumulate before failure depend on the nature of the mastic. This is critically important because it essentially states that a mastic that is well designed will tolerate more damage prior to failure than one that is not. Kim et al. showed that mastics with the proper amount of and type of filler can accommodate more damage prior to failure than unfilled systems and that polymer-modified systems can accommodate more damage prior to failure than nonmodified systems. This indicates that the nature of the mastic (and the impact of the filler or modifier) strongly affects moisture damage because it helps control whether a cohesive or an adhesive bond failure occurs.

Figure 4 is a plot of accumulated dissipated pseudostrain energy (DPSE) versus number of torsional DMA load cycles to failure of representative mastics. The filled asphalts or mastics allow a higher accumulation of DPSE prior to failure than neat asphalt. The type of filler and its physicochemical interaction with the asphalt have a strong impact (Lesueur and Little 1999). The proposed mechanism of fatigue life extension is that properly designed mastics or modified asphalts affect the rate of microdamage accumulation and resist rapid, catastrophic failure via microcrack coalescence. The process may be a redistribution, redirection, or “pinning” of crack energy.

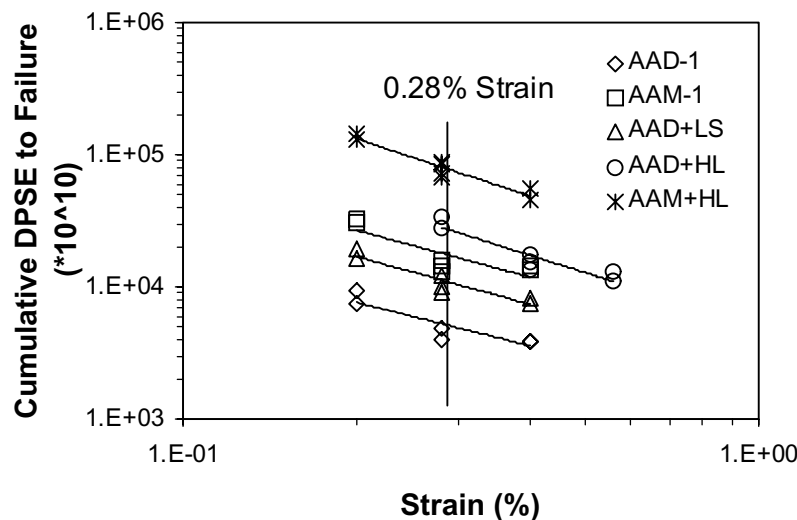


FIGURE 4 Relationship between cycles to failure (DMA) and DPSE for various mastics.
(After Kim et al. 2002.)

Little et al. (1999) have shown that microcrack damage rates are related to cohesive mastic surface energies based on Schapery's viscoelastic fracture theory. Cohesive bond strength can be calculated on the basis of cohesive surface energy measurements of the dry or water-saturated mastic (Cheng et al. 2002). Moisture intrusion weakens the cohesive bond and makes the resulting mixture more susceptible to damage (Table 2).

Effect of Aggregate Characteristics

A general hypothesis has been that acidic aggregates are hydrophobic while basic aggregates are hydrophilic. However, there are notable exceptions (e.g., Majidzadeh and Brovold 1968; Maupin 1982). The general conclusion is that few if any aggregates can completely resist the stripping action of water (Tarrer and Wagh 1991).

Tarrer and Wagh (1991) list a number of factors that influence the asphalt-aggregate bond: surface texture, penetration of pores and cracks with asphalt, aggregate angularity, aging of the aggregate surface through environmental effects, adsorbed coatings on the surface of the aggregate, and the nature of dry aggregates versus wet aggregates.

Surface texture of the aggregate affects its ability to be properly coated, and a good initial coating is necessary to prevent stripping (Maupin 1982). Cheng et al. (2002) have demonstrated that the adhesive bond, calculated from basic surface energy measurements of the asphalt and aggregate, between certain granites and asphalt was higher than between limestone aggregate and asphalt when the bond was quantified as energy per unit of surface area. However, when the bond was quantified as energy per unit of aggregate mass, the bond energy was far greater for the calcareous aggregates than for the siliceous. These results agreed well with mechanical mixture testing. They point out clearly the importance of the interaction of the physical and the chemical bond. Besides the importance of a good mechanical bond promoted by an amenable surface texture, stripping has been determined to be more severe in more angular aggregates (Gzemski et al. 1968) because the angularity may promote bond rupture of the binder or mastic, leaving a point of intrusion for the water. Cheng et al. (2002) substantiate this as they have shown that, regardless of the strength of the bond between the asphalt and aggregate, the bond between water and aggregate is considerably stronger. Table 5 shows adhesive bond strengths calculated in ergs/cm² for five different liquids or semisolids (four binders and water) and three different aggregates. Note that the bond between water and either of the aggregates is at least 30% stronger than for any of the asphalts.

TABLE 5 Adhesive Bond Energy per Unit Area of Sample (ergs/cm²) (After Cheng et al. 2002)

Binder	Aggregate		
	Georgia Granite	Texas Limestone	Colorado Limestone
AAD-1	153	141	124
AAM-1	198	205	179
Rubber asphalt	212	189	166
Aged rubber asphalt	171	164	145
Water	256	264	231

The effects of crushing of the aggregate are very interesting. One might expect that a freshly crushed aggregate surface would have a greater free energy than an uncrushed aggregate surface. This is because broken bonds due to fracture should substantially increase the internal energy even though having something of a countereffect on randomness (entropy increase). However, there is another side to consider. Tarrer and Wagh (1991) point out that sometimes newly crushed faces tend to strip faster than stockpiled aggregates. They state that it is characteristic of many aggregates that one or more layers of water molecules become strongly adsorbed on the aggregate surface as a result of electrochemical attractions. Thelen (1958) states that upon aging, the outermost adsorbed water molecules may become partially replaced or covered by organic contaminants present in air (e.g., fatty acids and oils) that reduce stripping potential. However, this seems unlikely because these fatty acids are relatively heavy and are not likely to volatilize. A general oxidation process reduces free radicals at the oxidation sites and may make weathered aggregates more resistant to stripping than freshly crushed aggregates. On the other hand, if the freshly crushed aggregate can be effectively coated with asphalt and the adsorption of the water layer can be prevented from the outset, the asphalt–aggregate bond developed may be the most effective. Certainly there is much room for advancement in the state of knowledge here.

Tarrer and Wagh (1991) and Hindermann (1968) discuss the effect of crushed aggregate surface on bond strength in light of the ways the aggregate surface may react to broken bonds created by crushing or cleavage. They discuss two potential reactions. In one, new coordination bonds may be formed by redirection inward to the atomic lattice. If this were the case, the aggregate would have no affinity for asphalt or water. This is a very unlikely process. In the second and more likely process, water, oil, or other contaminants in the air are attracted to the fresh surface to satisfy broken bonds. Since water is normally available, the driving force for the adsorption of water on the freshly crushed aggregate faces is that it reduces the free energy of the system. Although asphalts and other organics may also spread over the crushed faces of the aggregate, the rate at which they spread depends largely on their viscosity. Water is more prevalent and spreads much more quickly (Tarrer and Wagh 1991). Apparently, asphalt and organic materials spread over water films on an aggregate surface and tend to be stripped from water films by water (Tarrer and Wagh 1991), further complicating the process.

Clearly, Tarrer and Wagh (1991) make the case that heating aggregates that contain free water and adsorbed water films may remove free water and the outermost adsorbed water molecules, causing the interfacial tension between the aggregate and the asphalt to decrease (Thelen 1958; Majidzadeh and Brovold 1968), resulting in a reduction in stripping potential. The heating effect probably also reduces asphalt viscosity and allows better penetration into the aggregate surface, promoting a more effective physical bond.

According to Tarrer and Wagh (1991), the asphalt–aggregate bond is enhanced by three processes: (a) preheating the aggregate, (b) weathering the aggregate, and (c) removing aggregate coatings. When the aggregate surface is heated, the outermost adsorbed water layer is released, improving the state of interfacial tension between the asphalt and aggregate and, in turn, improving the bond between asphalt and aggregate. The weathering process results in a replacement of the adsorbed water layer with organic fatty acids from the air. This results in an improved asphalt–aggregate bond (Fromm 1974). A dust coating on the aggregate surface promotes stripping by preventing intimate contact between the asphalt and aggregate and by creating channels through which water can penetrate (Castan 1968).

