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**CHARACTERIZING
SURFACE PROPERTIES
OF AGGREGATES USED
IN HOT MIX ASPHALT**

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16. Abstract Physical and chemical properties of aggregates at the micro scale strongly impact the adhesive bond (strength and durability) between bitumen and aggregate. These properties include surface free energy, chemical interaction potential, and specific surface area. This report describes testing methods developed for the Universal Sorption Device (USD), the Wilhelmy Plate (WP), and the microcalorimeter (MC) to measure these surface properties of aggregates. Test results from five different asphalt binders and nine different aggregates are presented to demonstrate how these surface properties can be used to: (1) select combinations of bitumen and aggregates that are more resistant to moisture damage, (2) select additives that can be used to improve the performance of asphalt mixtures based on the physico-chemical nature of the bitumen and aggregate, and (3) predict the resistance of the mixture to moisture-induced damage.			
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Chapter I

Introduction

Introduction and Background

Physical and chemical properties of aggregates at a macro and micro scale influence the performance of asphalt mixes. Examples of physical properties at the macro scale are angularity, form, and texture of the aggregate. These properties are correlated with distress modes such as rutting in asphalt mix pavements. Specifications based on empirical and semi-empirical methods are used to control the flat, elongated, and rounded aggregates in asphalt mixes. Recent developments in automated aggregate imaging methods provide a more refined and quantitative way to measure these properties (Masad et al. 2005).

Examples of physical and chemical properties at the micro scale are, surface free energy, chemical interaction potential, and specific surface area of the aggregates. According to the literature, these properties directly influence the nature and durability of the bond between the aggregates and the bitumen in wet and dry conditions. This in turn affects the durability of the asphalt mix in terms of its resistance to moisture induced damage and fatigue cracking. However, test methods to efficiently measure these micro scale physical and chemical properties have not been investigated until recently.

Objective and Scope

The universal sorption device (USD) was used to measure the surface free energy and specific surface areas of aggregates. A microcalorimeter was used to measure the surface free energy of aggregates and identify the presence of chemical interactions between different aggregate types and bitumen. Developments of test methods from this study have made it feasible to use these test methods to measure the aggregate properties on a routine basis. Potential benefits of measuring micro scale physical and chemical properties using these methods include,

- The ability to select combinations of bitumen and aggregates that are more resistant to moisture damage,
- The ability to select additives that can be used to improve the performance of the mix based on the physio-chemical nature of the bitumen and the aggregate,
- The ability to predict performance of the asphalt mix in conjunction with other physical properties of the mix.

The purpose of this report is to present the developments made in the aforementioned test methods, and the test protocols to measure the micro scale physical and chemical properties of aggregates that are related to the performance of asphalt mixes.

Chapter II Universal Sorption Device

Introduction

Aggregates are a heterogeneous combination of various naturally occurring minerals. It is reasonable to regard aggregates as high energy solids, since the surface free energy of clean aggregates is typically higher than the surface free energy of the commonly used probe liquids. A gas sorption approach was used by Li (1997) and Cheng (2002) to determine surface energies of aggregates. Some of the results from Cheng (2002) indicate that there is a need for further refinement of this methodology for use as a test procedure for aggregates. For example, in some cases different probe liquids resulted in different specific surface areas for the same aggregate. Specific surface area is an important input in computing spreading pressures and eventually the surface energy components. Therefore, any discrepancy or error in specific surface areas of aggregates is also reflected in the computed surface free energy components. Since measurement of an adsorption isotherm is inherently a time consuming and sensitive procedure, manual control can lead to unwanted variability in the test results. In order to reduce this variability, a completely automated manifold was developed to facilitate testing and improve precision of the test method. Experimental and analytical methods to accurately measure and compute the surface free energy components were also developed.

Background and Theory

Spreading pressure is defined as the reduction in the surface free energy of the solid due to the adsorption of vapor molecules on its surface. Spreading pressure based on the equilibrium mass adsorbed at the maximum saturated vapor pressure is referred to as the equilibrium spreading pressure of the vapor with the solid, denoted by the symbol π_e . Based on this definition, equilibrium spreading pressure is expressed as:

$$\pi_e = \gamma_s - \gamma_{sv} \quad (2.1)$$

where, γ_s and γ_{sv} are the surface free energies of the solid in vacuum and in the presence of the vapor at maximum saturated vapor pressure, respectively.

The equilibrium spreading pressure of a vapor on a solid surface and their interfacial work of adhesion are related as follows,

$$W_{SL} = \pi_e + 2\gamma_{LV} \quad (2.2)$$

The above equation is valid for high surface energy materials such as aggregates. Further, using the Good-van Oss-Chaudhury (GVOC) theory for the work of adhesion (van Oss et al. 1988; van Oss, 1994), the spreading pressure of a vapor on a solid surface and their surface free energy components are related as follows,

$$\pi_e + 2\gamma_{LV} = 2\sqrt{\gamma_s^{LW} \gamma_L^{LW}} + 2\sqrt{\gamma_s^+ \gamma_L^-} + 2\sqrt{\gamma_s^- \gamma_L^+} \quad (2.3)$$

The three surface energy components of the solid are the unknowns in equation (2.3). The surface energy components of the liquid are known, and the spreading pressure between the

liquid vapor and solid is experimentally measured. Spreading pressure with at least three different liquid vapors must be measured experimentally and used with equation 4.3 to result in three simultaneous linear equations. This set of three equations can be solved to determine the three unknown surface energy components of the solid (aggregates).

The spreading pressure of a vapor over the aggregate surface is determined from its adsorption isotherm using equation (2.4) (Jura and Harkins, 1944):

$$\pi_e = \frac{RT}{MA} \int_0^{p_0} \frac{n}{p} dp \quad (2.4)$$

where, R , is the universal gas constant, T is the test temperature, n is the mass of vapor adsorbed per unit mass of the aggregate at vapor pressure, p , M is the molecular weight of the probe vapor, p_0 is the maximum saturation vapor pressure of the liquid, and A is the specific surface area of the aggregate.

Specific surface area of the aggregate is calculated using the classical Branauer, Emmett and Teller (BET) equation (Gregg and Sing, 1967) as shown below:

$$A = \left(\frac{n_m N_0}{M} \right) \alpha \quad (2.5)$$

where, N_0 is the Avogadro's number, M is the molecular weight of the probe vapor, and α is the projected area of a single molecule of the probe vapor, and n_m is the monolayer capacity of the aggregate surface.

Monolayer capacity is the number of molecules required to cover the aggregate surface in a single layer. This is calculated using equation (2.6) from the slope 'S' and intercept 'I' of the best fit straight line between $\frac{P}{n(p_0 - p)}$ versus $\frac{P}{p_0}$, where p , p_0 , and n are the partial vapor pressure, maximum saturation vapor pressure, and mass of vapor adsorbed on aggregate surface, respectively. The straight line fit is done only for partial vapor pressure, or $\frac{P}{p_0}$, ranging from 0 to 0.35, since the BET equation is valid only for this range.

$$n_m = \frac{1}{S + I} \quad (2.6)$$

Figure 2.1 summarizes the analytical steps to obtain surface energy components of an aggregate. Note that the specific surface area is determined using n-hexane to calculate the spreading pressures from all three probe vapors. Detailed explanation for this is provided in the section entitled "Experimental Variables".

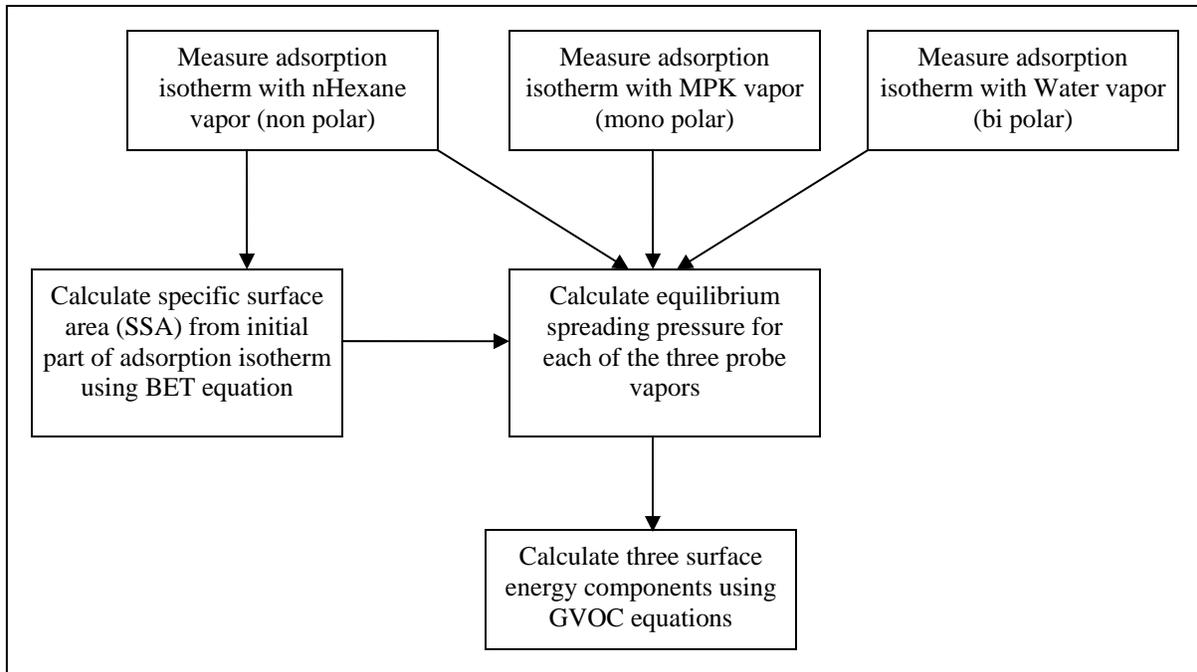


Figure 2.1 Flow Chart of Steps to Determine Aggregate Surface Energy.

Development of Test Method

Surface energy components of aggregates are calculated from the spreading pressures of three probe vapors on the aggregate surface. Spreading pressure of a probe vapor is determined by measuring the full adsorption isotherm of the probe vapor on the aggregate surface. Therefore, to determine surface energy of aggregates the main experimental task is to measure its adsorption isotherm with different probe vapors.

In this study, the aggregate was exposed to ten equal increments of partial probe vapor pressure from vacuum to maximum saturation vapor pressure to obtain a full adsorption isotherm. For each increment, the adsorbed mass was recorded after it reached equilibrium. Ten points were found to be sufficient to establish a good fit to the data within a reasonable test period. The time taken for the adsorbed mass to attain equilibrium was considerable for some aggregates and resulted in long overall test times. Furthermore, sensitivity of measurements and the human judgment required to determine if equilibrium was achieved, introduced variability and human error in the experiment. In order to avoid the influence of these factors on the test results, an automated test system capable of executing the entire test procedure with minimal operator effort and interference was developed. More details of the test method and set up are described in the following sub sections.

