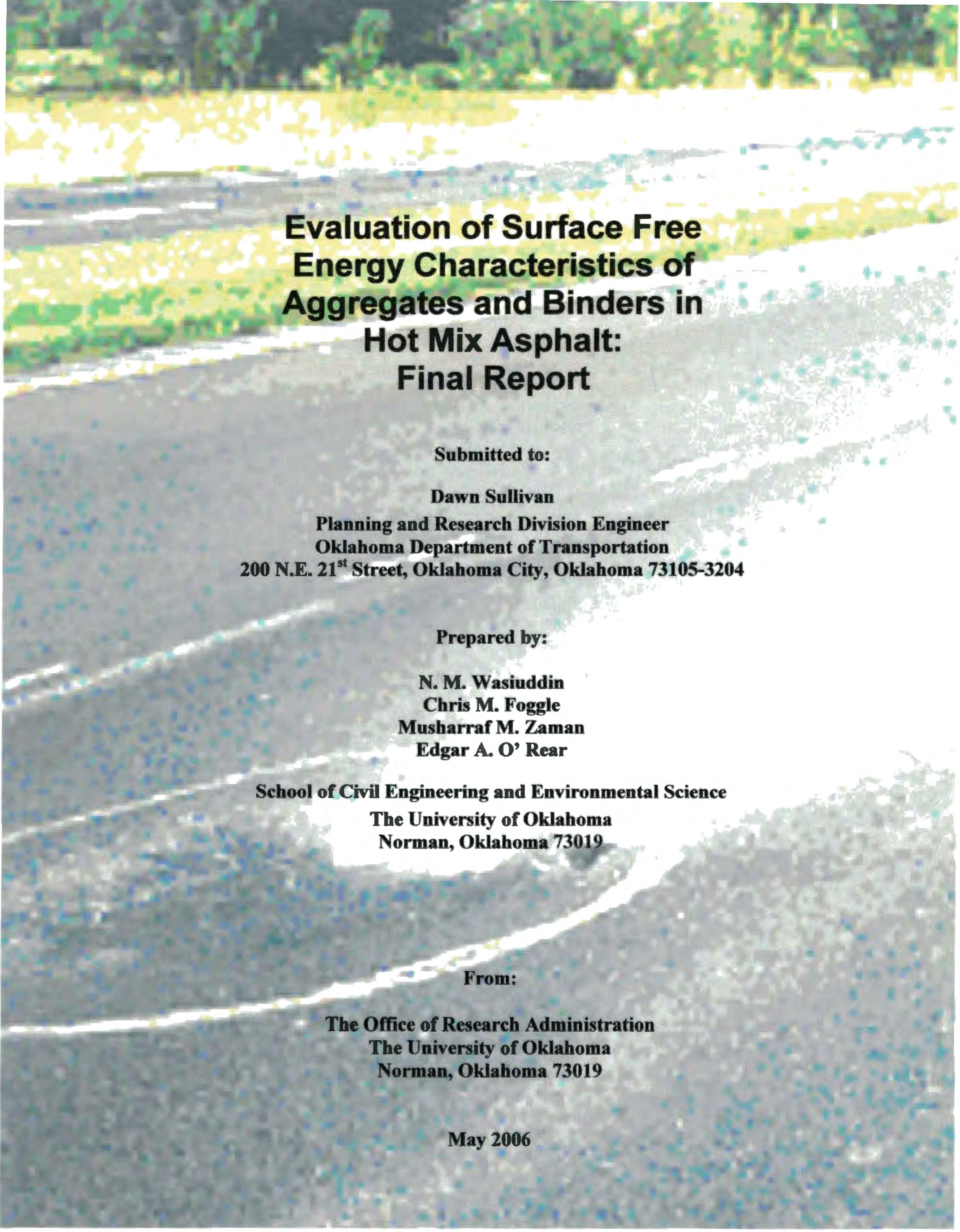

Evaluation of Surface Free Energy Characteristics of Aggregates and Binders in Hot Mix Asphalt: Final Report