Calculation of Asphalt–Aggregate Bond Strength

Fundamental Mechanisms

In 1984 Schapery proposed a basic viscoelastic fracture theory, which was derived from first principles of materials science and based on an energy balance. This theory states that the load-induced energy that causes fracture damage is balanced by the energy stored on newly formed crack faces. The energy imparted to the system can be quantified as the product of two properties of the materials in question: tensile creep compliance over the time of loading and the strain energy per unit of crack area produced from one tensile load to the next. The energy stored on fracture faces can be quantified by surface energy measurements of the material.

Fortunately, the material properties required to assess this energy balance can be effectively measured. Si et al. (2002) and Kim et al. (2002) demonstrate how to measure tensile creep compliance and the strain energy that causes damage (pseudostrain energy) during cyclic fatigue testing of asphalt mixtures. This concept of pseudostrain energy is not mysterious; it is merely a mathematical calculation that allows one to separate the dissipated energy that actually causes damage from the energy that is recovered over time and does not cause damage. Surface energies can also be measured. Cheng et al. (2001; 2002) have demonstrated how surface energy measurements on the aggregate and asphalt cement can be used to calculate surface energies of cohesion (related to fracture within the mastic—asphalt and filler) and adhesion (related to fracture at the asphalt–aggregate interface).

Using this fundamental look at fracture damage, it is easy to relate surface energy to pavement distress and to understand the wide-ranging importance of surface energy as an indicator of distress in asphalt pavements. Obviously, surface energy can be used to directly assess fracture potential: both cohesive and adhesive. But surface energy is also related to permanent deformation distress, the fatigue failure process, and cohesive strength reduction and adhesive failure (stripping) in the presence of moisture. It is important to briefly develop this connection.

As previously described, Bhairampally et al. (2000) used a tertiary damage model developed by Tseng and Lytton (1987) to demonstrate that well-designed asphalt mixtures tend to “strain harden” upon repeated loading. As previously discussed, this microcracking or tertiary damage leads to a departure from the typical “strain hardening” stress–strain curve representing an accelerated rate of damage due to the development of microcracking and the ultimate acceleration of microcrack growth. Cheng et al. (2002) have shown that the acceleration in damage, or tertiary damage, is related to cohesive and adhesive bond strengths of the mastic and asphalt mixtures in question. Table 1 presents the strong relationship between the number of cycles to failure in repeated load permanent deformation testing and cohesive and adhesive bond energies (which were calculated from bitumen and aggregate surface energy measurements). In Table 1 the free energy of adhesion in the presence of water is calculated. The negative sign indicates a preference of the aggregate for water over asphalt, and a less negative value represents a lower driving force to replace the asphalt in question with water. Thus it is consistent that asphalt AAM bonds more strongly with either the limestone or granite aggregate than asphalt AAD and that it is less likely to strip.

Two back-to-back studies for the Federal Highway Administration performed at Texas A&M University’s Texas Transportation Institute have established the importance of the healing phenomenon in the fatigue damage process. Field validation of healing that occurs during rest periods was presented by Williams et al. (1998). Here the researchers measured a substantial

recovery in modulus via surface wave measurement following rest periods. Little et al. (1999), Kim et al. (1997), Kim et al. (2002), and Si et al. (2002) measured the healing effect during repeated load tensile and torsional shear fatigue testing. They quantified the effect of healing in terms of recovery of dissipated energy during the rest period and in terms of extended fatigue life due to the cumulative effect of a number of rest periods. Little et al. (1999) further established that the healing process is composed of a short-term effect governed by the Lifshitz–Van der Waals component of surface energy and a long-term effect governed by the acid–base component of surface energy. All of these studies are consistent in their findings that a higher acid–base component of surface energy and a lower Lifshitz–Van der Waals component of surface energy produce a superior healing asphalt. Each of the studies referenced provide consistent and convincing experimental data substantiating this assertion.

The fact that surface energy of dewetting is fundamentally related to fracture and that surface energy of wetting is fundamentally related to healing is discussed by Little et al. (1998) and Little et al. (1999). In fact, Schapery presented a corollary to his viscoelastic fracture theory for healing in which he related long-term healing to surface energy and found that an increase in surface energy resulted in better healing. After studying the results of a large experimental matrix comparing surface energy with healing rate plots, Lytton discovered that healing has two components: short term and long term. He determined that the short-term healing rate (and magnitude) is inversely correlated with the Lifshitz–Van der Waals component of surface energy while the long-term healing rate (and magnitude) is directly related to the acid–base component of surface energy. When this is coupled with Schapery’s theory of viscoelastic fracture, a much more complete understanding of the entire fracture fatigue process is achieved, because the fatigue process consists of fracture during loading and healing during rest periods between load applications. Lytton et al. (1993) showed that the healing process is responsible for the major component of the laboratory-to-field fatigue shift factor. Since this shift factor historically ranges between about 3 and more than 100, healing is indeed a significant part of the fatigue damage process.

A logical extension can be made from understanding adhesive fracture based on surface energy to understanding the debonding process between bitumen and aggregate in the presence of moisture (stripping). Cheng et al. (2002) present a detailed methodology by which to measure the surface energies (all components) of asphalt using the Wilhelmy plate method and the surface energies of aggregates (all components) using the universal sorption device (USD). They then show how to compute the adhesive bonding energy between the bitumen and the aggregate both in a dry state and in a wet state (in the presence of a third medium—water). Table 5 (Cheng et al. 2002) demonstrates that the adhesive bond calculated per unit area of aggregate is highly dependent on the aggregate and asphalt surface energies and that the values of the adhesive bond vary over a significant range. They further point out that the affinity of the aggregate for water is far greater than it is for asphalt, so that if water has access to the aggregate interface it is likely to replace the asphalt (strip), and the rate of replacement is a function of the aggregate–asphalt bond strength. In Table 6 the same results are presented in terms of energy per unit mass instead of energy per unit area. Energy per unit mass takes the surface area into account. This is shown to be very important as the rank order of adhesive bond energy changes when this conversion is made. The far greater surface area of the limestone ranks it ahead of the granite in terms of bonding energy per unit mass even though this particular granite actually has a higher bonding energy per unit area.

**TABLE 6 Gibbs Free Energy per Unit Mass (ergs/gm $\times 10^3$)
(After Cheng et al. 2002)**

Binder	Aggregate		
	Georgia Granite	Texas Limestone	Colorado Limestone
AAD-1	158	614	375
AAM-1	206	889	536
Rubber asphalt	219	819	497
Aged rubber asphalt	178	714	435

Cheng et al. (2002) also measured the diffusivity and moisture-holding potential of various bitumens using the USD. Lytton developed a method by which to solve Fick's second law to differentiate adsorption from absorption in the sorption process so that diffusivity and moisture-holding potential could be determined. Using this approach, Cheng et al. (2002) found that diffusivity and water-holding potential vary significantly among bitumens and that the ultimate water-holding potential is related closely to damage. For example, asphalt AAD-1 has a lower diffusivity than asphalt AAM-1, but it has much greater water-holding potential (Table 2). This leads to a much higher level of damage in mixtures with AAD-1 than in mixtures with AAM-1. This damage may be due to two factors: the weakening of the mastic due to diffusion of water into the bitumen and the migration of water through the mastic to the mastic–aggregate interface causing stripping.

Fundamental Principles Shared by Material Processes

The preceding section points out that surface energy can be fundamentally related to material processes and failure mechanisms. From this background a set of principles can be established that can be used to measure material properties required to assess the basic distress processes. These principles are as follows:

1. All materials have surface energies, both asphalts and aggregates.
2. All surface energies have three components, all of which can be measured.
3. The theory of adhesive and cohesive bonding has been developed in industrial surface chemistry and chemical engineering and is used reliably and with confidence.
4. Fracture and healing involve two types of material properties: chemical and physical. Neither fracture nor healing can be properly described without the use of both properties: *chemical*—surface energies; *physical*—modulus and tensile strength and the way they change with age.
5. The presence of moisture at the asphalt–aggregate interface interrupts the bond and accelerates the rate of fracture damage. The presence of moisture in the mastic reduces cohesive strength and fracture resistance and, therefore, reduces the potential for microcracks in the mastic to heal.
6. On the basis of their surface energy characteristics, some combinations of aggregates and asphalts can be determined by calculations to bond well and heal well, whereas other combinations will not. In selecting materials for an asphalt pavement mixture from among

several available alternatives, it will always be possible to select the best combination of all of the available aggregates and asphalts to resist fracture, heal, bond well, and resist moisture damage. Predicting their performance will require the measurement of physical properties as well.