Sample Preparation

The aggregates to be tested were sampled from a representative stockpile. Aggregates passing ASTM sieve #4 and retained on ASTM sieve #8 were used for testing. The aggregates were sieved and cleaned with distilled water. About 25 grams of the aggregate were required for one replicate test with each probe vapor. After cleaning the aggregate with distilled water, they

were dried in an oven at 150°C for 6 hours and allowed to cool to room temperature inside a vacuum desiccator for about 6 more hours. Once the sample was cleaned and ready to test, it was placed in a wire mesh sample basket for testing.

Test Setup

The adsorption measurements were carried out in an air tight sorption cell. The sample basket was suspended in the cell from a hook connected to a microbalance via a magnetic suspension coupling. The magnetic suspension coupling enables accurate measurement of mass without the balance coming into any physical contact with the sample or vapors in the sorption cell. The sorption cell and micro balance together form the sorption apparatus manufactured by Rubotherm of Germany.

In order to automate the test procedure, a test manifold was developed and connected to the sorption apparatus. Software (SEMS, Surface Energy Measurement System) was developed to regulate the vapor pressure in the sorption cell and acquire mass, pressure, and temperature data via a series of solenoid valves and transducers. Figure 2.2 illustrates a schematic of the manifold and the sorption apparatus. Figure 2.3 shows a snapshot of the SEMS software for running the sorption test. The probe liquids were stored in air-tight cylinders connected to the manifold. The cylinders were degassed after connection to remove any trapped air and ensure the presence of only pure vapors from the probe liquid. The cylinders were connected to the sorption cell via a solenoid valve that was regulated by a computer to maintain the desired amount of vapor pressure in the sorption cell.

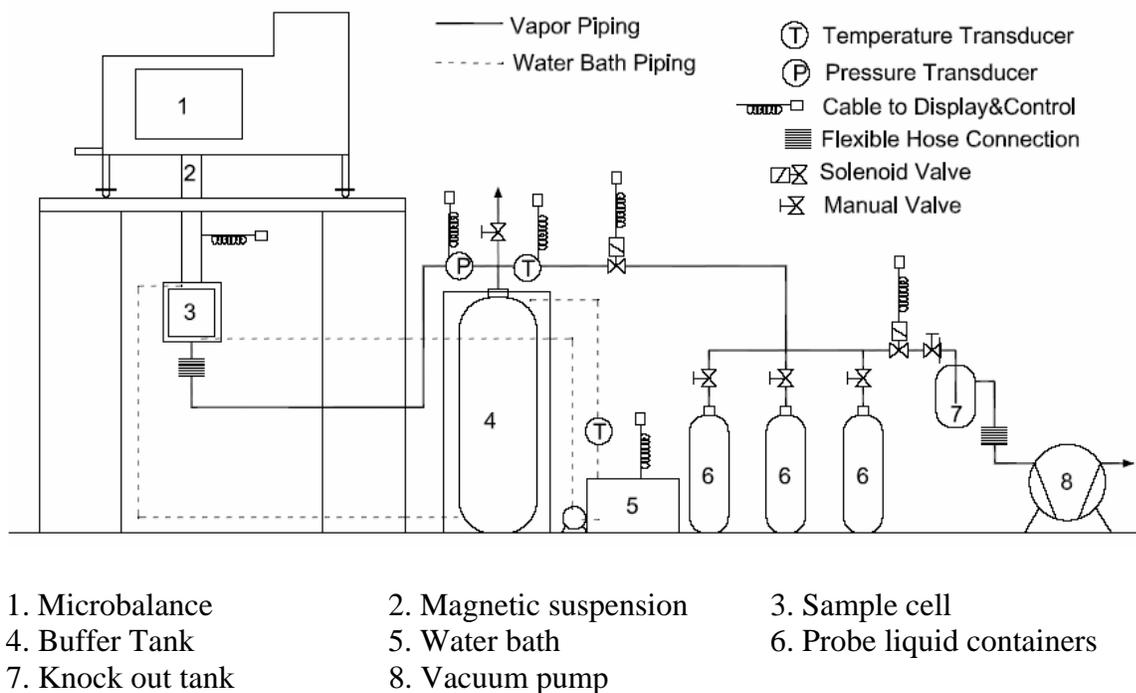


Figure 2.2 Layout of Universal Sorption Device System.

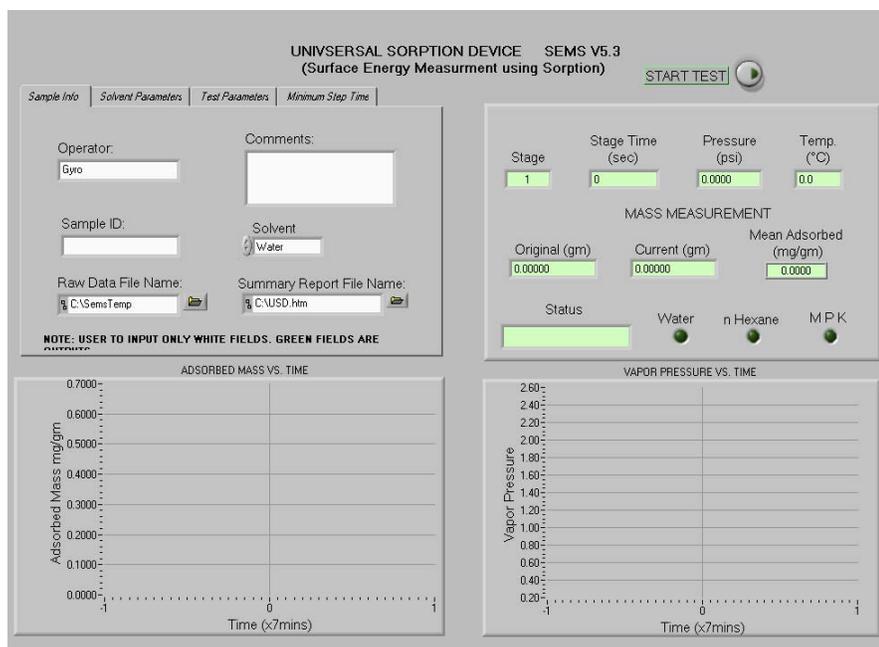


Figure 2.3 Snapshot of SEMS Software Used for Sorption Measurement.

Test Method

After the sample was suspended from the magnetic suspension hook, the sorption cell was sealed using a viton O-ring. The sorption cell was degassed using a mechanical vacuum pump. Degassing was carried out at 70°C under a vacuum of about 5 millitorr for a period of 2 hours followed by cooling to 25°C under vacuum for 4 hours. The temperature of the sorption cell was maintained using a water bath controlled by SEMS.

After completion of degassing, the adsorption isotherm of a probe vapor with the aggregate was obtained using SEMS. The following is a typical sequence of steps executed to obtain a full isotherm:

- Mass of the aggregate is measured in vacuum after complete degassing.
- Small doses of vapors from the probe liquid are allowed into the sorption cell to achieve a vapor pressure of approximately one-tenth the maximum saturated vapor pressure of the probe.
- Mass of adsorbed vapor is calculated as the difference between equilibrium mass after exposure to the vapor and the mass under vacuum.
- The previous two steps are repeated by increasing the vapor pressure in increments of approximately one-tenth of its maximum vapor pressure until saturated vapor pressure was achieved in the adsorption cell.

In order to determine whether the adsorbed mass has reached equilibrium, SEMS calculates the slope of the adsorbed mass versus time for the last five minutes of the test. If the slope is less than a pre-specified significant threshold value, the adsorbed mass is considered to have reached equilibrium and the next increment of partial vapor pressure is applied. Correction for buoyancy is automatically made to the measured mass as follows:

$$B = \frac{MpV}{RTz} \quad (2.7)$$

where, M is the molecular weight of the vapor, p is the partial vapor pressure at the time of measurement, V is the volume of the aggregate sample, R is the Universal gas constant, T is the test temperature, and z is the compressibility factor that can be calculated using empirical equations or obtained from physical tables (Pitzer and Brewer, 1961).

Following completion of the test, the SEMS software uses equations (2.4), (2.5) and (2.6) to calculate the specific surface area of the aggregate and the spreading pressure of the probe vapor from the test data. Equations (2.2) and (2.3) were used to determine the three surface energy components of the aggregates based on the spreading pressures from the three probe vapors and specific surface area calculated using n-hexane. The three probe vapors used in this research were n-hexane, methyl propyl ketone (MPK), and water. Table 2.1 presents the surface energy components of these three probes (van Oss et al. 1994).

Table 2.1 Surface Energy Components of Probe Vapors

Probe Vapor	γ^{LW} (erg/cm ²)	γ^+ (erg/cm ²)	γ^- (erg/cm ²)	γ (erg/cm ²)
Water	21.8	25.5	25.5	72.8
Methylpropylketone	21.7	0	19.6	21.7
Hexane	18.4	0	0	18.4

Experimental Variables

Chemisorption versus Adsorption

Bond strength between two materials due to their surface energies is typically an order of magnitude or smaller than the chemical bond strength. The main causes for the development of a bond between two materials are physical adsorption due to their surface energies and chemical adsorption or chemisorption due to formation of chemical bonds between the two materials. For example, physically adsorbed vapors on a solid surface can be removed by degassing at normal temperatures, while chemisorbed vapor molecules bond more tenaciously to the solid surface and usually cannot be removed without the aid of very high temperature and vacuum. Adsorption measurements may be used to measure the surface energy of aggregates only when the adsorbed mass is mostly due to physical adsorption and not chemisorption. In earlier experiments Cheng (2002) determined that there was no appreciable difference in the adsorption and desorption isotherms of typical aggregates such as granite, limestone, and gravel using the same probe vapors. Based on this data and similar results from other studies (Chen and Dural, 2002), it is reasonable to consider that the adsorption of selected probe vapors on the aggregate surface are primarily physical in nature.

Specific Surface Area

Surface energy is expressed in units of energy per unit area. Since the adsorption isotherm is measured in terms of mass of vapor adsorbed per unit mass of aggregate, specific surface area is an important input to compute the spreading pressure and surface energy of aggregates. Equations (2.5) and (2.6) shown earlier are used to calculate the specific surface areas of aggregates from their adsorption isotherms with different probe vapors. The physical interpretation of these equations is as follows. Equation (2.5) determines the number of molecules required to form a monomolecular layer or monolayer over the aggregate surface. Thus, the total number of molecules forming a monolayer is multiplied by the projected area of each molecule, results in the specific surface area of the aggregate.

