

INVESTIGATION OF ASPHALT-AGGREGATE INTERACTIONS IN ASPHALT PAVEMENTS

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ABSTRACT

Asphalt-aggregate interactions in asphalt pavements directly influence the adhesion of asphalt to aggregate and determine the strength of the bond between them. These interactions also determine how well the bond is maintained in the presence of water. This investigation examined the physicochemical phenomena that occur at the asphalt-aggregate interface as well as the long-range effect of the interstitial asphalt on the asphalt-aggregate bond. The adsorption behavior of model asphalt components, asphalt fractions and asphalts on aggregates of various petrography was evaluated. The effect of water on the bond between asphalt and aggregate was described through desorption studies. The adsorption and desorption behaviors between asphalt and aggregate were more strongly influenced by the aggregate chemistry and properties than those of the asphalt. Although the influence of asphalt chemistry was smaller than that of the aggregate, asphalt chemistry did affect asphalt-aggregate interactions. A test was developed that evaluated the affinity of different asphalt-aggregate pairs and their susceptibility to water.

INTRODUCTION

Asphalt-aggregate interactions are important in the adhesion of asphalt cement to aggregate because the asphalt must adhere to the aggregate for the adhesive binding action of asphalt to occur. In a road pavement, aggregate composes 94 to 95% by weight of the mix while asphalt makes up the other 5 to 6%. Any additives that are added to improve the performance of the pavement are typically added to the asphalt. The aggregate is present in a multiplicity of sizes ranging from 3/4 inch fraction to fines that are in the -200 mesh range. The larger aggregate sizes are distinct entities in the asphalt pavement while the finer particles can be visualized as an extended portion of the asphalt itself. As asphalt contacts aggregate and forms the mix that is used for the various road courses, the asphalt molecules interact directly with the active sites on the aggregate surface. The surfaces of the aggregates vary considerably in their chemistry, surface area, pore-size distributions, and rugosity. Hence, the aggregate, which can be limestone, gravel, granite, greywacke, basalt, to name a few, can have markedly different active surface sites that are available for interaction with asphalt molecules. Asphalts, being the bottoms product from petroleum refining of crude oils, also vary considerably in their chemistry, because of the differences in their source crudes. Hence, the interaction between the asphalt and aggregate is dependent on the chemistries of both.

Many factors influence the strength and longevity of the bond between asphalt and aggregate. Environmental and traffic factors take their toll. Water, in the form of rainfall or humidity, can have a direct and insidious effect on the adhesive bond between asphalt and aggregate. Moisture damage to the asphalt-aggregate bond results in the deterioration of the

bond through adhesive failure at the interface or cohesive failure within the asphalt or aggregate. These failures cause the asphalt to separate or strip from the aggregate, leaving the aggregate loose without a binder to keep the aggregate particles and, hence, the pavement together.

The overall objective of this work was to investigate and understand fundamental aspects of asphalt-aggregate interactions including both chemical and physical processes. A number of different aspects of this problem was evaluated including chemistry of the interaction between asphalt and aggregate, the effect of the interstitial asphalt on the bond, the effect of the aggregate on aging, and the water sensitivity of the asphalt-aggregate pair. This work, performed under the Strategic Highway Research Program Contract A-003B, covered many different aspects of asphalt-aggregate interactions which are summarized in this paper. A number of researchers was involved in this study who will be referenced in the text.

ASPHALT-AGGREGATE INTERACTIONS

The initial model of asphalt-aggregate interactions that was postulated was the adherence of asphalt at the asphalt-aggregate interface, followed by the development of a structured interphase region, which lay between the interface and the bulk, unstructured asphalt. A new understanding and model of asphalt-aggregate interactions have emerged out of the research performed. During hot mix processing, asphalt components contact and adhere to the interfacial surface of the aggregate with the more polar constituents, those compounds containing heteroatoms of sulfur, nitrogen, or oxygen, being the most competitive for the active sites on the aggregate. Physisorption rather than chemisorption usually occurs with most of the interactions being electrostatic, dipole-dipole, or Van der Waals interactions. Asphalt once contacted with the aggregate surface remains relatively stationary; although under high temperature and stressful conditions the molecules have an opportunity to move, change orientation and diffuse (Hicks, 1991).