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16. ABSTRACT

The objectives of this project is to demonstrate whether the Surface Free Energy (SFE) concept reported by Cheng et al. (2002) can be utilized to characterize the moisture-induced damage potential of selected asphalt binders and aggregates that are widely used in Oklahoma. Pursuit of this objective, the SFE components of two selected binders, PG 64-22 and PG 70-28 from Valero Refinery, Oklahoma, were evaluated with and without anti-strip additives in Phase II – Year 1. Two anti-strip additives, AD-here HP Plus and Redicote E-6 from Arr-Maz, Florida and Akzo Noble, Texas, respectively, were used at three percentages, 0.25%, 0.75% and 1.5%. The total SFE of PG 64-22 and PG 70-28 increases with an increase in additive content. 1.5% AD-Here HP Plus and 1.5% Redicote E-6 increased the total SFE of PG 64-22 by 67% and 208%. The corresponding increases in total SFE of PG 70-28 are 23.6% and 24.4%, respectively. The acid component of PG 64-22 and PG 70-28 are 2.9 dyne/cm^2 and 2.5 dyne/cm^2, respectively whereas, the corresponding base components is 0.4 dyne/cm^2 for both. Basic chemicals in the form of anti-strip additives (such as amines) can reduce the acid component and increase the basic components of asphalt binder. With the addition of 1.5% Redicote E-6 in PG 64-22, the acid component of asphalt binder decreases by 92% and the base component increases by 1141%. The SFE components of aggregates were evaluated by a Universal Sorption Device (USD) using water, methyl propyl ketone and n-hexane. The SFE of limestone and chat are 166.6 ergs/cm^2 and 132.2 ergs/cm^2, respectively. The higher surface energy of limestone provides better adhesion strength between limestone and asphalt binder. The basic component of SFE of limestone and chat are 390.8 ergs/cm^2 and 219 ergs/cm^2, respectively. It is evident that limestone is more basic than chat. It was observed that both the anti-strip additives have detrimental effect on limestone and chat in the presence of water. Comparatively, both the anti-strip additives have improved the free energy of adhesion in the presence of water between Georgia granite and asphalt binders (both PG 64-22 and PG 70-28). This is due to the fact that Goergia granite is a highly acidic aggregate. Therefore, liquid anti-strip additives can improve the adhesion between highly acidic aggregate such as granite and asphalt binders (based on their SFE characteristics). Finally, it can be concluded that SFE method is an excellent tool for measuring acid-base characteristics of aggregates and asphalt binders with and without anti-strip additives.

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Approximate Conversions to SI Units					*Approximate Conversions from SI Units*				
Symbol	**When you know**	**Multiply by**	**To Find**	**Symbol**	**Symbol**	**When you know**	**Multiply by**	**To Find**	**Symbol**
		LENGTH					**LENGTH**		
in	inches	25.40	millimeters	mm	mm	millimeters	0.0394	inches	in
ft	feet	0.3048	meters	m	m	meters	3.281	feet	ft
yd	yards	0.9144	meters	m	m	meters	1.094	yards	yds
mi	miles	1.069	kilometers	km	km	kilometers	0.6214	miles	mi
		AREA					**AREA**		
in^2	square inches	645.2	square millimeters	mm^2	mm^2	square millimeters	0.00155	square inches	in^2
ft^2	square feet	0.0929	square meters	m^2	m^2	square meters	10.764	square feet	ft^2
yd^2	square yards	0.8361	square meters	m^2	m^2	square meters	1.196	square yards	yd^2
ac	acres	0.4047	hectacres	ha	ha	hectasres	2.471	acres	ac
mi^2	square miles	2.590	square kilometers	km^2	km^2	square kilometers	0.3861	square miles	mi^2
		VOLUME					**VOLUME**		
fl oz	fluid ounces	29.57	milliliters	mL	mL	milliters	0.0338	fluid ounces	fl oz
gal	gallon	3.785	liters	L	L	liters	0.2642	gallon	gal
ft^3	cubic feet	0.0283	cubic meters	m^3	m^3	cubic meters	35.315	cubic feet	ft^3
yd^3	cubic yards	0.7645	cubic meters	m^3	m^3	cuic meters	1.308	cubic yards	yd^3
		MASS					**MASS**		
oz	ounces	28.35	grams	g	g	grams	0.0353	ounces	oz
lb	pounds	0.4536	kilograms	kg	kg	kilograms	2.205	pounds	lb
T	short tons (2000 lb)	0.907	megagrams	Mg	Mg	megagrams	1.1023	short tons (2000 lb)	T
		TEMPERATURE (exact)					**TEMPERATURE (exact)**		
°F	degrees Fahrenheit	(°F-32)/1.8	degrees Celsius	°C	°C	degrees Fahrenheit	9/5(°C)+32	degrees Celsius	°F
		FORCE and PRESURE or STRESS					**FORCE and PRESURE or STRESS**		
lbf	poundforce	4.448	Newtons	N	N	Newtons	0.2248	poundforce	lbf
lbf/in^2	poundforce per square inch	6.895	kilopascals	kPa	kPa	kilopascals	0.1450	poundforce per square inch	lbf/in^2