The projected cross sectional area of a probe vapor molecule is theoretically obtained using a liquid density equation that assumes the hexagonal packing model. Adsorbed molecules of polar probes such as MPK and water may have a preferred orientation resulting in different projected cross sectional areas for different aggregates. As a result, using the theoretical cross sectional area of the molecule may result in inaccurate estimation of specific surface areas of the aggregates. The projected cross sectional area of n-hexane (non polar probe) calculated based on liquid density formula is 36\AA^2 . Gases such as nitrogen or argon are commonly used as probes to determine specific the surface area of solids on account of their relatively inert and non polar nature. Based on the comparison of specific surface areas of various standard materials using one or more probe vapors including inert gases, the projected area of n-hexane molecules is estimated as 56\AA^2 (McClellan and Harnsberger, 1967) which is larger than the value calculated using the liquid density formula. It is recommended that this value of projected area of n-hexane molecules be used to calculate the specific surface areas of the aggregates. This proposition is supported by experimental data presented later in this chapter.

Sample size and preconditioning

Although measuring adsorption isotherms is not a new technique, certain modifications were required in order to implement it for measuring aggregate surface energies. Most of the vapor sorption methods described in the literature use very finely divided solids and a sample mass of about 1gm or less (Jura and Harkins, 1944; Chen and Dural, 2002; Bilinski and Holysz, 1999). Furthermore, most of these tests are based on measurement of relatively pure and homogenous solids and employ preconditioning temperatures as high as 250°C for time durations as long as 24 hours.

Aggregates used in hot mix asphalt are heterogeneous and are often combined from different size fractions to achieve a desired gradation. Surface energy of an aggregate is an intrinsic material property and therefore must be independent of its geometry. This eliminates the requirement to test every size fraction of the same aggregate to obtain its surface energy characteristics. This is true unless the size fraction is extremely fine such that differences in individual crystals become significant. Such fines are more likely to be considered as a part of the bitumen mastic rather than an aggregate bound by the bitumen. It is important to select a sample size and quantity that represents the mixture properties. Approximately 25 grams of aggregate passing the ASTM #4 sieve and retained on the ASTM #8 sieve was found to be the most appropriate quantity and size for surface energy measurements using the sorption apparatus. The quantity of the sample is determined by the range (5-100 grams) and sensitivity (10 micro grams) of the balance. Typically smaller aggregate sizes will result in larger total surface areas and vice-versa. A large total surface area improves the precision of measurement

because larger amounts of vapor mass are adsorbed, but also results in longer degassing and equilibrium times. On the other hand, a smaller total surface area reduces the test duration but at the expense of precision of measurement. The size fraction, between the #4 and #8 sieves optimizes precision and minimizes time of testing.

In this study, preconditioning of aggregates was done in two stages. In the first stage the aggregate sample was cleaned with distilled water to remove any physical or organic impurities from the surface. The sample was then heated in an oven at 150°C for 12 hours and allowed to cool to room temperature in a desiccator. Calcium sulfate crystals were added to the desiccator to lower the humidity in the desiccator. In the second stage of preconditioning the aggregates were transferred into the sample basket and suspended in the sorption cell. A vacuum of about 5 millitorrs was applied for a period of two hours at a temperature of 70°C and the cell was allowed to cool back to test temperature under vacuum for three to four hours. The adequacy of this preconditioning procedure was determined in two ways. First, the mass of aggregate was monitored during degassing and no appreciable change in mass was observed after about 2 hours of degassing indicating that there was no further significant desorption from the aggregate surface. Second, in another experiment isotherms of the same aggregate subjected to different durations of degassing were compared and found to be indifferent. Figure 2.4 illustrates this comparison for a gravel sample with MPK as a probe vapor. It is evident from the figure that the preconditioning procedure described above is adequate for testing this aggregate size fraction.

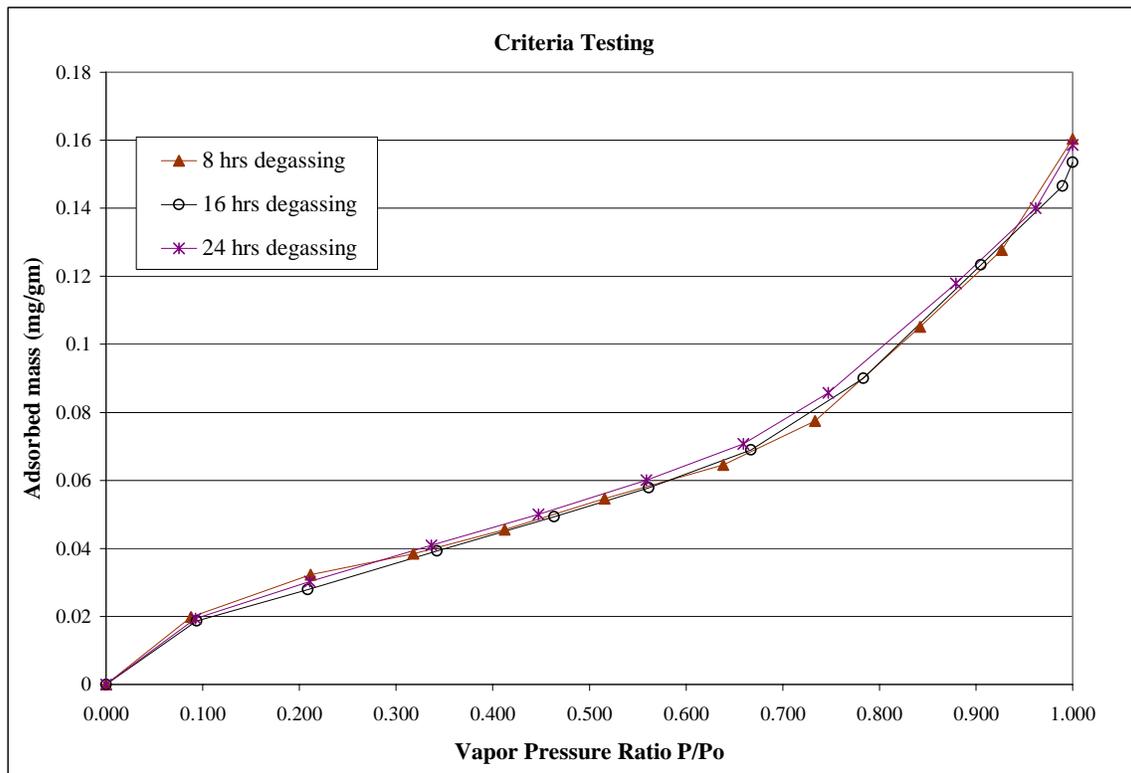


Figure 2.4 Evaluation of Preconditioning Time.

Test Results

Surface energies of five different aggregate types and four minerals were measured in this study. The aggregates were obtained from the Strategic Highway Research Program, Materials Reference Library (MRL), Reno, Nevada. These aggregates were from different sources and represent a range of mineral compositions. Three replicates of each aggregate were tested with each of the three probe vapors.

The developed manifold and accompanying SEMS software was used to carry out the adsorption test. Figure 2.5 shows a typical output from the SEMS software after completion of a test with a probe vapor. The specific surface area and spreading pressure for the aggregate with the probe vapor are calculated using equations (2.4) and (2.5), respectively. In order to calculate the surface energy characteristics of the aggregate, spreading pressures from different probe vapors are combined using equations (2.2) and (2.3). Table 2.2 presents the spreading pressure measured using the USD and the coefficient of variation of the results based on three replicate measurements. The specific surface areas of the aggregates were computed from the adsorption isotherm of n-hexane and with a projected area of nHexane molecule as 56\AA^2 .

Table 2.2 Spreading Pressure

Aggregate	M P K		n Hexane		Water	
	Spreading Pressure (erg/cm ²)	CV (%)	Spreading Pressure (erg/cm ²)	CV (%)	Spreading Pressure (erg/cm ²)	CV (%)
RD	32.1	16.0	20.1	6.7	94.4	8.6
RL	69.7	7.2	28.3	14.1	293.2	4.0
RK	31.1	12.4	25.3	15.8	59.3	5.6
RA	20.3	17.0	23.9	5.5	124.5	16.4
RG	61.5	10.5	28.7	15.3	252.9	6.0
Quartz	8.7	10.9	22.8	5.1	142.7	8.6
Albite	28.4	1.9	23.4	9.0	85.6	6.5
Calcite	29.4	3.5	39.6	3.5	139.6	6.2
Microcline	18.4	3.9	20.0	1.3	72.7	3.7