Effect of Asphalt Composition on Adhesion

Asphalt Composition

The chemistry of asphalt is complex. This brief overview is certainly a simplification of the complex nature of asphalt and is meant to provide (a) definitions of basic terms and (b) descriptions of basic asphalt components, which are used in discussion throughout this paper.

Elemental Composition

Asphalt molecules are comprised primarily of carbon and hydrogen (between 90% and 95%) by weight. However, the remaining atoms, called heteroatoms, are very important to the interaction of asphalt molecules and hence the performance of asphalt. They include oxygen, nitrogen, sulfur, nickel, vanadium, and iron.

Molecular Structure

Asphalt atoms are linked together to form molecules. Perhaps the simplest is the aliphatic carbon-carbon chain saturated with hydrogen bonds. The carbon-carbon bonds can also form rings saturated with hydrogen. These saturates are essentially nonpolar and interact primarily through relatively weak Van der Waals forces. A second class of asphalt molecules involves aromatics. This molecule has six carbon atoms in the form of a hexagonal ring. This ring possesses a unique bond with alternating single and double bonds between carbon atoms. Figure 5 shows representative examples of saturates (aliphatic and cyclic) and aromatic structures.

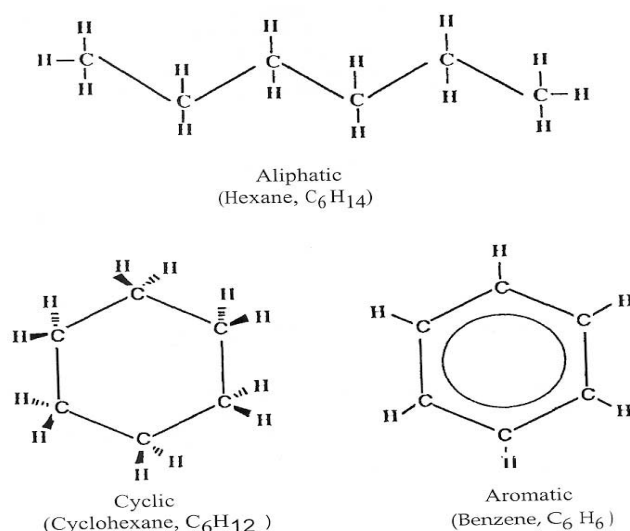


FIGURE 5 Types of asphalt molecules. (From Jones 1992.)

Bonds Among Asphalt Molecules

Strong covalent bonds link atoms together to form asphalt molecules. These molecules interact with one another through much weaker bonds (Jones 1992): pi-pi bonds, hydrogen or polar bonds, and Van der Waals bonds. These are represented in Figure 6.

Pi-pi bonds are unique to aromatic molecules. They provide polarity and the ability of aromatic molecules to link together in unique configurations, including a stacked arrangement as shown in Figure 6. Heteroatoms among asphalt molecules develop polarity and link together by forming hydrogen bonds. Figure 6 shows a hydrogen bond between two very important asphalt functional groups: a sulfoxide and a carboxylic acid. Van der Waals bonding is the weakest of the secondary bonds. They form when molecules cool or stress is removed. Van der Waals bonding is responsible for the free-flowing nature of asphalt at high temperatures versus the semisolid nature at lower temperatures (Jones 1992). As a point of reference, it is important to understand that covalent primary bonds within the molecule are from 10 to 100 times stronger than secondary bonds.

Polar Versus Nonpolar Molecules

Polar molecules form “networks” through hydrogen and pi-pi bonds that give asphalt its elastic properties. Nonpolar materials form the body of the material in which the network is formed and contribute to the viscous properties of asphalt (Jones 1992). Degree of polarity is the most important property of polar molecules, while degree of aromaticity is the second most important. Highly polar and highly aromatic molecules form the most interactive and strongest molecular networks.

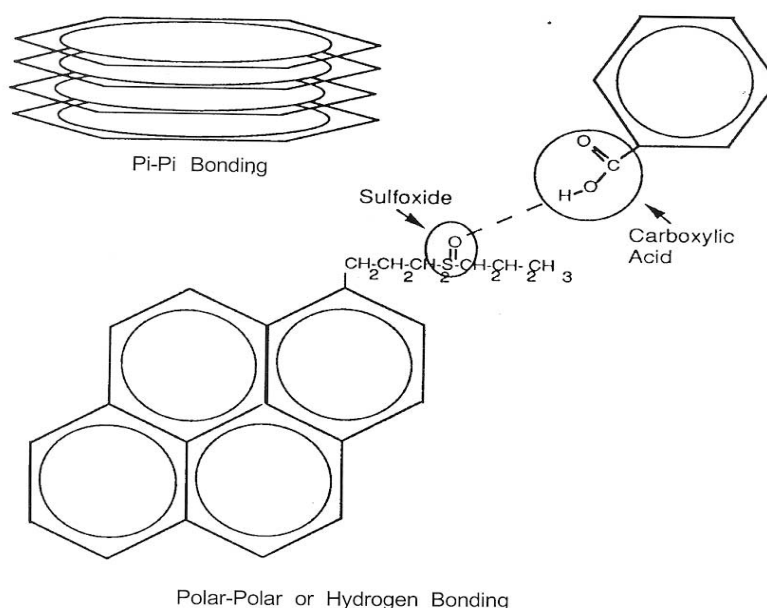


FIGURE 6 Types of intermolecular asphalt bonds. (After Jones 1992.)

Nonpolar molecules do not interact strongly enough to form networks, but they do substantially influence asphalt performance. The molecular weight of nonpolar molecules is related to low temperature performance (Jones 1992). A preponderance of high-molecular-weight nonpolar molecules will lead to asphalts that stiffen and perform poorly at low service temperatures. If nonpolar molecules are waxy, they will crystallize at low temperatures and become crack susceptible.

Nonpolar and polar molecules must interact in an acceptable manner or be “compatible.” If polar and nonpolar molecules are relatively similar in chemistry, they will be compatible; however, if they are very different, the polar network will not stay in solution, and phase separation can be a substantial problem.

Asphalt Model

Jones (1992) explains the history of development of an asphalt model. He describes how analytical techniques including size exclusion chromatography and ion exchange chromatography have led to viewing asphalt as a two-phase system. The polar molecules interact with each other through polar–polar or hydrogen bonding. These bonds form associations that create a network within the nonpolar solvent molecules. However, as explained by Jones, both phases make a significant contribution to asphalt performance. Figure 7 illustrates the model described by Jones (1992)—the Strategic Highway Research Program (SHRP) model.

The associations of polar molecules are due to polar sites on the asphalt through hydrogen bonding. Other interactions take place through pi–pi bonding and Van der Waals bonding. These interactions provide the major contribution to viscoelastic properties of the asphalt. Actually, the term phase is not accurate in the description of polar versus nonpolar components because the mixture is homogeneous and the bonds between the polar molecules are rather weak and form and break constantly.

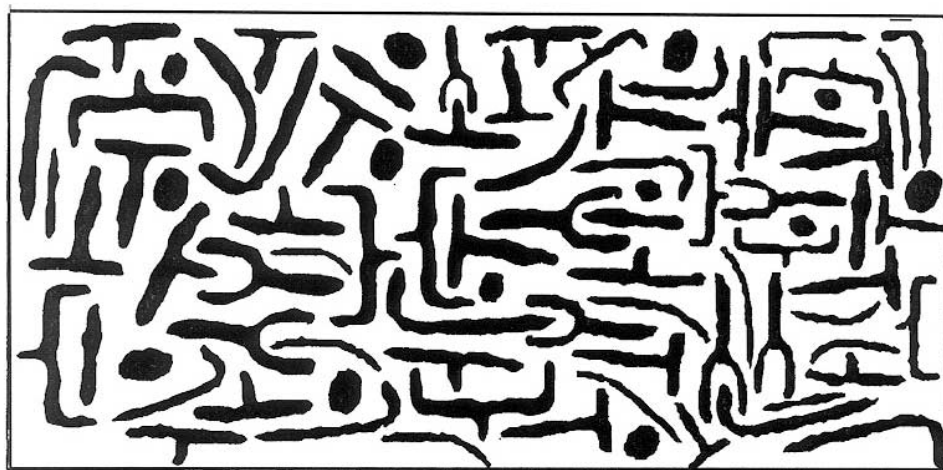


FIGURE 7 SHRP asphalt model. (After Jones 1992.)