Effect of Chemistry on Adhesion

Asphalt is a complex material composed primarily of hydrocarbons but contains a variety of functional groups containing heteroatoms of C, N, H, and metals such as vanadium and nickel, which are present primarily in the asphaltene fraction. A study by Scott (1978) has shown that when asphalts were contacted with aggregates, oxygen-containing groups from asphaltenes were preferentially adsorbed on the aggregate surface. Fritschy and Papier (1978) observed a similar behavior from the polar asphaltenes. Likewise, Curtis et al. (1989a, b) have shown that asphaltenes adsorbed more on sandstone and limestone than did the parent asphalt.

Asphalt is a complex material with many different types of compounds and functional groups present. Adsorption studies were performed with both asphalt model compounds, that represented the type of functional groups present in asphalt, asphalt and asphalt fractions. Adsorption tests involving model compounds gave the following ranking averaged over a series of aggregates, including granites, limestones, gravels, and greywacke: sulfoxide > carboxylic acid > nitrogen base > phenol > ketone > pyrrole > 4-ring aromatic > 2-ring aromatic. The adsorption of polar asphalt model compounds on the different aggregates was much larger than the less polar or nonpolar compounds. Likewise, the larger molecular size

fraction of asphalt, that contains the most polar groups, adsorbed more on the aggregate surface than did the smaller molecular size fraction and, usually, even more than the asphalt itself.

Water attacks the bond between asphalt and aggregate. Evaluation of the effect of water on the adsorbed models showed that models with carboxylic acid and the basic sulfoxide functional groups desorbed readily while the phenolic and nitrogen-base models were more able to withstand the effects of water and remain on the surface of the aggregate. Components that had the most affinity for the aggregates also tended to have the most sensitivity to water.

Aggregate chemistry plays a key role in the adsorption of asphaltic components, the adhesion of the asphalt to the aggregate, and the retention of the asphaltic components in the presence of water. Each aggregate of a given bulk mineralogical type has a unique surface chemistry. These active sites promote adsorption of asphaltic components, particularly ones with polar functional groups. The covering of those active sites by nonpolar C_8 or C_{18} hydrocarbons completely masks their activity, while changing the chemistry of the sites by adding amine groups affects the adsorption behavior of both asphaltic models and asphalts themselves (Curtis et al., 1992). Dust coatings occurring naturally on aggregate surfaces can change the chemistry of adhesion and result in weak bonding between the dust and aggregate surface, leading to attrition of the bonding forces that help maintain the adhesion and, hence, the pavement.

Evaluation of asphalt-aggregate interactions in terms of the adsorption and desorption isotherm behavior of three different asphalts from solutions onto four different aggregates showed that aggregate chemistry is much more influential than asphalt chemistry for both adhesion and sensitivity to water. For a given asphalt, large differences were observed in the amount of asphalt adsorbed and retained after exposure to water when using both siliceous and calcareous aggregates (Brannan et al., 1991). Likewise, for a given aggregate, the differences observed in the adsorption of three different asphalts was much less than that for a single asphalt and several aggregates.

Net Adsorption Tests. A test that provides a method for determining the affinity of an asphalt-aggregate pair and its sensitivity to water was developed. This test is called the Net Adsorption Test. The test is composed of two steps: first, asphalt is adsorbed from toluene solution and the amount of asphalt adsorbed is measured; and second, a small amount of water (~280 mM) is introduced into the system, asphalt is desorbed from the aggregate surface, the amount of asphalt desorbed is measured and the net amount of asphalt remaining on the aggregate surface is measured. This value is termed the net adsorption and provides a means of directly comparing the affinity and water sensitivity of different asphalt-aggregate pairs (Curtis et al., 1992).