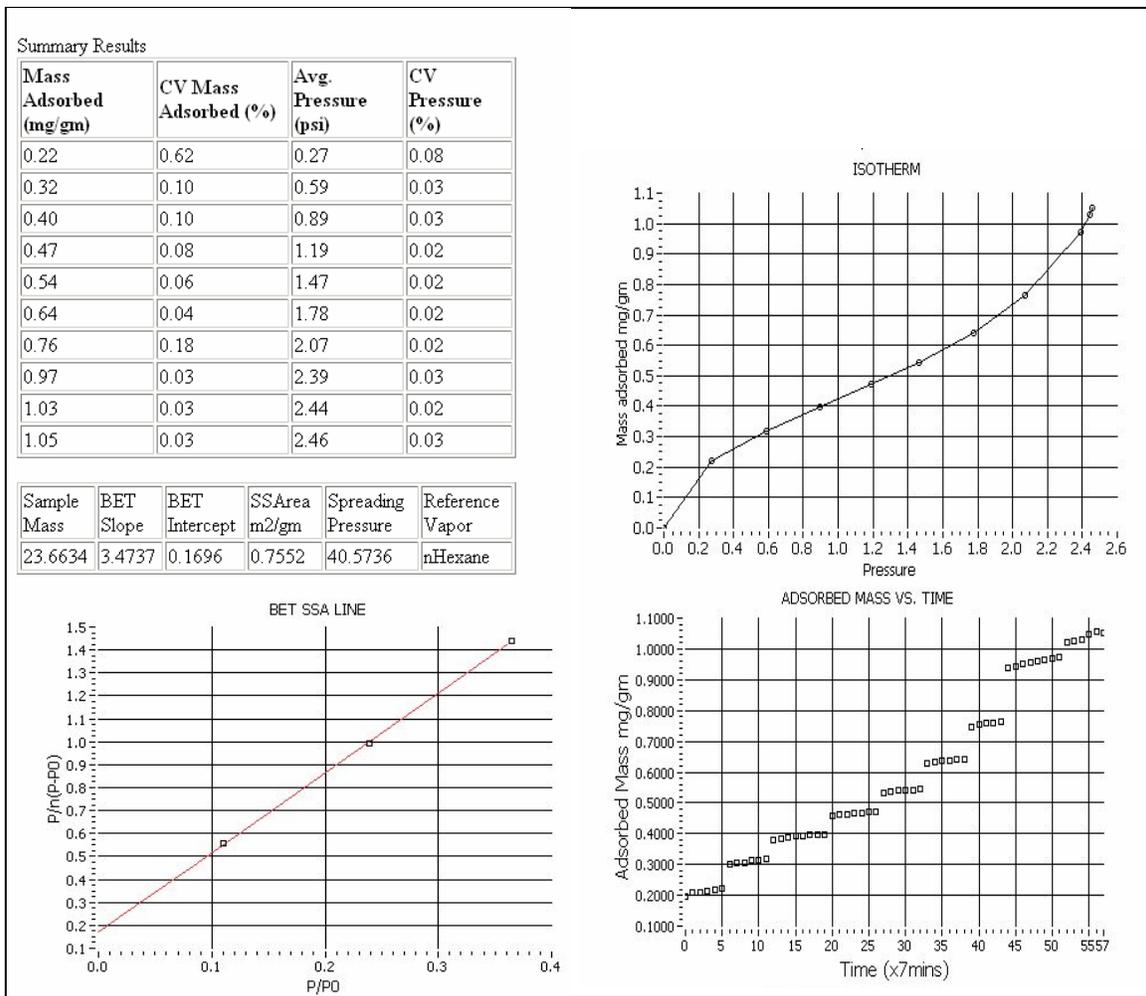


Figure 2.5 Typical Report Generated Using SEMS Software.

Table 2.3 summarizes surface energy characteristics for the five aggregates and four minerals. Figures 2.6 through 2.8 illustrate the three surface energy components of the aggregate and minerals that were tested along with their standard deviations. Results from these figures show that this test method can be used to determine the surface energy components of the three aggregates with reasonable precision. Standard deviations for the surface energy components were calculated using propagation of errors.

Table 2.3 Surface Energy Components

Aggregate	γ^{LW} (erg/cm ²)		γ^+ (erg/cm ²)		γ^- (erg/cm ²)		γ^{AB} (erg/cm ²)	γ^{Total} (erg/cm ²)
	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.		
RD: Limestone	44.1	1.25	2.37	1.08	259	18	49.57	93.6
RL: Gravel	57.5	4.09	23	4.15	973	39	299.2	356.8
RK: Basalt	52.3	4.77	0.64	0.74	164	10	20.5	72.8
RA: Granite	48.8	0.49	0		412	83	0	48.8
RG: Sandstone	58.3	4.52	14.6	4.01	855	34	223.2	281.5
Mineral: Quartz	37.2	1.0	0.0		525	32.2	48.3	96.6
Mineral: Albite	47.5	0.5	0.7	0.1	245	10.1	21.3	77.1
Mineral: Calcite	67.0	1.6	0.0		427	20.8	0	67.0
Mineral: Microcline	43.9	0.4	0.0		239	8.0	0	46.6

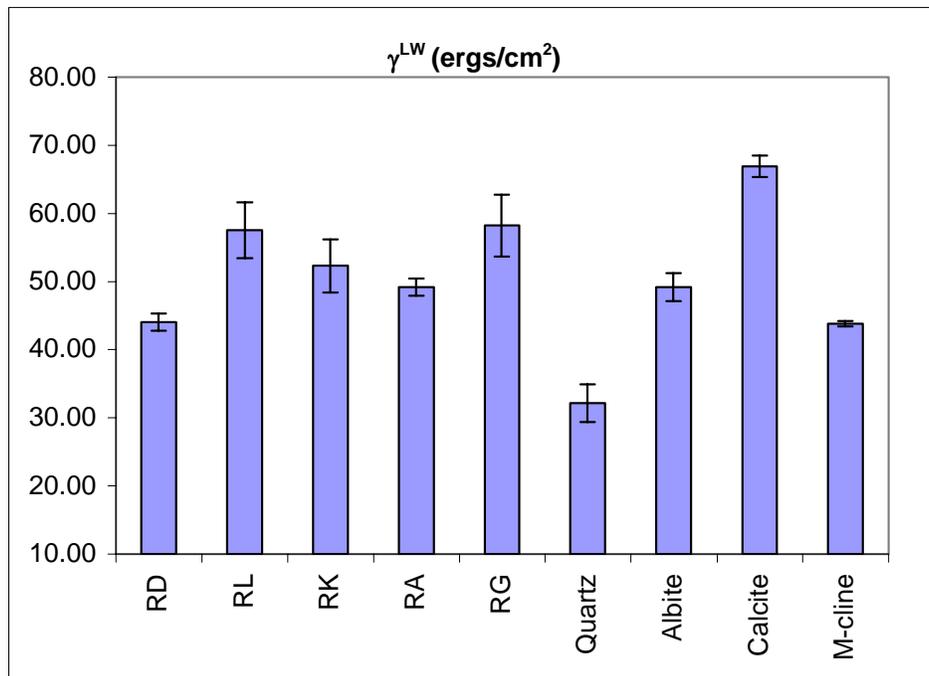


Figure 2.6 LW Component of Aggregates.

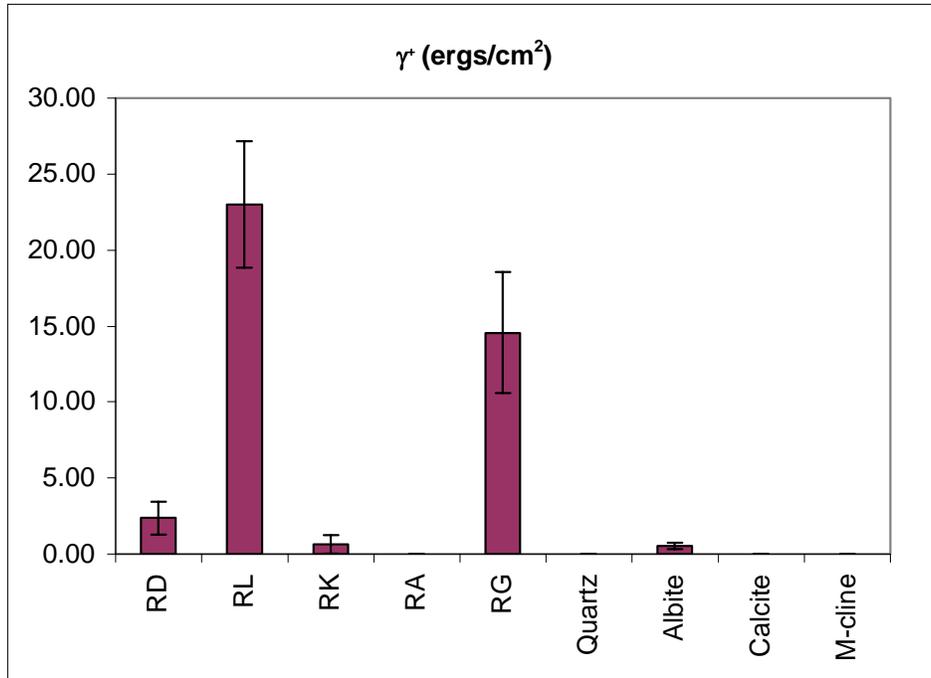


Figure 2.7 Acid Component of Aggregate.

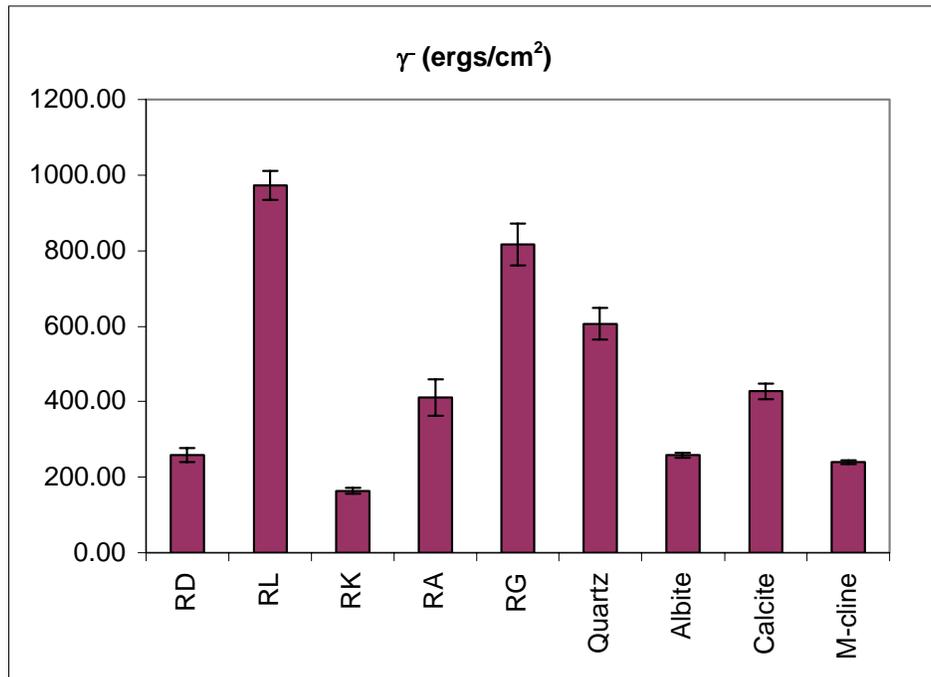


Figure 2.8 Base Component of Aggregate.

Validating Test Method Based on Specific Surface Area

Table 2.4 presents the specific surface areas of five different aggregates measured using the three probe vapors and considering the projected cross sectional area of the probe molecule based on the liquid density formula. Differences in cross sectional area determined using polar (MPK and water) and non-polar (n-hexane) vapors are evident. The table also includes surface areas of aggregates calculated using n-hexane but with a projected molecular cross sectional area of 56\AA^2 as adopted from the literature (McClellan and Harnsberger, 1967). Earlier it was proposed that n-hexane must be used with a projected cross sectional area of 56\AA^2 to compute the specific surface area of the aggregates since n-hexane molecules are non-polar and therefore their orientation is not affected by different surface polarities of different aggregate surfaces. In order to validate this, the specific surface area of the same size fraction of two aggregates was measured using a commercially available nitrogen sorption device manufactured by Micromeritics Inc. Data from Table 2.5 shows that the specific surface areas measured using this device agree well with the areas obtained using the adsorption equipment. This comparison also provides a limited validation of the accuracy of measurement of this test method.