Multifunctional Organic Molecules

Data show that having two or more functional groups on the same molecule makes it possible to form chains of weak polar-polar interactions. According to Jones (1992), these chains are the foundation of the polar networks. An example of a multifunctional organic molecule is one with both a carboxylic acid ($R\text{-COOH}$) and a sulfoxide ($S=O$) on the same molecule. Figure 8 is an example of two multifunctional organic molecules. The first one contains three heteroatoms in its structure: a phenol group ($O\text{-H}$), a sulfoxide ($S=O$), and a ketone ($C=O$). The second example is a linear chain molecule that contains a carboxylic acid ($R\text{-COOH}$) and a mercaptan (SH) group.

Multifunctional organic molecules have a major impact on aging. This is because for polar molecules to generate significant physical changes, it is necessary for them to interact in chainlike structures or form networks. Figures 9 and 10 illustrate how oxidation of molecules with a single active site results in a “quenching” of the effect of oxidation, while the oxidation of molecules with multiple active sites develops a continuous network.

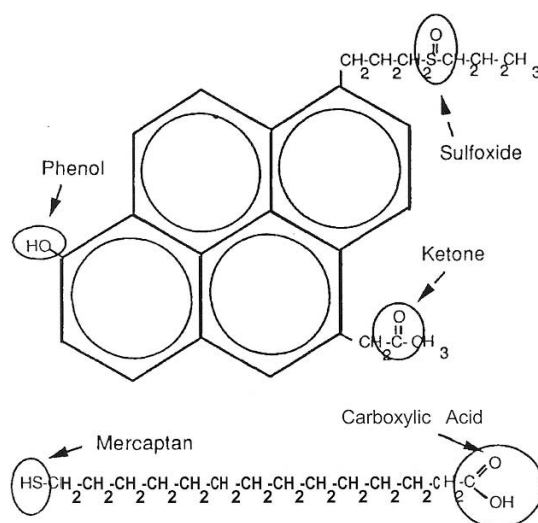


FIGURE 8 Types of multifunctional organic molecules. (After Jones 1992.)

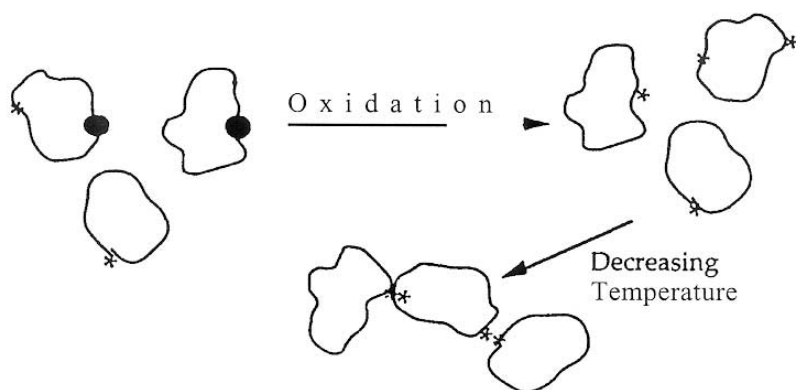


FIGURE 9 Asphalt with simple active sites. (After Jones 1992.)

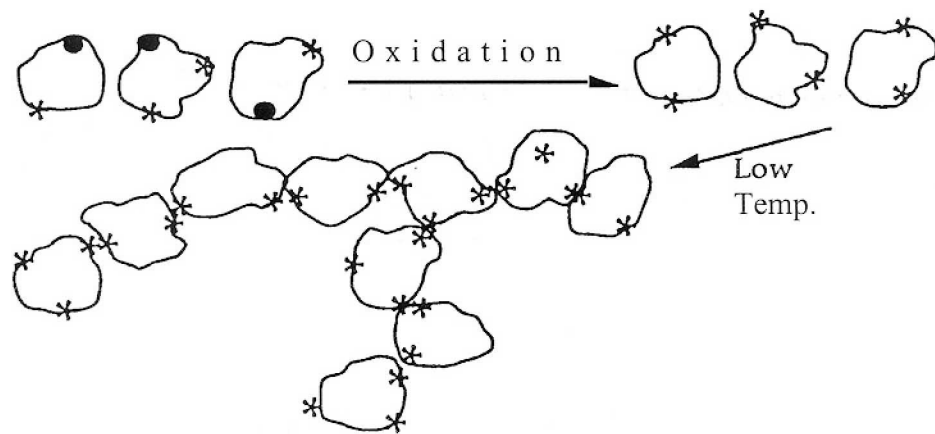


FIGURE 10 Asphalt with multiple active sites. (After Jones 1992.)

Asphalt Chemistry and Adhesion

Polarity or separation of charge within the organic molecules promotes attraction of polar asphalt components to the polar surfaces of aggregates. Although neither asphalt nor aggregate has a net charge, components of both have nonuniform charge distributions, and both behave as if they have charges that attract the opposite charge of the other material. Curtis et al. (1992) have shown that aggregates vary widely in terms of surface charge and are influenced by environmental changes. Robertson (2000) points out that adhesion between asphalt and aggregate arises between the polars of the asphalt and the polar surface of the aggregate. He also points out that polarity alone in asphalt is not sufficient to achieve good adhesion in pavements because asphalt is affected by the environment. Robertson (2000) further states that asphalt has the capability of incorporating and transporting water. Absorption of water varies with asphalt composition and changes further as asphalt is oxidized. Cheng et al. (2002), as discussed previously, have shown that a substantial quantity of water can diffuse through and be retained in a film of asphalt cement or an asphalt mastic, substantially changing the rheology of the binder. Robertson (2000) states that at the molecular level in asphalt, basic nitrogen compounds (pyridines) tend to adhere to aggregate surfaces tenaciously. Carboxylic acids are easily removed from aggregate in the presence of water if the acids form a monovalent salt by interaction at the aggregate surface, but divalent (calcium) salts of acids are much more resistant to the action of water.

Curtis (1992) ranked the affinity of various asphalt functional groups to bond to aggregate surfaces by using adsorption isotherms (UV adsorption spectroscopy). In general she found acidic groups, carboxylic acids, and sulfoxides to have the highest adsorptions, while ketone and nonbasic nitrogen groups had the least. However, the sulfoxide and carboxylic acids were more susceptible to desorption in the presence of water. According to Curtis (1992), the general trend of desorption potential of polar groups from aggregate surfaces is sulfoxide > carboxylic acid > nonbasic nitrogen \geq ketone > basic nitrogen > phenol.

Effect of Aggregate Properties on Adhesion

A number of aggregate properties affect the adhesive bond between asphalt and aggregate: size and shape of aggregate, pore volume and size, surface area, chemical constituents at the surface, acidity and alkalinity, adsorption size surface density, and surface charge or polarity.

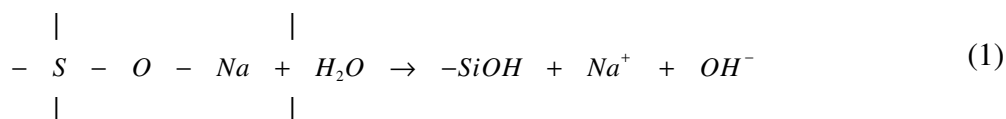
Pore Volume and Surface Area

Yoon and Tarrer (1988) investigated five aggregates (granite, dolomite, chert gravel, quartz gravel, and limestone). They measured pore volume, surface area, average pore size, and percentage coating after boiling. Their study showed that stripping resistance is defined by the level of physical bond that is achieved between the asphalt and aggregate, and this is, in turn, defined by surface area, pore volume, and pore size. The optimal resistance to stripping was developed in aggregates that provide a large surface area for bonding as well as a favorable pore size for adequate (deep) asphalt penetration. This is probably because when asphalt cement coats a rough surface with fine pores, air is trapped and the asphalt has difficulty penetrating the fine pores (Yoon and Tarrer 1988). However, the penetration of asphalt cement into pores is synergistically dependent not only on the pore structure but also on the viscosity of the asphalt cement at mixing temperatures.

Yoon and Tarrer (1988) also determined that aggregates with approximately equal physical properties (e.g., pore volume and structure and surface area) can have very different properties depending on their basic chemistry and mineralogy, which define surface activity. Yoon and Tarrer found substantially higher bonding power for limestone than for quartz gravel even though both had similar physical surface structures. The results of Cheng et al. (2002) were very similar; they found that a certain granite aggregate has a much higher surface energy per unit area than a certain limestone, but when bonding energy was computed in terms of unit mass instead of unit surface area (incorporating effects of surface area), the limestone was predicted to have a much greater potential to resist damage in repeated loading tests of asphalt samples at 85% saturation.

pH of Contacting Water

Hughes et al. (1960) and Scott (1978) reported that adhesion between asphalt cement and aggregate in the presence of water became weakened when the pH of the buffer solution was increased from 7.0 to 9.0 (Scott 1978). Yoon and Tarrer (1988) showed that if different aggregate powders (chert gravel, quartz sand, quartz gravel, granite, limestone, and dolomite) were added to water and allowed to react with water for up to about 30 minutes, the pH of the blend will increase to some asymptotic value (Figure 11). Even granite, known to be acidic, showed an increase in pH over time to about 8.8. The granite reaction in water, which leads to this gradual pH increase, is, according to Yoon and Tarrer, due to the silicate lattice reaction with the water to impart excess hydroxyl ions as follows:



This is a typical hydrolytic reaction of the salt of a weak acid.