The net adsorption of an asphalt aggregate pair is dependent on both the asphalt composition and the aggregate chemistry and morphology. The amount of asphalt adsorbed for eleven aggregates, which were composed of limestones, granites, greywacke, gravels, and basalt, ranged over an order of magnitude for a given asphalt at a preselected asphalt solution concentration (Figure 1). Water sensitivity was also strongly dependent on the chemistry of the aggregate. For some aggregates, half or more of the initial asphalt adsorbed desorbed into a toluene solution that contained only a very small amount of water. For those aggregates that showed substantial water sensitivity, the asphalt chemistry seemed to have a larger influence than on those aggregates that were not sensitive to water.

Bonding Energy. The influence on the composition and chemistry of the aggregate on the amount of heat released or bonding energy was substantial (Ensley, 1990). The bonding energy of the asphalt-aggregate mixture is measured by immersing the aggregate in the asphalt and measuring the resulting exotherm. Eleven aggregates were evaluated with a series of different asphalts. The aggregates could be ranked according to their bonding energy because of the large differences observed among them. By contrast, the ranking of asphalts in conjunction with a given aggregate was not easily discernable.

Interphasal Asphalt. Early research involving determining the bonding energy associated with asphalt-aggregate resulted in an initial exotherm followed by a small release in energy over a fairly long time period (Ensley and Scholz, 1972). These results were interpreted as the development of an interphase region between the asphalt-aggregate interface and the bulk, unstructured asphalt. The interphase region was hypothesized to be a structured region where asphalt molecules were ordered according to their dipole-dipole interactions. However, the research performed recently (Ensley, 1992) did not show the same long-term, low energy release. Additionally, autoradiographic measurements of asphalt contacted to aggregate gave no evidence of the formation of a structured interphase region (Ross, 1990). Aging experiments, performed to evaluate the effect of aggregate on asphalt oxidation, examined the region between the asphalt-aggregate interface and 100 μm out from the aggregate surface. This region, which was sampled every 24 μm , showed no differentiation in the chemical composition that was detectable by infrared analysis.

Asphalt-Aggregate Model. The evidence obtained in this research indicated that the asphalt-aggregate mixtures can be modeled as a system in which large, small, and fine aggregate particles are either coated with asphalt or suspended within the asphalt. Asphalt adheres to the outer surface and penetrates into the pores, crevices, and interstices of the aggregate. The active sites on the aggregate particle attract the most polar and bondable asphalt species upon initial contact. Competition exists among the various asphaltic constituents with the polar components being most competitive (Jeon and Curtis, 1992). Most asphalt molecules are directly contacted with an aggregate or with another asphalt molecule in contact with or close to an aggregate surface. The fines that compose 5 to 8% of the aggregate are interspersed with the aggregate forming a mastic, a medium in which it is difficult to distinguish macroscopically between asphalt and aggregate.

Aging. Aging studies showed that carboxylic acids, ketones, and sulfoxides increased with oxidative aging, at the interface and in the asphalt at distances of 25 μm to 100 μm from the aggregate surface (McKay, 1992). The number and type of oxidative aging products appear to be directly related to the compositional chemistry of the asphalt. The higher the indigenous sulfur content is in a particular asphalt, the higher the sulfoxide formation is under oxidative conditions.

The changes caused by oxidative aging can potentially affect the nature of the chemistry of the interface. The compounds typically produced are sulfoxides, carboxylic acids and ketones. Both sulfoxides and carboxylic acids have a high affinity for the aggregate surface. However, when the moisture sensitivity of these model compounds was evaluated, these two models with the high affinity for the aggregate showed the most sensitivity to water.