Table 2.4 Specific Surface Area of Aggregates

Aggregate	Water ¹ (10\AA^2)		MPK ¹ (35\AA^2)		Hexane ¹ (39\AA^2)		Hexane ² (52\AA^2)
	SSA (m^2/gm)	CV(%)	SSA (m^2/gm)	CV(%)	SSA (m^2/gm)	CV(%)	SSA (m^2/gm)
RD	0.17	4	0.23	10	0.18	5	0.26
RL	2.01	6	1.40	7	0.69	10	1.00
RK	4.15	12	6.49	7	7.20	8	10.38
RA	0.10	18	0.05	6	0.07	4	0.10
RG	1.62	4	0.99	10	0.51	7	0.74

Value in parenthesis is projected area of molecule used for calculation. ¹ is value calculated using liquid density formula and ² is value adopted from literature

Table 2.5 Specific Surface Area Using Different Methods

Aggregate	USD SSA (m^2/gm)	Micromeritics SSA (m^2/gm)
RK	10.38	10.10
RA	0.10	0.13

Surface Energy Components and Interpretation

The test results indicate that the sorption test controlled by the SEMS software measures spreading pressures of aggregates with reasonable precision. The Lifshitz-van der Waals (LW) or dispersive component of surface energy varies from 44 to 58 ergs/cm², for different aggregates. Although differences in the dispersive component between aggregates is not large, it contributes

significantly to adhesion keeping in perspective the dispersive component of bitumen surface energy that typically varies from 12 to 35 ergs/cm². Also, from existing literature (Bilinsky and Holysz, 1999; Douillard et al., 1995; Bilinsky and Chibowski, 1983) the dispersive component of finely divided minerals commonly found in aggregates, such as quartz and calcite is reported to be between 35 to 80 ergs/cm². These values were determined using various other techniques such as the Wicking method, microcalorimeter and inverse gas chromatography. The values obtained from the USD measurements are in agreement with this range.

The magnitude of the acid component is very small, and the magnitude of the base component is very high and significantly different for all five aggregates. The acid and base interactions between the bitumen and aggregate are geometrically combined in a complimentary fashion (acid component of aggregate with base component of bitumen and vice-versa) to compute the total work of adhesion. Therefore, the large magnitude of base component of aggregates is a significant contributor to the adhesion between the bitumen and aggregate with the acid component of bitumen, although small, acting as a scaling factor. This is in concurrence with other adhesion theories that attribute adhesion between bitumen binder and aggregate to the weakly acidic character of the bitumen and a basic character of the aggregate (Petersen et al., 1974).

Summary

The test method developed in this project offers a convenient way to measure surface energy components of aggregates that can be combined with the surface energy components of bitumen to compute the dry work of adhesion, and work of debonding in presence of water to estimate the moisture sensitivity of asphalt mixes. Discrepancies in specific surface areas of aggregates reported by previous researchers were resolved. Precision of the test method was improved significantly by developing an automated test manifold controlled by a computer. Specific surface areas of aggregates measured using this test method compare well with specific surface areas measured using industry standard method and provide a limited validation for the accuracy of this device. Surface properties of pure minerals such as quartz and calcite measured using this method are also in reasonable agreement with similar data available in the literature based on other test methods.

Chapter III

Applications of Calorimeter

General

Adhesion between bitumen and aggregate and their debonding in the presence of water are key factors that influence the moisture sensitivity of an asphalt mix from a materials point of view. Mechanical interlocking, physical adhesion and chemical bonding are the three main mechanisms responsible for adhesion and debonding. The previous chapter describes development of a test method to measure the surface free energy components of aggregates. These values can be combined with the surface free energy components of bitumen to quantify the moisture sensitivity of asphalt mixes. When surface free energy is used to compute the work of adhesion between the aggregate and bitumen and their work of debonding in the presence of water, it accounts for only the contribution of the physical adhesion between these materials. However, when chemically active aggregates such as limestone are used, or when active fillers such as hydrated lime, or liquid anti strip agents are added to the bitumen, chemical interactions may contribute significantly to adhesion. One way to quantify the effect of chemical bonding, if any, is by measuring the heat of adhesion when bitumen comes into contact with the aggregate surface.

A micro calorimeter can be used in different ways to quantify adhesion and debonding between the bitumen and aggregate. The three different ways of using the microcalorimeter explored in this project are as follows:

- To rapidly measure the enthalpies of immersion of aggregates with different probe liquids, this is then used to determine the surface free energies of aggregates.
- To measure the enthalpy of immersion of aggregates with water, this is a direct measure of the total reduction in energy of the aggregate-water system when water coats the surface of a clean dry aggregate.
- To measure the enthalpy of immersion of aggregates with bitumen at mixing and compaction temperatures (approximately 150°C), which is a direct measure of the total reduction of energy of the aggregate-bitumen system when bitumen coats the surface of a clean dry aggregate.

This chapter presents a description of the tests and results for the above three applications for a subset of materials used with the USD. Comparisons between results based on surface energy measurements and the results from the micro calorimeter indicate that this device can be used to measure various thermodynamic parameters related to the moisture sensitivity of the asphalt mixes with adequate sensitivity.

Surface Energy of Aggregates

When a clean solid (such as an aggregate) is immersed in a liquid, a new solid-liquid interface is formed and the clean solid surface is eliminated. This interaction is associated with a change in the total energy of the system and evolution of heat, referred to as the enthalpy of

immersion. The enthalpy of immersion represents the strength of surface interactions at the solid-liquid interface. In the absence of any chemical reactions the enthalpy of immersion represents the reduction in total energy of the system due to the total surface energies of the two materials. If the interfacial surface free energy at the aggregate-liquid interface is represented by γ_{AL} , and surface free energy of the clean solid surface is represented by γ_A , then based on the above explanation, the change in free energy of the system due to immersion, ΔG_{imm} is given by,

$$\Delta G_{imm} = \gamma_{AL} - \gamma_A \quad (3.1)$$

The right hand side of equation (3.1), can be replaced by the surface energy components of the solid and liquid using the GVOC theory. Furthermore, based on the classic Gibbs free energy equation, ΔG_{imm} , can be replaced by the enthalpy of immersion ΔH_{imm} , and entropy of immersion ΔS_{imm} , to obtain the following equation:

$$\Delta H_{imm} - T\Delta S_{imm} = \gamma_L - 2\sqrt{\gamma_A^{LW} \gamma_L^{LW}} - 2\sqrt{\gamma_A^+ \gamma_L^-} - 2\sqrt{\gamma_A^- \gamma_L^+} \quad (3.2)$$

In equation (3.2) the subscript “A” refers to the aggregate and “L” refers to the liquid and other terms are as described before.

Douillard et al. (1995) determined the heats of immersion and adsorption isotherms for various pure minerals with different probe liquids. Based on the comparisons of adsorption isotherms and heats of immersion, they demonstrate that the entropy term, $T\Delta S_{imm}$, in equation (3.2) can be approximated as 50% in magnitude of the enthalpy term, ΔH_{imm} . Since aggregates are composed of minerals which belong to the same class of materials used by Douillard et al. it is reasonable to extend this approximation to heats of immersion with aggregates. If a calorimeter is used to measure enthalpy of immersion, ΔH_{imm} of a solid immersed in a probe liquid with known surface energy components, and the magnitude of the entropy term, ΔS_{imm} , is approximated as 50% of the magnitude of the enthalpy term, then the only unknowns in equation (3.2) are the three surface energy components of the solid. Just as with the USD, measuring enthalpy of immersion with three probe liquids will generate a set of three linear equations that can be solved to determine the three surface energy components of the aggregate.

Test Description

The microcalorimeter used in this study was an isothermal differential calorimeter manufactured by Omnical, Inc. The differential calorimeter is comprised of two cells, a reaction cell and a reference cell. The net enthalpy is measured as the difference between the enthalpies of the reaction and reference cell using a series of thermocouples connected in series between the two cells. Figure 3.1 shows a schematic of the differential microcalorimeter.

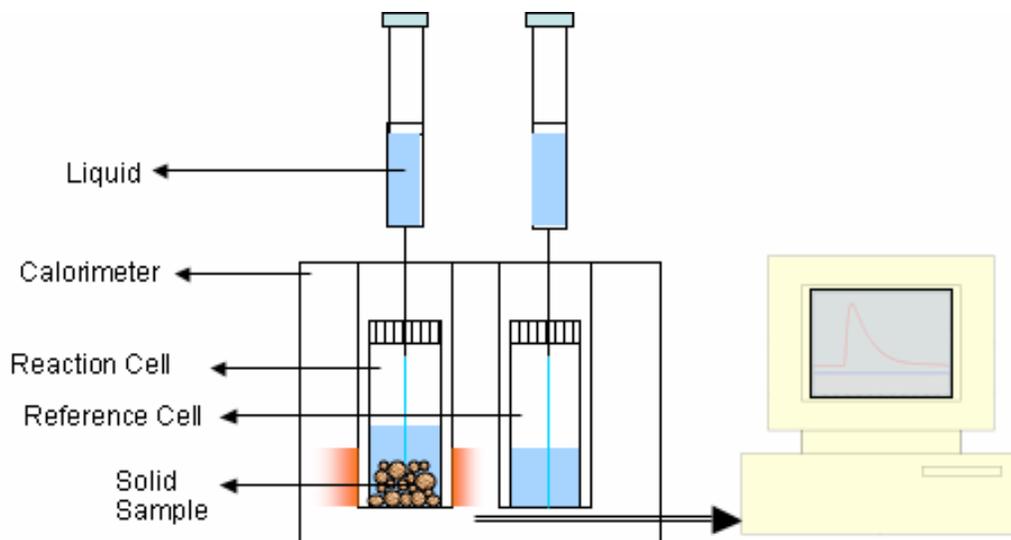


Figure 3.1 Schematic Layout of the Micro Calorimeter.

The aggregates included in this study were RD (limestone), RG (sandstone), RK (basalt), and RL (gravel). The three probe liquids used to measure the enthalpies of immersion were, heptane, benzene, and chloroform. These three probe liquids were selected because heptane is a non polar liquid and benzene and chloroform are mono polar liquids with a Lewis base and a Lewis acid character, respectively. Enthalpy of immersion of at least two replicates was measured in random order for each aggregate-probe pair.

