

# In Situ Measurement of Water at the Asphalt/Siliceous Aggregate Interface

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## Abstract

Water at the asphalt/aggregate interface is the major contributor to the debonding of asphalt from mineral aggregates (stripping). This paper describes a spectroscopic technique to detect and measure *in situ* water at the interface between an asphalt and a siliceous aggregate, and the application of the technique to studies of several asphalts. The technique employs Fourier transform infrared (FTIR) spectroscopy in the multiple internal reflection (MIR) mode. An asphalt layer of any thickness is coated on an  $\text{SiO}_2$ -covered Si internal reflection element (IRE) and a water chamber is attached to the asphalt-coated substrate. Spectra are taken automatically at specified time intervals without disturbance of the specimens. In the study, water at the asphalt/aggregate interface for five Strategic Highway Research Program (SHRP) core asphalts (AAC-1, AAD-1, AAG-1, AAK-1 and AAM-1) of about 60  $\mu\text{m}$  thick on an  $\text{SiO}_2$ -Si substrate was measured using the technique. The amount and thickness of the water layer at the asphalt/siliceous aggregate interface were determined based on internal reflection spectroscopy theory, the water concentration-intensity calibration curve obtained using a series of  $\text{H}_2\text{O}/\text{D}_2\text{O}$  mixtures, and the water uptake of the asphalts. The results indicated that the thickness of the water layer at the asphalt/siliceous aggregate interface increased as time of exposure increased. Water adsorption characteristics at the asphalt/ $\text{SiO}_2$ -Si substrate interface were different for the five asphalts. The technique should be useful for evaluating asphalt/siliceous aggregate mixtures in terms of water diffusion, water susceptibility, effectiveness of antistripping agents, and effects of aggregate surface contamination on water stripping.

**Keywords:** asphalt/aggregate interface, *in situ*, water

## INTRODUCTION

The debonding of asphalt from mineral aggregates in the presence of water (stripping) "has been observed at times ever since asphalt paving came into existence" (1). Since stripping was first recognized as a problem, many studies have been devoted to the search for a solution to this problem. Still, stripping continues to occur in many areas. Whether asphalts fail prematurely or in the range of the expected service life, they require large replacement costs that could probably be reduced through development of effective methods for measuring the effects of water on the stripping of asphalt from an aggregate and for evaluating the effectiveness of antistripping agents. A major technical barrier to overcoming the problem of stripping is the lack of a technique for measuring water at the asphalt/aggregate interface. Measuring water at bonded interfaces has been the subject of much interest, not only in the asphalt pavement area, but also in many areas involving a polymer film on a substrate, such as in the fields of coatings, adhesives, and fiber composites. However, until recent research at the National Institute of Standards and Technology (NIST) that led to a technique for measuring water *in situ* at the coating/metal interface (2-4), there has been no suitable technique available. The main objective

of this study was to develop a technique for measurement of water *in situ* at the interface between asphalt and a model siliceous aggregate.

The technique developed for studying water *in situ* at the asphalt/siliceous aggregate interface is based on Fourier transform infrared - multiple internal reflection (FTIR-MIR) spectroscopy, commonly known as FTIR-ATR (attenuated total reflection) spectroscopy. The theory and principles of FTIR-MIR are well understood (5). The application of this technique for measuring *in situ* (2) and quantifying (4) water at the interface between a polymer and a substrate has been described.

## EXPERIMENTAL

The model siliceous aggregate used in this study was a 50x10x3mm, spectroscopic grade, SiO<sub>2</sub>-covered Si internal reflection element (IRE). The asphalts were five of the Strategic Highway Research Program (SHRP) core asphalts: AAC-1, AAD-1, AAG-1, AAK-1, and AAM-1. Asphalts were heated to 60°C in air and applied on the model aggregate using a "drawdown" technique. The thickness of the asphalt films on the model aggregate was  $63 \pm 15$   $\mu\text{m}$ . A water chamber was attached to the asphalt-coated aggregate and water was introduced into the chamber. Figure 1 illustrates the specimen configuration and experimental setup. At specified time intervals, FTIR-MIR spectra were taken automatically without realignment of the instrument accessory and without disturbance of the specimens. Difference spectra between the water-exposed and unexposed asphalt-coated aggregate specimens as a function of exposure times were recorded. All spectra were the result of 32 coadditions and were collected at 4  $\text{cm}^{-1}$  resolution throughout the 1200-4000  $\text{cm}^{-1}$  range. Unpolarized light at an incident angle of 45° was used. Quantitative analyses were performed using the peak height method. Since this was an *in situ* measurement, no random errors due to specimen changing, spectrometer and environmental chamber conditions, and optical alignments were introduced in the measurement. Thus, any changes in the spectra were a direct result of water entering the asphalt/aggregate specimen. Further, because asphalt was directly applied to the IRE, errors resulting from variations in contact between the asphalt and the IRE were avoided.