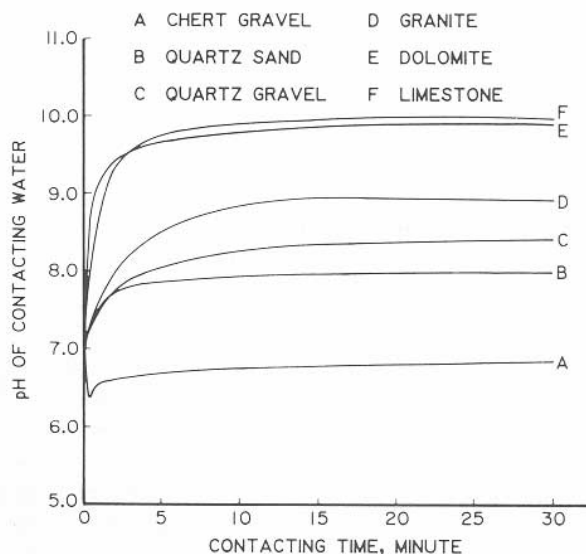


FIGURE 11 Changes in pH of water in which aggregates were immersed. (After Yoon and Tarrer 1988.)

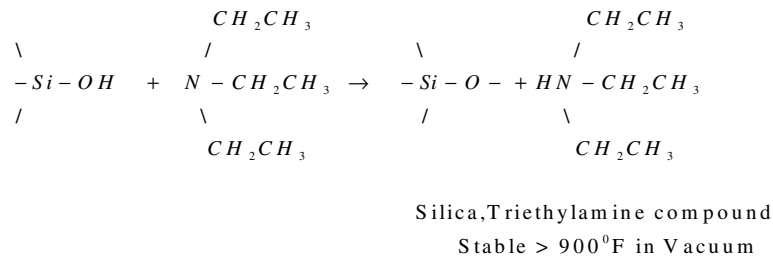
Yoon and Tarrer (1988) assessed the sensitivity of stripping to changes in pH of water in contact with the aggregate surface. They performed boiling stripping tests to verify the sensitivity. The pH of the water was modified by using a solution of HCl or NaOH. The stripping became more severe as the pH increased. Yoon and Tarrer explain that when an aggregate is being coated with asphalt, the aggregate selectively adsorbs some components of the asphalt—the more polar compounds and hydrogen bonds or salt links are formed. Obviously, the type and quantities of the adsorbed components affect the degree of adhesion. Yoon and Tarrer state that the presence of ketones and phenolics is thought to improve stripping resistance, whereas carboxylic acids, anhydrides, and 2-quinolenes are thought to increase stripping sensitivity because of the substantial water susceptibility of the associated bonds.

According to Yoon and Tarrer (1988), the water susceptibility of the hydrogen bonds and salt links between the adsorbed asphalt components and the aggregate surface would increase as the pH of the water at the aggregate surface increases. Therefore, it seems reasonable to conclude that stripping sensitivity will increase as the pH of the water increases. Experimental results of Yoon and Tarrer (1988) substantiate this hypothesis. However, they warn that other surface aggregate properties also play a role. Different types of metal ions affect stripping potential. For example, alkaline earth metals in limestone associate strongly with the asphalt components in carboxylic acids to form alkaline earth salts, and the bonds formed are not dissociated easily in water even at a high pH. In other words, the adsorption is strong because of the insolubility of the alkaline earth salts formed between the limestone and the bitumen acids.

The addition of hydrated lime offers a mechanism to tie up carboxylic acids and 2-quinolenes so they cannot interact with hydrogen bonding functionalities on the aggregate surface to produce moisture-sensitive bonds. Thomas (2002) points out that the interaction of lime with components in the asphalt not only prevents the formation of moisture-sensitive bonds but also subsequently allows more resistant bonds (e.g., with nitrogen compounds from the asphalt) to proliferate. He points out that an additional benefit of the use of lime is to react with or adsorb compounds that can be further oxidized and enhance the increase in viscosity as a

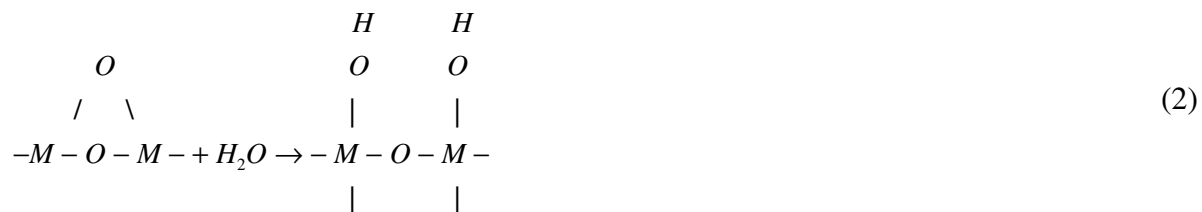
result of oxidation. In fact, experiments at Western Research Institute (2002) show a substantial improvement in moisture resistance after severe freeze–thaw experiments when lime is added directly to the bitumen and before the bitumen is coated on the aggregate. Western Research Institute is currently studying the effect of bonds between the aggregate surface and bitumen components including sulfonic acids, ketones, and 2-hydroquinolines on moisture damage.

In a manner similar to the reaction between acidic compounds such as carboxylic acids in asphalt and alkaline aggregate or with lime, an amine compound either if present in asphalt or added in the form of an antistripping additive will react with acidic surfaces as in the case of siliceous aggregates to form a surface compound. Evidence of the formation of such a surface compound between siliceous surfaces and amine compounds was demonstrated by Titova et al. (1987).



Surface Potential

Interfacial activity between asphalt cement and the aggregate surface is fundamentally important in assessing stripping potential. Yoon and Tarrer state that the functional groups of asphalt that are adsorbed on the aggregate surface come mainly from the acid fraction of the asphalt. Yoon and Tarrer offer the example of carboxylic acid (R-COOH), which in the presence of water separates into the carboxylate anion (R-COO⁻) and the proton (H⁺). This causes the asphalt surface to have a negative polarity at the interface. Aggregates with water present are negatively charged, and as a result, a repulsive force develops between the negatively charged aggregate surface and the negatively charged asphalt surface at the interface. Payataki (1975) states that solid surfaces in contact with water usually acquire charges through chemical reactions at the solid surface and adsorption of complex ions from the solution. For example, metal oxide surfaces in water hydrolyze to form hydroxyl groups:



which subsequently dissociate as



A high pH value of the water in contact with the mineral surface will cause the surface to be more negatively charged.

Yoon and Tarrer (1988) report that the intensity of the repulsion developed between the asphalt and aggregate depends on the surface charge of both the asphalt and aggregate. They used zeta potential as a method to measure aggregate surface charge and found a general trend that aggregates that have a relatively high surface potential in water are more susceptible to stripping (see Figure 12).

SHRP Research on Aggregate Surface Chemistry

General

Labib (1991) confirmed the existence of a range of acid–base types among various SHRP aggregates using zeta potential measurements and electrophoretic mobility. He reported that it is significant that the initial pH of aggregates was greater than 9.0, irrespective of aggregate type. This would neutralize the bitumen carboxylic acids at the interface and cause hydrolysis of bitumen–aggregate bonds. The high pH was attributed to basic soluble salts even in acidic aggregates.