Aggregates passing the #100 sieve and retained on the #200 sieve were found to be of suitable size for these tests. This was based on the minimum surface area required to generate heat that can be measured by the instrument with adequate precision. Crushed aggregates were sieved to obtain sufficient material of the desired size. The aggregates were then washed in the #200 sieve with distilled water and oven dried. About 8 grams of the sample to be tested was placed in a 16ml capacity glass vial. The tare weight of the vial was recorded before filling it with the sample. This vial was used in the reaction cell. Another empty vial sealed with a similar cap and septa was used in the reference cell. The vials have a polypropylene open top cap sealed with a PTFE lined silicone septa. Prior to testing, both vials were preconditioned by heating at 150°C for four hours under vacuum below 300millitorr. Vacuum was drawn in both vials using a 26 gauge syringe needle passing through the silicone septa. Once preconditioning was complete the needle was quickly withdrawn allowing the silicone septa to seal it and retain the contents of the vial under vacuum. The vials were then allowed to cool to the test temperature of 25°C. The test set up developed in this study enables preconditioning of four vials simultaneously. Once the samples were preconditioned and cooled, the vial with the aggregate sample was weighed again to obtain the exact dry weight of the test sample and placed in the reaction cell. The empty vial was placed in the reference cell. Four syringes of 2ml capacity each were filled with the probe liquid. Two of these syringes were positioned on top of the reaction vial and the other two on top of the reference vial. Accompanying software with the micro calorimeter recorded the differential heat between the two cells within an accuracy of 10 μ watts. As soon as thermal equilibrium was reached (typically 30 to 40 minutes) the syringes were pushed simultaneously piercing through the septa and the probe liquid was injected in both vials. Since differential heat

between the two cells is recorded, heat generated due to the process of piercing and injection is compensated during measurement. The net heat measured in the reaction cell is due to,

- enthalpy of immersion in the reaction cell, and
- difference in heat of vaporization of the probe liquid on account of the difference in free volume of the reaction and reference cell.

The latter is corrected by calculating heats of vaporization for the corresponding probe liquids.

Specific surface area of the aggregates is an important input for determining their surface energy. In this research, the specific surface areas of the materials used were determined using adsorption measurements with the USD. In practice, this can be done using any commercial nitrogen adsorption equipment. The total enthalpy of immersion is divided by the mass of the sample to obtain the enthalpy of immersion in ergs/gm and then by the specific surface area to obtain the heat or enthalpy of immersion in ergs/cm². The surface energy components of the aggregates were determined by solving the three simultaneous equations generated using each of the three probe liquids from equation 3.2.

Results and Discussion

Table 3.1 presents the average enthalpy of immersion of different aggregate-probe pairs and Table 3.2 presents the coefficient of variation for these measurements.

Table 3.1 Enthalpy of Immersion in ergs/cm²

Aggregate	Liquid Probe		
	Benzene	Chloroform	Heptane
RD	159	345	108
RG	204	386	99
RK	63	137	38
RL	130	416	76

Table 3.2 Coefficient of Variation (%) for Measured Enthalpy of Immersion

Aggregate	Liquid Probe		
	Benzene	Chloroform	Heptane
RD	3	0	4
RG	0	1	5
RK	2	0	1
RL	7	2	4

Based on the data presented above it is evident that the micro calorimeter has very good repeatability. The device also has adequate sensitivity to differentiate between the heats of immersion of different aggregates with the same probe and heats of immersion of different probes with the same aggregate. Table 3.3 presents a comparison of the surface energy components of the aggregates measured using the Universal Sorption Device and the Micro calorimeter.

Table 3.3 Surface Energy Components of Aggregates in ergs/cm²

Aggregate	Surface Energy Components					
	LW		Acid		Base	
	USD	MC	USD	MC	USD	MC
RD	44	52	2	11	258	469
RG	58	48	15	162	855	920
RK	52	18	1	16	162	154
RL	57	38	23	42	973	1652

USD = Universal Sorption Device, MC = Micro Calorimeter

With the exception of the acid component of RG, the order of magnitude of the surface energy components derived from both methods are similar. Micro calorimeter appears to be more sensitive than the USD in differentiating between the Lifshitz-van der Waals (LW) component of surface energy of different aggregates. Figures 3.2 through 3.4 present a graphical comparison of the three surface energy components determined using the microcalorimeter and the USD.

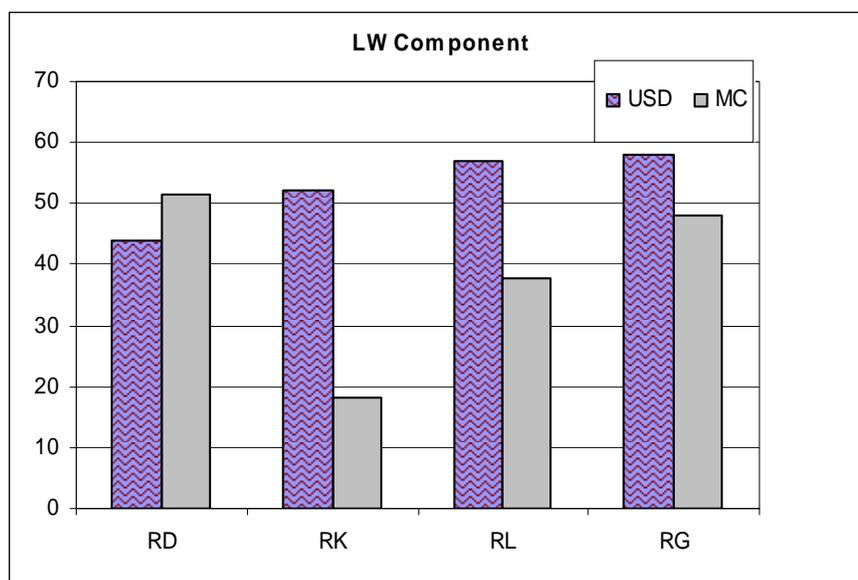


Figure 3.2 Comparison of the LW Component of Surface Energy.

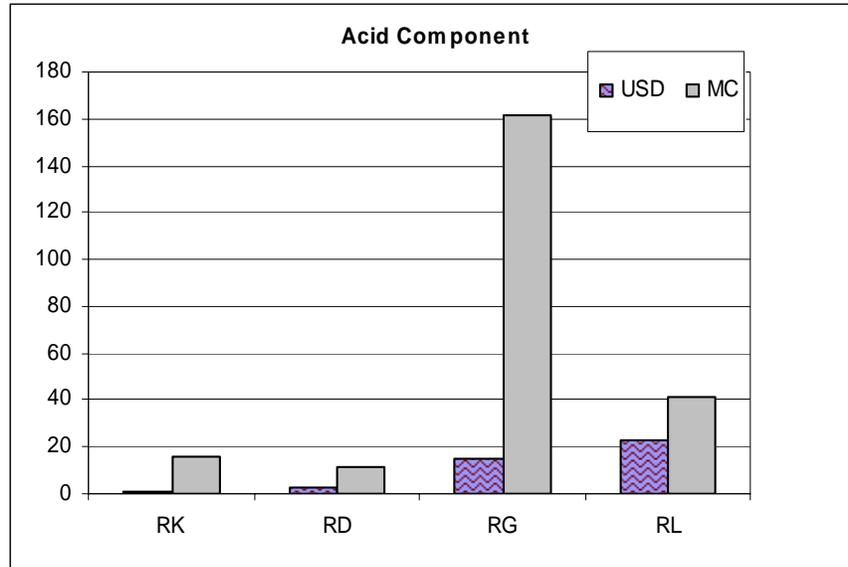


Figure 3.3 Comparison of the Acid Component of Surface Energy.

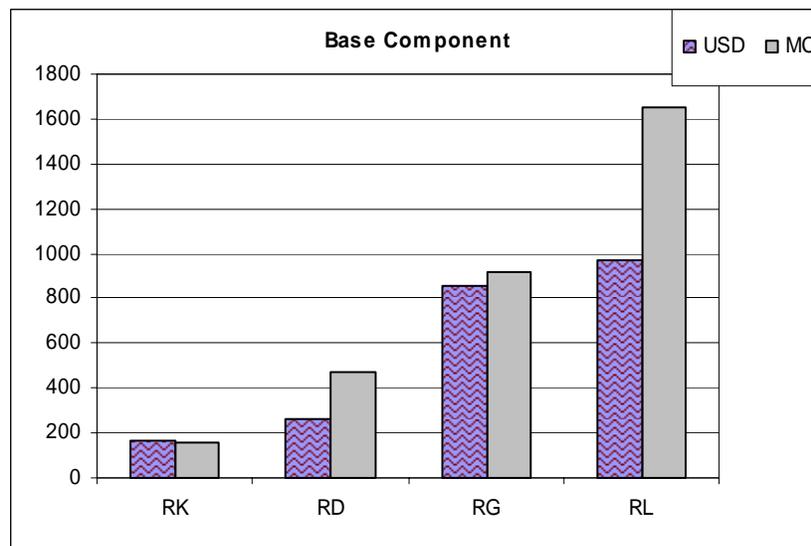


Figure 3.4 Comparison of the Base Component of Surface Energy.

The base component of surface energy derived from the USD and the micro calorimeter show similar trends. The important application of determining aggregate surface energy components is not to rank aggregates based on their surface energy components, but to calculate the work of adhesion and work of debonding for different bitumen-aggregate combinations, and predict the moisture sensitivity of different asphalt mixes. Therefore, it more reasonable to compare the work of adhesion and work of debonding obtained by combining surface energies of aggregates and bitumen from the USD and Wilhelmy plate, respectively, with the values obtained by combining surface energies of aggregates and bitumen from the micro calorimeter and Wilhelmy plate methods, respectively. Surface energies of nine different types of bitumen

measured in another study using the Wilhelmy plate method were used for this comparison resulting in a total of 36 combinations with the four aggregates. Figures 3.5 and 3.6 illustrate this comparison for the dry work of adhesion and wet work of debonding, respectively.

The dry work of adhesion calculated using results from the micro calorimeter compares well with the values calculated using results from the USD. The wet work of debonding calculated using results from the micro calorimeter correlates well with the values calculated using results from the USD, although there is a bias in the results.

In the preceding comparisons, results from the micro calorimeter are compared with results from the USD. If the USD is used as a reference for accurate and true surface energies of aggregates then the bias and scatter between results from the micro calorimeter can be largely attributed to the assumption made for the contribution of the entropy term. However, both of these are indirect methods to measure surface energy components of aggregates and there is no concrete evidence that results from the USD represents the “true values” for these components.