Hence, oxidative aging may produce substantial changes in the chemistry of the asphalt-aggregate interface, particularly with an asphalt-aggregate pair that is particularly susceptible to aging. The adhesion of the asphalt to the surface is dependent upon the types

of species at the interface and their ability to bond strongly to the surface. The resistivity of that bond to environmental factors, particularly the intrusion of water, is essential for maintaining long pavement life. Since several of the functional groups present after oxidative aging are susceptible to water, the resistivity of the asphalt-aggregate bond may be weakened by the presence of water.

Water Sensitivity

Stripping of asphalt from aggregate stems from the intrusion of water into the asphalt-aggregate system. The modes of failure depend upon the character of the system and include:

- Separation of the bond at the interface
- Cohesive failure within the asphalt
- Cohesive failure within the aggregate
- Phase separation of components when the presence of water increases the solubility of polar compounds through hydrogen bonding.

If the water-proofing layer of asphalt surrounding an aggregate particle is continuous, then water can penetrate the system by diffusing through the asphalt film removing along the way those asphaltic components that are solubilized. If cracks occur in the film, then water can intrude to the asphalt-aggregate interface, causing failure at or near the interface. The failure can be interfacial or cohesive either in the asphalt or in the aggregate. Reduction in water damage can be attained by modifying the aggregate surface through silylation or the addition of antistripping agents. However, complete covering of the particle by an asphalt film should decrease the quantity of water reaching the aggregate and reduce the deleterious effect of water on the aggregate. Building of roads with low air voids or good drainage may be most influential in reducing water damage, by limiting the exposure of the asphalt-aggregate bond to water.

Resilience of Asphalt-Aggregate Bonds. Adhesion between an asphalt-aggregate pair can be promoted or inhibited by processing and environmental factors. As part of this research, the effect of pH on the asphalt-aggregate bond was investigated. High pH found in a very basic medium was detrimental to most asphalt-aggregate bonds; however, treatment at somewhat lower but still basic pH did not affect the bond substantially (Tarrer, 1992). Curing at elevated temperatures after mixing promoted adhesion in some asphalt-aggregate pairs. A test involving the factors of increased pH and curing was incorporated into the modified Lottman (T-283) test and has been suggested as a means of differentiating among asphalt-aggregate combinations. Those particular asphalt-aggregate combinations that did not perform well under chemical preconditioning (high pH) or curing were treated with additives, either liquid antistripping agents or lime, to improve their performance. Retesting the treated mixture under the stringent pH conditions offers a means of determining the effectiveness of the treatment.

SUMMARY AND CONCLUSIONS

Asphalt-aggregate interactions are strongly influenced by the composition and surface chemistry of the aggregate. Aggregate properties are much more influential in determining adsorption and stripping behavior than are asphalt properties. The net adsorption test demonstrated the large differences in asphalt affinity and stripping propensity occur among aggregates of different mineralogy. Asphalt compounds with polar functional groups are

highly competitive for the active sites (i.e., those sites that contain metals or charged species) on the aggregate surface. Some polar compounds that adhere competitively to the aggregate surface are highly susceptible to water and are readily removed from the aggregate surface. Changes in pH, particularly very basic pH, can be detrimental to the bond between asphalt and aggregate. Curing of the asphalt-aggregate bond can improve bonding between a particular asphalt-aggregate pair although that interaction is highly specific. Specificity among the different asphalt-aggregate combinations was readily apparent in both the adsorption and desorption studies and the bonding energy measurements. The interactions between asphalt and aggregate are dominated by aggregate chemistry. Asphalt chemistry also has an influence, though much smaller than that of the aggregate, on asphalt-aggregate interactions.

Nomenclature for Figure 1.

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| RA = granite | RE = gravel | RG = gravel |
| RB = granite | RF = glacial gravel | RH = basalt |
| RC = limestone | RG = sandstone | RL = gravel |
| RD = limestone | RH = greywacke | |

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**Figure 1. Net Adsorption of Asphalts
on MRL Aggregates**