Labib (1991) documented the sensitivity of the bitumen–aggregate bond to pH. He identified three pH regions. At pHs above about 8.5 (Region 3), dissolution of the surface silica occurred in quartz or silica aggregates. In carbonate-based aggregates at pHs between about 1 and 6 (Region 1), calcium ion dissolution occurred, and the presence of carboxylic acids enhanced stripping in this region through cohesive failure in the aggregate. Podoll et al. (1991)

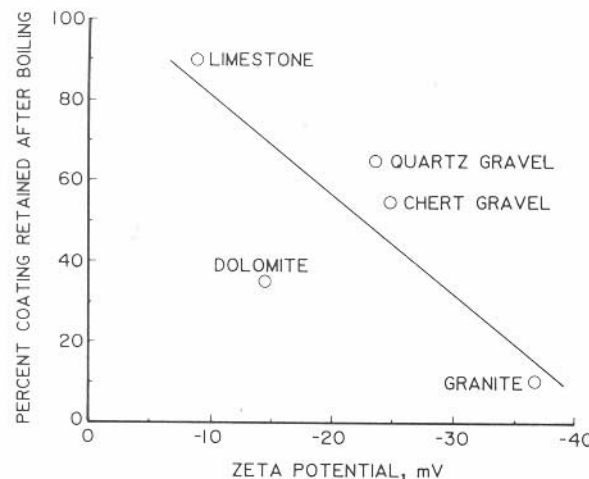


FIGURE 12 Comparison of aggregate surface potential and stripping propensity as determined by the boiling water tests. (After Yoon and Tarrer 1988.)

used surface analysis by laser ionization to confirm that bitumen–aggregate bond disruption occurs within the aggregate and not at the interface. They found notably less sodium, potassium, and calcium in the top monolayer of aggregate in stripped areas than in unstripped areas. This indicates that dissolution of the cations was greater where bitumen had been stripped away. Scott's (1978) work on bitumen-coated glass slides supports Podoll et al. He found that debonding occurred in the more water-soluble glasses and not in the more stable opal glasses.

Jamieson et al. (1995) conclude that net adsorption of bitumen on aggregate is a function of five aggregate variables: potassium oxide, surface area, calcium oxide, zeta potential, and sodium oxide. Alkali earth metals (sodium and potassium) are detrimental to adhesion. Higher surface area provides more active sites per unit mass for interaction. Calcium forms water-resistant bonds, and aggregates with a more negative surface charge may provide more potential for adsorption.

SHRP Adhesion Model

The SHRP adhesion model concludes that aggregate properties have a greater impact on adhesion than do various binder properties. Adhesion is achieved mainly by polar constituents in the bitumen bonding with active aggregate sites through hydrogen bonding, Van der Waals interaction, or electrostatic forces. The general trend is that sulfoxides and carboxylic acids have the greatest affinity for aggregates. However, in the presence of water, sulfoxides and carboxylic acid groups are more susceptible to debonding, whereas phenolic groups and nitrogen bases are more effective in providing a durable bond (Jamieson et al. 1995). It is also apparent that aromatic hydrocarbons have much less affinity for aggregate surfaces than the polar groups.

SHRP Stripping Model

The SHRP view is that stripping is controlled by cohesive failure within the aggregate rather than at the bitumen–aggregate interface (Jamieson et al. 1995). Surfaces rich in alkali metals are more susceptible to debonding than surfaces rich in alkaline earth metals because the latter form water-insoluble salts with acid and other groups with the bitumen.

Podoll et al. (1991) state that stripping of siliceous aggregate may be associated with the presence of water-soluble cations and aluminosilicates. The mechanism is probably dissolution of salts, dissociation of silica due to the high pH environment generated by solubilization of alkaline earth cations, electrostatic repulsion between negatively charged aggregates and ionic components of the bitumen at the surface, and dissolution of soaps formed between acid anions on the bitumen surface and alkali metal cations on the aggregate surface.

The superior stripping resistance of some limestones is due to the formation of water-insoluble (covalent) bonds between calcium sites on the aggregate and bitumen constituents, but stripping of calcareous aggregate can occur where their water solubility is high.

WAYS TO IMPROVE ADHESION

Interaction of Acidic Aggregates and Asphalt with Alkaline Amine Compounds

Amines have a long hydrocarbon chain. The chain is compatible in asphalt cement, and, in the presence of water, the amine is ionized to form an amine ion, $R-NH_3^+$, which has a positive charge (cationic). The physical properties of fatty amines can be altered by changing the nature of the hydrocarbon chain while the chemical nature can be altered by changing the number of amine groups and their positions in the molecule (Porubszky et al. 1969). Taken together, the

chain length and number of amine groups greatly influence the adhesion of the asphalt. Optimum performance is typically achieved with 14 to 18 carbon chain amines with one or two amine groups (Porubszky et al. 1969; Tarrer and Wagh 1991).

Fatty amines enable asphalt to wet aggregate surfaces. The amine group reacts with the aggregate surface while the hydrophobic hydrocarbon chain of the fatty amine is anchored in the asphalt. The net effect (Tarrer and Wagh) is that the long hydrocarbon chain acts as a bridge between the hydrophilic aggregate and the hydrophobic bitumen surface, encouraging a strong bond.

Effect of Hydrated Lime on Adhesive Bond

Plancher et al. (1977) hypothesized that hydrated lime improved binder–aggregate adhesion by interacting with carboxylic acids in the asphalt and forming insoluble salts that are readily adsorbed at the aggregate surface. This is an important reaction because hydroxyl (OH) groups are found on the surfaces of siliceous aggregates. These SiOH groups form hydrogen bonds with carboxylic acid groups from asphalt and strongly affect the adhesion between the asphalt and aggregate (Hicks 1991). But this hydrogen bond is quickly broken in the presence of water, and the two groups dissociate and reassociate with water molecules through hydrogen bonding. This means that the hydrogen bonding between the water molecules and the SiOH group and between the water molecule and the COOH group is preferred over the bond between SiOH and COOH.

When lime is added, some dissociation of the $\text{Ca}(\text{OH})_2$ molecule occurs, resulting in calcium ions (Ca^{++}). These ions interact with the carboxylic acids (COOH) and 2-quinolones (Petersen et al. 1987) to form rather insoluble calcium organic salts. This leaves the SiOH molecule free to bond with nitrogen groups in the asphalt (Petersen et al. 1987). These bonds are strong and contribute to adhesion. Figure 13 illustrates some of the important functional groups in asphalt.

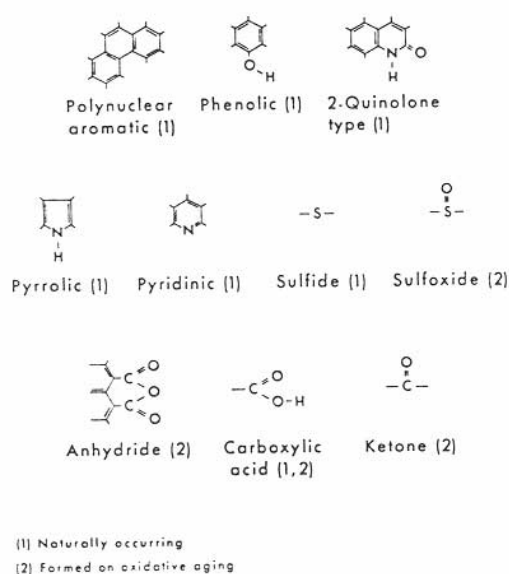


FIGURE 13 Chemical functionalities of importance in asphalt polarity and that contribute in the reaction with calcium. (After Petersen et al. 1987.)

Schmidt and Graf (1972) state that the effectiveness of hydrated lime as an antistripping agent cannot be completely explained by the reaction between calcium from lime and the acids in the asphalt. They state that lime provides calcium ions that migrate to the aggregate surface and replace hydrogen, sodium, potassium, or other cations.

In 1997 the Western Research Institute provided an excellent explanation of the hypothesized aggregate–asphalt interaction.

Susceptibility to water stripping depends, at least in part, on the water solubility of organic salts formed from the reaction of carboxylic acids in the bitumen with carbonates in the aggregates. High molecular weight magnesium and calcium salts are relatively hydrophobic and not very soluble in water. Sodium salts, being more soluble, lead to stripping. Further, it was found in SHRP research that carboxylic acids in bitumen hydrogen bond very strongly with hydroxyl groups on siliceous aggregates, these being highly concentrated on the aggregate surface. However, this hydrogen bond is highly sensitive to disruption by water, thus accounting, at least in part, for the high moisture sensitivity to moisture damage of pavement mixtures containing siliceous aggregates. Conversion of carboxylic acids to insoluble salts (e.g., calcium salts) prior to use in pavement mixtures could prevent adsorption of water-sensitive free acids on the aggregate in the first place. When pavement containing surface active materials is wet and is subjected to mechanical action of traffic, it is predictable that the surface activity of the sodium carboxylates (soaps) in the bitumen will help scrub the oil (bitumen) away from the rock. . . . The practical, perhaps conservative, solution to the historical problem of stripping is to convert all acidic materials in asphalt to water-insensitive (non-surface active) calcium salts at the time of production. This would require lime treatment at the refinery. Some refineries do this today (SHRP bitumen AAG). The recommendation here is that conversion of acids to calcium salts be made a universal requirement. The process recommended here reduces moisture susceptibility of the whole asphalt rather than just at the interface. Lime treatment of the aggregate will be desirable.