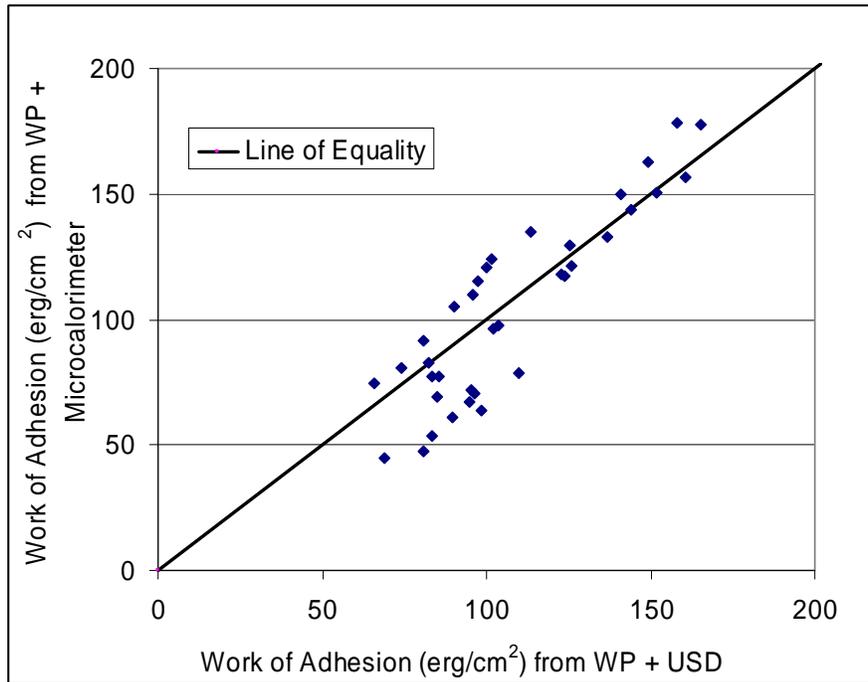


Figure 3.5 Comparison of Dry Adhesive Bond Strength between USD and Micro Calorimeter.

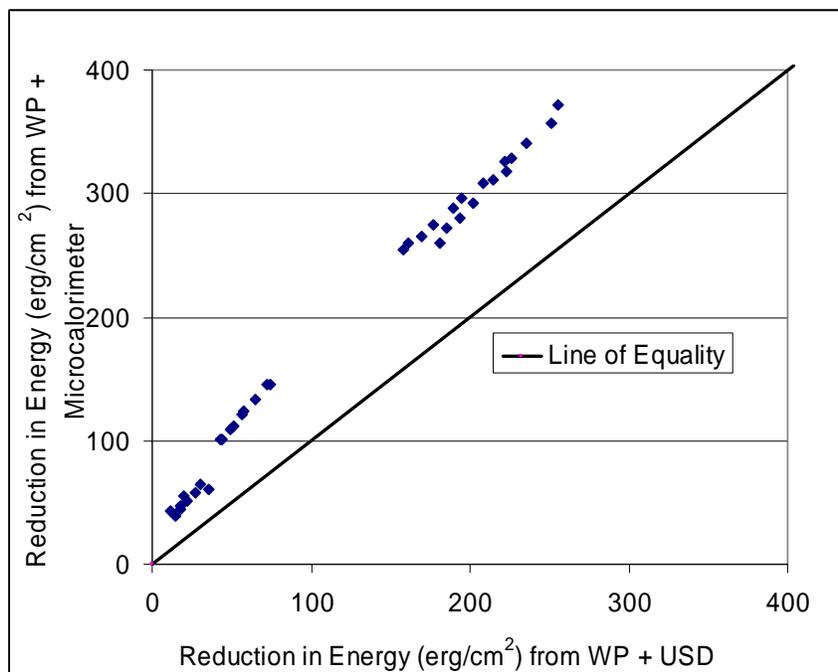


Figure 3.6 Comparison of Wet Adhesive Bond Strength between USD and Micro Calorimeter.

Hydrophilicity of Aggregates

The enthalpy of immersion of an aggregate in water can be used to quantify the hydrophilicity of different aggregates. In this context hydrophilicity of an aggregate is defined as the reduction in total energy of the system when water wets the surface of a clean dry aggregate. It can also be described as the thermodynamic drive for water to wet the surface of the aggregate or in a phenomenological sense it is the affinity of water molecules to adhere to the aggregate surface. The hydrophilicity of the four previously selected aggregates was measured as the heat of immersion of these aggregates with water. The test procedure was similar to the procedure used to measure heat of immersion of different aggregates with the probe liquids. Table 3.4 presents the values for heat of immersion of the four aggregates in water.

Table 3.4 Heats of Immersion in Water

Aggregate	Heat of Immersion	
	ergs/cm ²	ergs/gm
RD	348	515
RG	436	876
RK	373	7785
RL	977	4600

Results present in Table 3.4 show that the aggregates differ significantly in their affinity to water. The greater the hydrophilicity or the heat of immersion in water, the greater will be the thermodynamic drive for water to wet the surface of the aggregate. The hydrophilicity of an aggregate can also be theoretically computed if the surface free energy components of the aggregate and water are known. Mathematically this value is given by,

$$\gamma_{AW} - \gamma_A \quad (3.3)$$

There are two major differences between the hydrophilicity estimated from these two different methods. Firstly, although both terms measure the reduction in energy of the system when water wets the aggregate surface, hydrophilicity derived from equation 3.3 is the reduction in free energy of the system whereas the hydrophilicity measured using the microcalorimeter is the reduction in total energy of the system. In other words, the latter term includes the enthalpy and entropy effect. For this class of materials it is reasonable to assume that the contribution of entropy will be a fixed percentage of the enthalpy of immersion. Therefore, although hydrophilicity derived by either method may not be equal due to the contribution of entropy, these two terms must at least be linearly correlated.

The second difference is that hydrophilicity determined using equation 3.3 takes into account only the physical interaction between the aggregate and water due to their surface free energies. According to the literature, electrostatic interactions between the aggregate and water also exist during the process of adhesion between these materials. These interactions are also associated with the change in pH of the water that comes into contact with the aggregate surface. Although, the contribution of electrostatic interactions themselves is a very small percentage of the total work of adhesion between the aggregate and water based on their surface energy components (Hefer et al., 2005), change in pH of the water can alter its surface energy components, which in turn can effect the magnitude of physical adhesion between the aggregate and the water. It is proposed here that the hydrophilicity of aggregates measured using the microcalorimeter is due to the cumulative effect of all these interactions, which otherwise would be difficult to quantify individually and combine.

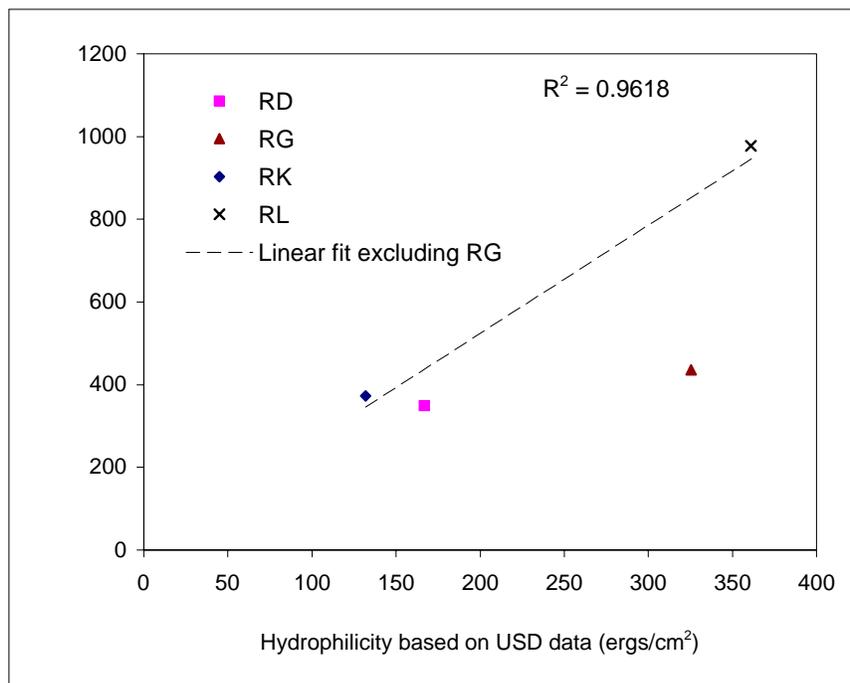


Figure 3.7 Hydrophilicity of aggregates from USD vs. Micro Calorimeter.

Figure 3.7 compares the hydrophilicity of aggregates based on equation 6.3 with the hydrophilicity of aggregates measured as the heat of immersion using the micro calorimeter. The correlation between hydrophilicity measured using both these methods for the three aggregates excluding RG, considering a straight line fit passing through the origin is significant. The bias of this straight line from 1:1 fit is due to the fact that the contribution of entropy is also included in the ordinate. This also explains the reason why the values of ordinate are generally higher compared to the values in the abscissa that includes only the free energy component of the total energy. The following paragraph explains the possible causes for deviation of RG from the general trend.

At first instance, the departure of RG from the general trend may be attributed to the fact that the acid component of surface energy of RG measured using the microcalorimeter was very high compared to the value measured using the USD. However, this deviation did not improve when the graph was plotted by hypothetically increasing the acid component of RG from the USD. The deviation is also not due to the entropy term since the relative contribution of entropy to the total energy of the system must be approximately the same for these materials. Eliminating these possible causes, the deviation of RG from the general trend can be explained based on the differences in electrostatic or other complex interactions associated with the change in pH of water after coming into contact with RG as compared to other aggregates. This provides a limited support to the proposition that the heat of immersion measured using the micro calorimeter is sensitive to the sum effect of different interactions that quantify the thermodynamic drive for water to wet the surface of the aggregate including the contribution

from surface energy of these materials. The following example further reinforces this proposition.

Consider moisture sensitivity of asphalt mixes with the two aggregates RG and RL. It is reasonable to compare the moisture sensitivity of these two aggregates based only on hydrophilicity since the base and LW component of surface energy of both these aggregates are approximately in the same range, and it was established earlier that these two are the main components that differentiate the adhesive bond strengths of different bitumen-aggregate combinations. Data from the USD indicates that RG has a very high affinity for water (325 ergs/cm^2) based on the surface energy terms alone. This is approximately the same as the affinity of RL to water (361 ergs/cm^2) compared to other aggregates (130 ergs/cm^2 for RK and 160 ergs/cm^2 for RD). Therefore, the moisture sensitivity of RL aggregate must be approximately the same as that of the RG aggregate if hydrophilicity based on the surface free energies from the USD is considered. This is contradictory to data from other studies (Western Research Institute, 2001) which show that RG is an aggregate with intermediate stripping tendency as compared to RL which has a very high tendency to strip. However, hydrophilicity of the two aggregates based on the heat of immersions measured by the microcalorimeter, corroborate well with these findings.