To translate FTIR information to the amount and thickness of the water layer at the asphalt/aggregate interface, an FTIR-MIR intensity-concentration calibration curve for water was established and the amount of water absorbed in the asphalt was determined. The calibration curve was established by an FTIR-MIR analysis of water at eight different concentrations in D<sub>2</sub>O. The amount of water absorbed in the asphalt was determined using the gravimetric method and 63- $\mu\text{m}$  asphalt films on thin aluminum plates. The asphalt-coated aluminum plates (three replicates for each asphalt) were immersed in distilled water, taken out, blotted, and weighed at desired intervals up to 310 hours; the amount of water gained was expressed in percent by mass of the original asphalt. Complete experimental details are given in Reference 6

## RESULTS

Figure 2 shows typical FTIR-MIR difference spectra of an asphalt/siliceous aggregate specimen exposed to water at different times. The intensities of the water bands (e.g. OH stretching near 3400  $\text{cm}^{-1}$ ) increased while those of the asphalt bands (e.g. CH band at 2922  $\text{cm}^{-1}$ ) decreased,

as a function of time of exposure. (The water bands were verified by the FTIR-MIR spectrum of the liquid water in contact with the asphalt-free siliceous aggregate.) The intensity-time plots of water (e.g. Figure 3) revealed that the increases and decreases were rapid initially, then slowed down. These results indicated that the technique is effective for detecting *in situ* water taken up by an asphalt-coated siliceous aggregate system. The effects of water on the asphalt-coated siliceous aggregate were different for the five asphalts. The intensities of the water bands of the AAD-1 asphalt increased substantially over the first 45 hours then levelled off, while those of the other asphalts increased more slowly (than AAD-1) but continued to increase even after much longer times.

The water detected in the asphalt/aggregate specimen was the sum of water absorbed in the asphalt within the FTIR-MIR probing depth and of the water at the asphalt/aggregate interface. This may be expressed mathematically as:

$$C_w(t) = A(t)[1-x] + x \quad [1]$$

$$x = l(t)/d_p(t) \quad [2]$$

$$d_p(t) = 0.243 - 0.018x \quad [3]$$

where  $d_p(t)$ , in  $\mu\text{m}$ , is the penetration depth of the evanescent wave in the samples as a function of exposure time,  $t$ ;  $d_p$  was calculated based on the internal reflection spectroscopy as presented in detail in References 4 and 6 for polymer/substrate and asphalt/siliceous aggregate systems, respectively.  $C_w(t)$  is the mass fraction of water within  $d_p$ ; this quantity was derived from the results in Figure 3 and the calibration curve.  $A(t)$  is the mass fraction of water absorbed in the asphalts within  $d_p$  thickness as a function of time;  $A(t)$  was determined from the water absorption experiment.  $x$  is the thickness fraction of  $d_p$  occupied by the water layer at the asphalt/aggregate interface and  $l(t)$ , in  $\mu\text{m}$ , is the thickness of the water layer at the asphalt/aggregate interface as a function of time. Equation 3 accounts for the change of  $d_p$  due to a replacement of asphalt ( $d_p = 0.243 \mu\text{m}$ ) by water ( $d_p = 0.225 \mu\text{m}$ ) during exposure.

Equations 1, 2, and 3 allowed the calculation of the amount and thickness of the water layer at the asphalt/model aggregate interface. A computer spreadsheet was designed to obtain the thickness,  $l(t)$ , of the water layer at the asphalt/siliceous aggregate interface. The results are presented in Figure 4 for five SHRP asphalts. The thickness values were calculated assuming that water was uniformly distributed on the entire surface area of the specimen. The mass of water at the asphalt/aggregate interface was determined by multiplying the thickness by the surface area within the chamber walls ( $329 \text{ mm}^2$ ) and by a water density of  $1 \text{ Mg/m}^3$ . Alternatively, the mass can be determined first, then converted to a thickness value. The results showed that the thickness of the water layer at the asphalt/model aggregate interface varied with exposure times and with the asphalt types. For example, after 50 hours immersion, AAD-1 had a 85 nm-thick water layer, while AAC-1, AAG-1, AAK-1, and AAM-1 had thicknesses ranging from 20 to 28 nm after the same period. The thickness of the water layer of AAD-1 reached a plateau value after 50 hours, but that of the other asphalts continued to increase for some time.

## CONCLUSIONS

A sensitive technique for measuring water *in situ* at the asphalt/model siliceous aggregate interface has been developed. The technique can detect and also quantify the water at the asphalt/siliceous aggregate interface. The technique will be valuable for understanding the water susceptibility of asphalt/siliceous aggregate mixtures. The technique is unique in providing information on the transport of liquid water through an asphalt layer of any thickness attached to an aggregate (6). Such information should be useful for predicting the performance of asphalt and asphalt/aggregate mixtures in service. The technique should therefore be useful for predicting water susceptibility and studying the effects of the aggregate, contamination of the aggregate, antistripping agents, and the asphalt on the water susceptibility of asphalt/siliceous aggregate mixtures. Further, the technique should be useful for measuring organic or inorganic materials, such as oil, lime, etc., *in situ* at the asphalt/aggregate interface. Similarly, it may also be useful for measuring the transport properties of water, organic, and inorganic materials through a layer of asphalt/aggregate mixture or concrete on a substrate. It is anticipated that the technique will have a wide range of applications in highway technology.