Yoon and Tarrer (1988) discuss the effect of water pH on stripping potential in asphalt mixtures with respect to antistripping additives. Their analysis showed that as the pH of the water increases, the adsorptive bonds between amine-type additives and aggregate surfaces are weakened. As a result, water can more easily displace asphalt from the aggregate surface. They point out that this is not the case with hydrated lime, where the resistance to stripping is independent of the pH of the contacting water. However, other research has shown that normally pHs as high as 10 will not dislodge amines from the aggregate, and pHs greater than 10 are very unusual. The effectiveness of the polyamine additives increases with curing time in studies by Yoon and Tarrer (1988). They found that by storing asphalt–aggregate mixtures for a few hours at 300°F, the effectiveness of some additives improved considerably even at a high pH value of contacting water. Yoon and Tarrer (1988) hypothesize that the reason for the improved performance with curing might be the development of a film of polymerized asphalt.

Other Chemical Treatments

Jamieson et al. (1995) describe three possible treatments to improve adhesion: addition of cations to the aggregate surface, addition of antistripping agents to the bitumen, and aggregate pretreatment with organosilanes. Jamieson et al. (1995) point to research that shows that enhanced bonding is associated with relatively large concentrations of iron, calcium, magnesium, and aluminum at the aggregate surface. Jamieson et al. describe that the principal role of antistripping agents is to trigger the dissociation of aggregations of bitumen components, thereby increasing the availability of bitumen functional groups for active sites on the aggregate surface. Bonding energy measurements indicate that the effectiveness of aggregate pretreatment with modifiers is dependent on aggregate type, probably because antistrip agents are usually amines with relatively similar properties, whereas aggregates vary widely (Jamieson et al. 1995). Organosilane pretreatment of aggregate increases the number of polar adsorption sites on the aggregate surface (DiVito and Morris 1982; Graf 1986). Research during SHRP ranked the overall performance of organosilane treatments as a function of hydrophobic bonding enhancements and determined the order of ranking to be amino > hydrocarbon > thiol.

DUSTY AND DIRTY AGGREGATES

General Mechanisms of Bond Disruption with Dirty or Dusty Aggregates

Dusty aggregates may generally be referred to as aggregates coated with materials smaller than 75 μm . This may cause a problem in developing an acceptable bond between fine and coarse aggregate because the asphalt binder tends to coat the dust and not the aggregate, leading to a greater probability for bond interruption and hence displacement.

Dirty aggregates normally refer to aggregates coated with clay mineral fines. While clay-sized materials are soil particles smaller than 2 μm , true clays are not only very small particles but also have a unique mineralogy and morphology. Clay minerals are made up of alternating layers of silica and alumina, which comprise particles that have a great affinity to adsorb water. This is why clay fines are plastic in nature and have a large plasticity index [range of moisture content between the plastic limit (where the soil acts as a plastic semisolid) and the liquid limit (where the soil acts as a liquid)]. The presence of clay particles on the aggregate surface is similar to that of dust. The asphalt bond with the fine and coarse aggregate is disrupted by the presence of the dust or clay. In fact, the situation is worse with clay fines because these particles have a tendency to swell when they take on water, and this swelling mechanism can break or disrupt an existing bond with asphalt. Furthermore, clay is more active than other soil particles. This can lead to other complex reactions between asphalt, water, and the clays, including emulsification. Clay particles adsorb cations because of their strong negative surface charge and their enormous specific surface area. The amount and nature of the cations adsorbed can affect bond interactions and emulsification potential.

In summary, aggregates coated with dust or clay disrupt the asphalt–aggregate bond and can also lead to more complex reactions among water, asphalt, and aggregate, such as emulsification.

Kandhal et al. (1998) evaluated aggregate tests to assess the potential for aggregate fines to cause stripping in asphalt mixtures. They considered the sand equivalent test, the plasticity index test, and the methylene blue test. They evaluated a set of 10 asphalt mixtures using a common coarse limestone aggregate but with different fine aggregates. They used two validation tests to assess moisture damage: American Association of State Highway and Transportation

Officials T283 and the Hamburg wheel-tracking test. After a careful statistical analysis of results, they found that the methylene blue test did the best job of identifying moisture sensitivity of the mixtures.

Modification of Dusty and Dirty Aggregates to Improve Asphalt–Aggregate Interaction

Hydrated lime has been used to treat dusty and dirty aggregates. The mechanism is partially because hydrated lime reacts with clay to change its properties. Two basic mechanisms are involved: cation exchange or molecular crowding of calcium hydroxide molecules at the surface of the clay and pozzolanic reaction.

Cation exchange or calcium hydroxide crowding provides an abundance of divalent calcium ions, which, because of their high concentration and divalent nature, replace the normally available cations in the clay environment. This leads to a substantial reduction in clay plasticity (Little et al. 1995) and causes clay colloids to flocculate into larger aggregates (Little et al. 1995). However, the most important reaction is the pozzolanic reaction, where caustic calcium hydroxide raises the pH of the lime-water-clay system to more than 12. At this high pH, clay minerals are attacked and the silica and alumina solubilize. Soluble silica and alumina then combine with free calcium cations to form calcium silicate and calcium aluminate hydrates, further reducing plasticity, stabilizing the clay, and forming more well-cemented agglomerates (Little et al. 1995). One might expect that the lime-modified clay coatings will “peal” from the aggregates and no longer remain as coatings but as “cemented” small aggregates of flocculated clay that can be separately coated with asphalt.

CONCLUSIONS

Although several separate mechanisms have been identified to explain the process of moisture damage in asphalt pavements, it is more likely that most asphalt pavements suffer moisture damage as a result of a synergy of several processes. From a chemical standpoint, the literature is clear that neither asphalt nor aggregate has a net charge, but components of both have nonuniform charge distributions, and both behave as if they have charges that attract the opposite charge of the other material. Researchers point out that certain polar asphalt compounds develop more tenacious and moisture-resistant bonds with the aggregate surface than others and that the development of the more tenacious and long-lasting bonds can be promoted by treatment of the asphalt mixtures with additives. The most durable bonds appear to be formed by interaction of phenolic groups and nitrogen bases from the bitumen. These form insoluble salts. While sulfoxides and carboxylic acids have a greater affinity for the aggregate surfaces, they are most susceptible to dissolution on water.

The asphalt–aggregate bond is affected by aggregate mineralogy, adsorbed cations on the aggregate surface, and the surface texture and porosity. Favorable chemical bonding between asphalt and aggregate alone will not optimize the adhesive bond and minimize moisture damage. The bond is part physical, and, therefore, the asphalt must be able to wet and permeate the aggregate surface. This process is dependent on asphalt rheology at mixing temperatures and the nature of the aggregate surface, pore size, pore shape, and aggregate mineralogy. To complicate matters somewhat, the ability to bond asphalt to aggregate is dynamic and changes with time. This is largely affected by the shift in pH at the aggregate–water interface, which can be triggered by dissociation of aggregate minerals near the surface or by the nature of the pore water (cation type and concentration).

Moisture damage is certainly not limited to adhesive failure, but weakening of the cohesive strength of the mastic due to moisture infiltration is equally important. Recent research has shown that water can diffuse into asphalt of mastics and that each can hold an appreciable amount of water. Research over many years has clearly shown that this water can weaken the asphalt mixture, making it more susceptible to damage. Thus the logical view is that the deleterious effects of moisture on the adhesive and cohesive properties, both of which influence asphalt mixture performance, must be considered. In fact, recent work at Texas A&M University points out that the propensity for either adhesive or cohesive failure in an asphalt mixture is dependent on the thickness of mastic cover. Since the distribution varies considerably within the mixture, the statistical distribution will determine which mechanism controls.

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TOPIC 2

Questions and Answers

DALLAS LITTLE

Texas A&M University, Speaker

Q1—Alan James, Akzo Nobel

As far as I understand the presentation, the asphalt contains good and bad players as far as the adhesion is concerned. Carboxylic acids are bad players and nitrogen compounds are good players. Can the surface energy measurements distinguish between good and bad players or do both contribute to the surface energy numbers?