Total Energy of Adhesion between Aggregates and Bitumen

Another application of the microcalorimeter is to measure the total energy of adhesion between different bitumen and aggregates at the mixing and compaction temperature. It is proposed that this instrument and method is sensitive to identify the presence of any chemical reaction that may contribute to the adhesion between the bitumen and aggregate. Earlier studies that report the measurement of work of adhesion between the bitumen and aggregate (Ensley et al., 1984; Ensley, 1973; Ensley and Scholz, 1972) were associated with several drawbacks. For example, the post test equilibrium heat flow was generally much higher than the pre test equilibrium heat flow. This difference was attributed entirely to the reduction in free energy as multiple layers of bitumen built beyond the first monolayer on the aggregate surface during the adhesion process, whereas it is likely that a significant part of this difference is due to the differences in specific heats of the reaction and reference cell due to the mixing of the bitumen and the aggregate. Also, these studies did not attempt to use results from the microcalorimeter in conjunction with the heat of immersion with water and surface energy components of bitumen and aggregate. The following paragraphs present a description of the test method to measure the total energy of adhesion between the aggregates and bitumen and a comparison of these results with the work of adhesion determined using the surface free energy of the bitumen and aggregate.

Materials and Test

The four aggregates used previously, RL, RK, RG and RD and two bitumen types, AAB and ABD were used in this experiment. This resulted in a total of eight bitumen-aggregate combinations. The microcalorimeter used was the same as before but with a different set up for holding the samples to conduct the tests at 150°C with bitumen in liquid form. Figure 3.8 shows the set up used for the high temperature experiments. The test procedure was similar to the heat of immersion experiments described earlier. The reaction vial (bitumen + aggregate) and reference vial (blank cell + aggregate) were placed in their respective cells. The aggregates were used immediately after oven drying at 160°C for 16 hours. The system was allowed to come to

equilibrium at 150°C, which usually took about 4 hours. During the equilibration time, aggregates in the glass columns are separated from the reaction vial with the bitumen or the blank vial using a filter paper. After equilibrium is reached, the glass columns are lowered by about 5 mm, puncturing the filter paper and allowing the aggregates to drop into the vial. Aggregates in the reaction vial readily mixed with the bitumen in the liquid form. This resulted in a reduction of energy of the system that is associated with the release of heat and is measured by the microcalorimeter. The amount of heat given out is the total energy of adhesion between the bitumen and the aggregate.

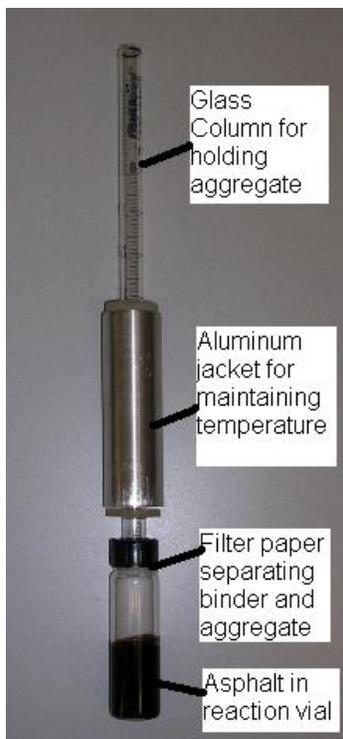


Figure 3.8 Reaction Vial to Conduct Immersion Experiments at High Temperatures with Micro Calorimeter.

Results and Discussion

At least two replicate measurements were made for the heat of immersion for each bitumen-aggregate combination. Figures 3.9 and 3.10 present a comparison of the heats of immersion measured for the four aggregates using bitumen AAB and ABD, respectively, with the theoretical work of adhesion between these aggregates and the bitumen calculated using their surface energy components from the Wilhelmy plate method and the USD.

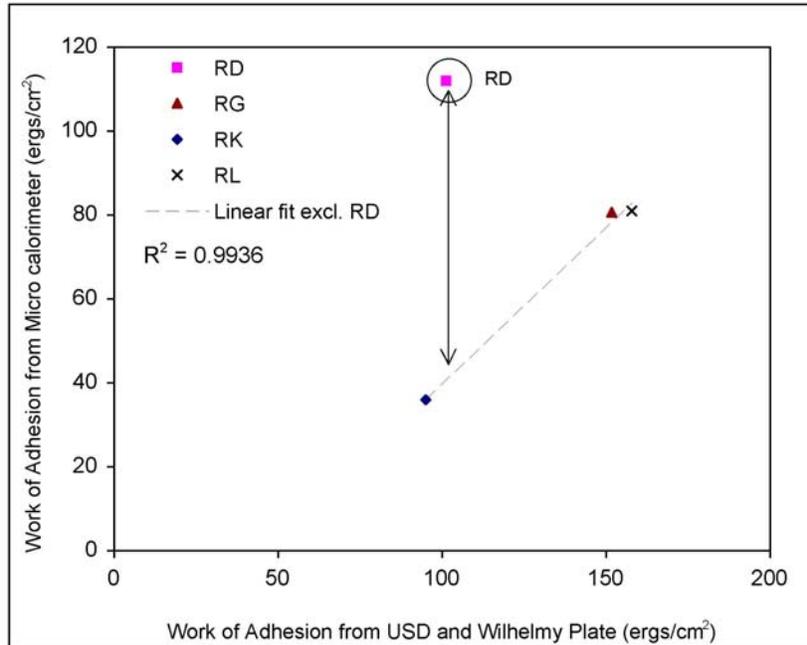


Figure 3.9 Measured Total Energy of Adhesion vs. Work of Physical Adhesion for AAB.

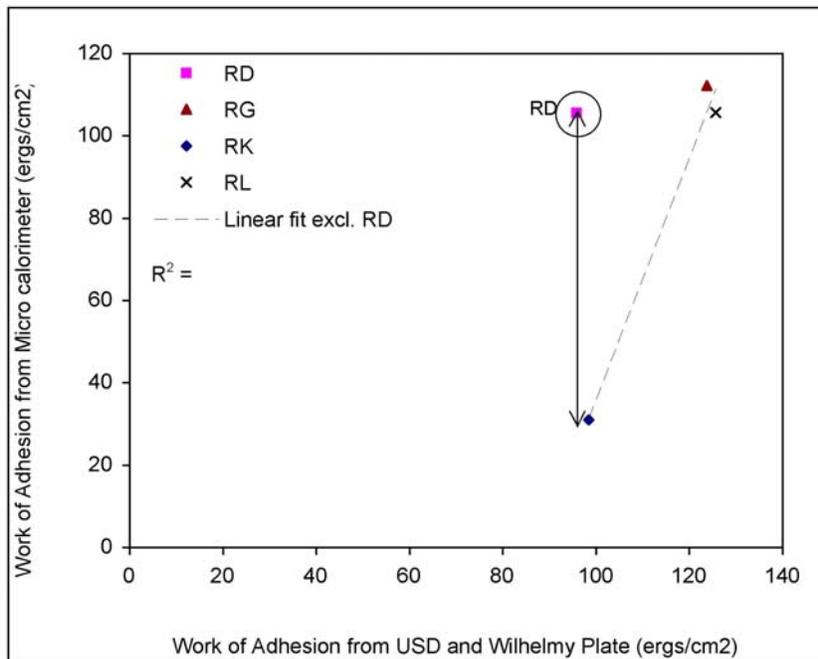


Figure 3.10 Measured Total Energy of Adhesion vs. Work of Physical Adhesion for ABD.

There are three possible reasons for the differences between the values measured using the micro calorimeter and the theoretical values calculated from the surface energies using the Wilhelmy plate method and the USD. Firstly, as mentioned before, the value computed from the surface energies is related to the free energy of adhesion, whereas the value measured using the microcalorimeter is due to the total energy of adhesion. However, under the assumption that the proportion of entropy does not change significantly for this class of materials when comparing one bitumen-aggregate combination with another, it is reasonable to expect that entropy will not affect the positive linear trend between the work of adhesion and total energy of adhesion. The second reason for difference between the two values is that the work of adhesion was computed based on surface energy values of the bitumen and aggregate at 25°C, whereas the total energy of adhesion was measured using the microcalorimeter at 150°C. Since the rate of decrease in surface energy of materials with temperature for these materials is usually small and similar, this difference will also not significantly affect the positive linear trend between the work of adhesion at 25°C and the total energy of adhesion at 150°C. The third and most important reason is that the work of adhesion based on the surface energy components of bitumen and aggregate quantifies only the physical adhesion between these two materials. In contrast, the total energy of adhesion measured by the micro calorimeter is due to all possible physical and chemical interactions that occur between the aggregate and the bitumen. This difference is not necessarily constant for all aggregates. As a result chemical interactions can cause deviations in any expected positive correlation between work of adhesion based on surface energy and total energy of adhesion based on heats of immersion.

Figures 3.9 and 3.10 show that the total energy of adhesion for RD is significantly greater than that expected for other aggregates based on the theoretical work of adhesion. Based on the above explanation, it is expected that there are significant chemical interactions associated with RD as compared to other aggregates. This is substantiated by the fact that while RD is predominantly a limestone, other aggregates are predominantly siliceous. Other studies suggest that the presence of calcium ions on the aggregate surface promote the formation of chemical bonds with functional groups such as carboxylic acids from the bitumen. Further, the heat dissipation curves for RD were predominantly exothermic but inevitably showed a small endotherm before finally achieving the post mixing equilibrium. This endotherm was more significant for RD than for other aggregates. Typically chemisorption is preceded by physical adsorption and in some cases there is a small energy barrier that needs to be overcome before chemisorption follows physical adsorption. It is suggested that low intensity chemical interactions continue even after wetting of the aggregate surface by bitumen and the endotherm prior to equilibrium is associated with the energy absorbed during the transition from physical adsorption to chemisorption. From these results, it is inferred that the microcalorimeter can be used to quantify the total energy of adhesion between aggregate and bitumen including effects of physical and chemical bonding. Also, this method used in conjunction with surface energies measured using the Wilhelmy plate method and the USD can be used to identify presence of any chemical bonding that contributes to adhesion.

Summary

The use of a microcalorimeter to measure thermodynamic properties related to moisture sensitivity of mixes was proposed. Results show that the micro calorimeter can be used to measure,

- surface energy components of aggregates,
- total energy of adhesion between the bitumen and aggregate including the cumulative effects of physical adsorption and chemisorption, and
- total energy of adhesion between aggregate and water including effects of physical absorption and effects due to electrostatic and other interactions.

Some other advantages of using a microcalorimeter are,

- lower capital cost of the equipment,
- excellent repeatability combined with adequate sensitivity,
- shorter test times as compared to adsorption methods,
- preconditioning of samples can be done independent of the equipment saving on sample preparation time, and
- less operator skill is required to operate the device and conduct tests.

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