## ACKNOWLEDGEMENTS

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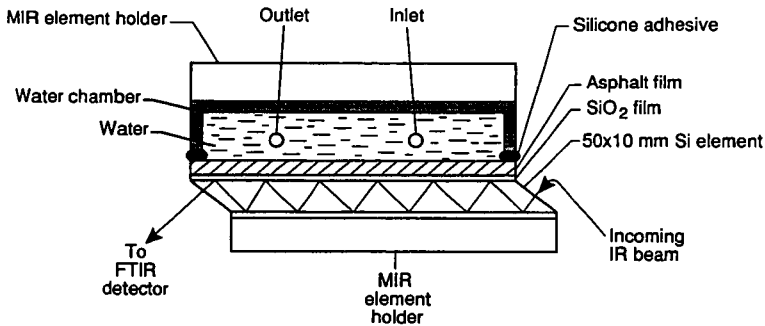


Figure 1. Specimen configuration and experimental setup for *in situ* measurement of water at the asphalt/siliceous aggregate interface.

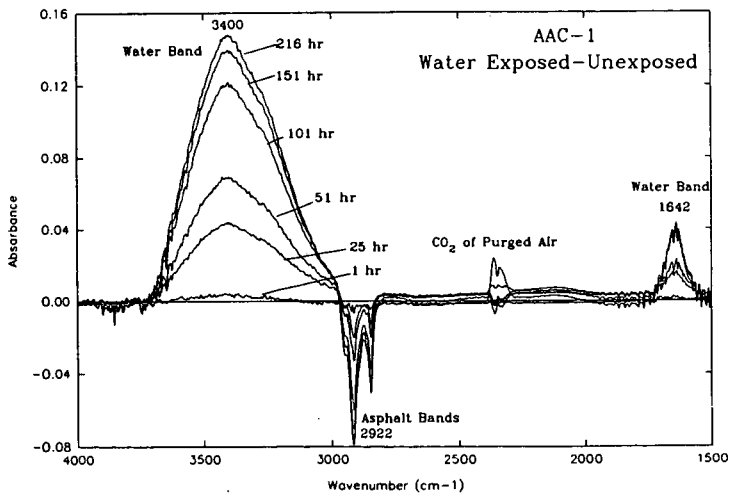


Figure 2. Typical FTIR-MIR difference spectra (water exposed - unexposed) of an asphalt/siliceous aggregate specimen for different exposure times in water.

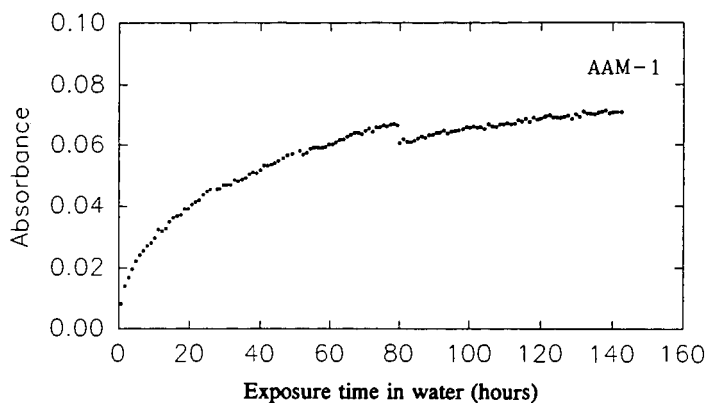


Figure 3. A typical water OH stretching intensity/time plot of an asphalt/siliceous aggregate specimen exposure to water. (Each dot represents one data point.)

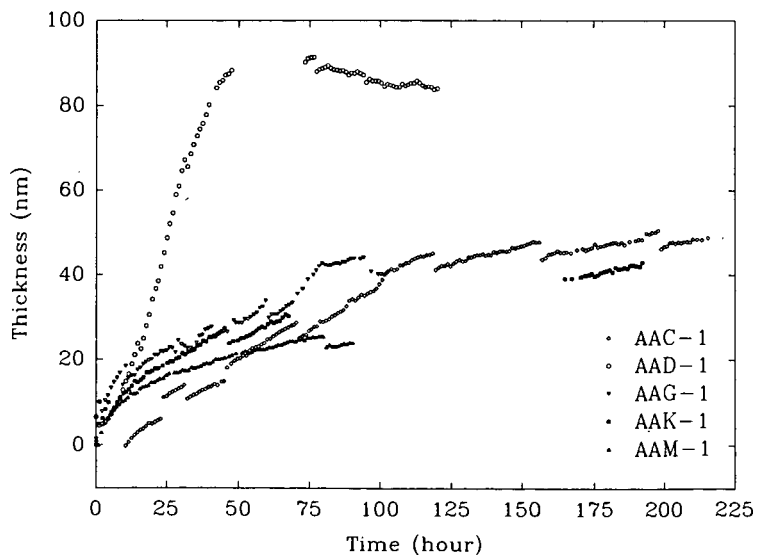


Figure 4. Thickness of the water layer at the asphalt/siliceous aggregate interface for five SHRP asphalts.