A—Dallas Little

In a sense surface energy measurements can differentiate, but perhaps not with the precision you imply in your question. Surface energy can differentiate between acid–base and Lifshitz–Van der Waals interactions, for example, but they cannot directly differentiate between, say, carboxylic acids and carbonyls or between carboxylic acids and nitrogen compounds. But the fact is that surface energy can give us a “global” sense of bond energy, and this is perhaps where we need to begin. Although I did not present it in this paper, we look at the impact of surface energy on moisture damage as sort of a two-step process. In the first part, the adhesive bond formed between the asphalt and the aggregate protects against damage. We obviously want this value to be high. In the second step, the bond energy or Gibbs free energy between the asphalt and aggregate demonstrates a preference of the aggregate to bond with water rather than asphalt. This free energy value turns out to be negative, which indicates a reduction in energy as water replaces asphalt at the aggregate surface, and hence this is a favored process. If the absolute value of this number is large, then the rate of debonding will be high; if it is smaller, then the rate of damage due to debonding will be lower. Therefore, we seek a large bond energy directly between the asphalt and aggregate (impeding bond interruption in the first place) and a less negative value of bond energy between the asphalt and aggregate in the presence of water (slowing the rate of debonding if water gets to the interface).

Q2—John Harvey, University of California at Davis

With the long-term chemical and pH changes that could occur in the field over a period of a few years, could benefits of treatment diminish? Most treatment benefits have been laboratory tested with accelerated tests lasting several weeks. Are you aware of any long-term testing confirming the benefits identified with short-term tests?

A—Ray Robertson, Western Research Institute

To answer your question, John, we have some field sites that several different states have very kindly put in for us where the comparison is among asphalts that are used. In other words, the principal variable at each site is the asphalt. We are looking at differences in the long-term performance characteristics of those asphalts. That, to me, is the gold standard measuring stick. While I’m up, can I make a comment on what was asked over here on surface energy measurements? You really don’t want to measure surface energy of individual components. The

real advantage of the method is to measure the positive and negative effects together. For any of you who weren't around the day after TRB, we had a pretty lively discussion on that subject for a while. Really, the surface energy measurement is to get the summation of the effects of all of the components of the asphalt. Can I make one more comment? To continue with what you have heard quoted here on carboxylic acids, one of the things we are going to have to watch more carefully is what happens with aging of asphalts, what kinds of new materials are formed. Again, to pick on Dr. Ken Thomas, he has identified some components from aging that cause substantially greater moisture sensitivity than carboxylic acids. How one treats these materials to "get them out of the way" is a subject we will probably discuss quite a bit more tomorrow.

A—Dallas Little

I really like the comment, Ray. I use the term global; you use the term summation effect. But the fact is we need something to simplify what we are looking at because, otherwise, the complexity of the interaction can be overpowering. So, if you can come up with a tool, even though it may be somewhat limited because you can't differentiate among the species, if it gives you this overall summation or global effect then it is valuable. It is kind of an unbiased measure of the bonding propensity between the asphalt mastic and the aggregate. That is what we are really looking at and see promise in.

Q3—Gayle King, Koch Pavement Solutions

Dallas, I am intrigued by your compression test, which applied multiple loads to a submerged specimen. I assume you are trying to create the pore pressures that we once hoped to simulate with the environmental conditioning system, but maybe missed. Best guess! Are you creating higher pore pressures than observed with the ECS, and how might it compare with the Hamburg WTD or other mechanical wheel-tracking devices? Any feel for whether you are creating the same kind of damage that the Texas Department of Transportation has seen in problem mixes where static immersion tests did not pick up moisture problems?

A—Dallas Little

Gayle, that's a very, very insightful question. I would have to say that, unfortunately, we haven't measured the pore pressures in the experiment. We brought the system to about 85% saturation pretty much without confinement prior to running the repeated low compression experiment. So we really don't have a handle on what those pore pressures are, but that is something that should be done. That is a very important part of the puzzle.

Q4—Barry Baughman, Ultra Pave

Dr. Little, have you looked at using polymeric aggregate treatments to protect the aggregate from the moisture while improving the adhesion to the asphalt?

A—Dallas Little

No, we haven't looked at it. Our research to this point has looked at basic aggregates, and I use the term "basic" to refer to natural, or unaltered, aggregate. We looked at just the basic aggregates and the bitumen. However, we do have a study under way with the International Center for Aggregate Research that is looking at different coating or modification effects on the aggregate to see how they might affect surface energy and how that might affect the resistance to damage.

Q5—Robin Graves, Vulcan Materials Co.

Looking at the difference between a lime mitigation situation, adding lime to the aggregate versus to the bitumen. Have you looked at the solubility of calcium hydroxide in the bitumen system and do you know how soluble the calcium is and whether there are any pH changes in that system?

A—Dallas Little

I have not done that, Robin. That is a good question. You know, this thing about adding lime to the bitumen is intriguing because over the years we have looked at adding it, not as an antistrip, but considering it as a filler to the bitumen. Today I showed you one slide where the amount of damage that an asphalt sample can handle before failure is strongly affected by the filler. This is because the filler acts to mitigate the damage by absorbing energy, redirecting microcracks, crack pinning, and all those mechanisms. Over the years, we've found that the impact of hydrated lime as filler is bitumen-dependent: it works better in some than it does in others. We have referred, in past publications, to lime as an interactive filler with some bitumens while it acts as an inert filler with others. This is probably because the surface of the lime forms an interactive layer or buffer region because of absorption of polars in some bitumens. For example, hydrated lime in SHRP asphalt AAD is much more effective than it is when mixed with AAM. Didier Lesueur with LCPC in Nantes, France, and I presented a paper in 1999 (Effect of Hydrated Lime on Rheology, Fracture, and Aging of Bitumen, *Transportation Research Record: Journal of the Transportation Research Board*, No. 1661, pp. 93–105) concerning this interactive effect. This goes all the way back to the work of Claine Petersen, Hank Plancher, and others who state that this interactive effect is due to functionalities such as carboxylic acids interacting with the surface of the lime. So all that is really interesting, but we have not at this point in time looked at the ionization potential of the lime within the asphalt, and that would be something we would need to do.

Q6—Joe Button, Texas Transportation Institute

Dallas, would you answer this question in the short term and the long term? Do you see the surface energy measurement process as a specification test in the future?

A—Dallas Little

Yes, I do. I think it will be a specification test. There is a project under negotiation right now where we are trying to look at it as a specification test, and I certainly see the potential for doing that. I see the potential for shortening the time period for the surface energy measurement on the aggregate. We can then use the bond energy between the aggregate and bitumen as a basis to specify aggregates and bitumens on the basis of compatibility with one another. The short answer is yes; the long answer is we've got a little bit of work to do to get there. We also have to keep in mind that it's not just surface energy that affects the response of the asphalt mixtures. Other factors do as well. Mixture properties such as mixture compliance, the time effects on compliance, and so forth affect the ability of the mixture to resist damage. The surface energy characteristics can also help us define crack potential. Not just bonding potential; they can help us define the potential of the mixture to crack. Dick Schapery in 1974 developed a viscoelastic fracture model, which says essentially that the energy you put into the system is balanced by the surface energy that is created on crack surfaces as they develop. So, there is a fundamental relationship between surface energy and crack growth and crack healing, as Schapery predicted

in the mid-1970s. If you can develop a mixture that is resistant to the propagation of cracks and enhances the healing of microcracks, then certainly you are reducing the damage potential. Systems that crack more and have more crack damage have a greater propensity for moisture damage because the moisture can migrate into the damaged crack areas. So surface energy is not just related to the bonding effect; it is also related to the propagation of damage through microcracking.

Q7—Roger Smith, Consultant

We've heard that certain fine fillers, such as hydrated lime, can be a benefit. I'd like to hear your thoughts on the general effect of high dust (P 200) on moisture sensitivity.

A—Dallas Little

I think I have tried to limit the discussion to what would be the appropriate amount of filler in the constraints of the overall mix design. If the appropriate amount of filler is present to pin the cracks, absorb some of the energy, and make the mixture more resistant to damage, then you are in good shape. Obviously, you can abuse that and add too much, and then you get into a whole line of other problems. You could develop a mix that is too dry, a mix that is so dry that you alter the adhesive bond between the mastic and the aggregate surface, and then you go down another route that might cause more damage than good for sure. So you know, asphalt is a very humbling material. It is a material that keeps us all in check and often surprised.

Q8—Bill Maupin, Virginia Transportation Research Council

Dallas, have you looked at time dependency effect on bond strength? In other words, could you initially have a strong bond that may become weak over time with certain asphalt–aggregate additive systems?

A—Dallas Little

I think you could, Bill, and we have not looked at that. I think that some research indicates that if you have some environmentally induced shifts in pH and so forth, certain types of additives or certain systems make a difference. We haven't looked at that, but it is certainly something important to look at.