TABLE OF CONTENTS

TABLE OF CONTENTS 01
LIST OF TABLES 03
LIST OF FIGURES 04
ACKNOWLEDGEMENTS 05
EXECUTIVE SUMMARY 06

1 INTRODUCTION

1.1 Background 11
1.2 Objectives 12
1.3 Tasks Performed in Phase II – Year 2 13

2 SURFACE FREE ENERGY (SFE) OF ASPHALT BINDER

2.1 SFE of Asphalt Binder 16
2.2 Dynamic Wilhelmy Plate Method (DWPM) 17
2.3 Calculation of SFE from Dynamic Contact Angle 18
2.4 Calculation of Free Energy of Adhesion from SFE 19
2.5 Experimental Setup and Procedure 20
2.6 Test Matrix 22
2.7 Advancing Contact Angle of Asphalt Binders 22
2.8 Effect of Anti-Strip Additives on SFE of Asphalt Binders 24
2.9 Effect of Anti-Strip Additives on Acid-Base Characteristics of Asphalt Binders 26
2.10 Interaction of Acidic Binder with Acidic Aggregate 29
2.11 Comparison between PG 64-22 and PG 70-28 30
2.12 Proposed Chemical Model of Asphalt Binder 30
2.13 Conclusions 31

3 SFE CHARACTERISTICS OF AGGREGATES

3.1 Introduction 39
3.2 Selection of Aggregates 39
3.3 Aggregate Properties Test 40
3.4 Principles of Operation of the USD 40
3.5 Theory and Methodology 42
3.6 Sorption Test 45
3.7 Specific Surface Area of Aggregates 45
3.8 Spreading Pressure 46
3.9 SFE Components of Aggregates 46

4 ASPHALT-AGGREGATE INTERACTIONS

4.1 Introduction 51
4.2 Free Energy of Adhesion between Asphalt Binder and Aggregate 51
4.3 Free Energy of Adhesion between Asphalt Binder and Aggregate in the Presence of Water 52
4.4 Moisture Susceptibility Test (AASHTO T-283) 53

5 SFE METHOD AS A TOOL FOR MEASURING MOISTURE SUSCEPTIBILITY AND CONCLUDING REMARKS

5.1 Shortcomings of the Currently Used Moisture Susceptibility Test (AASHTO T-283) 57
5.2 SFE Method as a Tool for Measuring Moisture-Induced Damage Susceptibility 58
5.3 SFE Approach – An Alternate Method? 60
5.4 Recommendations for Future Research 61

REFERENCES 62
APPENDIX A 64

LIST OF TABLES

Table 2.1	Test Matrix	33
Table 2.2	Average Contact Angle with Standard Deviation	33
Table 2.3	SFE Components of Asphalt Binders with and without Additives	33
Table 3.1	Engineering Properties of Limestone and Chat	48
Table 3.2	Surface Areas and Spreading Pressures of Aggregates	48
Table 3.3	SFE Components of Limestone and Chat	48
Table 4.1	Free Energy of Adhesion	55
Table 4.2	Free Energy of Adhesion in the Presence of Water	55
Table 4.3	Tensile Strength Ratio of Different HMA Mixes	56

LIST OF FIGURES

Figure 1.1 Three Stages of Stripping: White Stains, Flushing and Pothole (I-40, Oklahoma) 14
Figure 1.2 Potholing in the Inside Wheel Track of Slow Lane (Will Rogers Parkway, Oklahoma) 14
Figure 1.3 (a) Loss of Adhesion and 15
(b) Loss of Cohesion 15
Figure 1.4 (a) Free Energy of Cohesion and 15
(b) Free Energy of Adhesion 15

Figure 2.1 Dynamic Wilhelmy Plate Method for
(a) Advancing contact angle and 34
(b) Receding contact angle 34
Figure 2.2 Samples in a Sample Holder 34
Figure 2.3 Wilhelmy Plate test results from DCA Analyzer for PG 64-22 with water 35
Figure 2.4 Effect of AD-Here HP Plus and Redicote E-6 on total SFE of PG 64-22 35
Figure 2.5 Effect of AD-Here HP Plus and Redicote E-6 on total SFE of PG 70-28 36
Figure 2.6 Effects of AD-Here HP Plus and Redicote E-6 on Acid Component of PG 64-22 36
Figure 2.7 Effects of AD-Here HP Plus and Redicote E-6 on Acid Component of PG 70-28 37
Figure 2.8 Effects of AD-Here HP Plus and Redicote E-6 on Base Component of PG 64-22 37
Figure 2.9 Effects of AD-Here HP Plus and Redicote E-6 on Base Component of PG 70-28 38

Figure 3.1 Schematic Diagram of the Universal Sorption Device 49
Figure 3.2 Different Components of a Universal Sorption Device 50

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EXECUTIVE SUMMARY

Currently, the performance of HMA due to moisture exposure is evaluated by the retained strength test (AASHTO T283 and OHD L36). This test, however, does not directly address any mechanisms that govern stripping, and it only serves as an indicator of moisture-induced damage. Recently, Texas Transportation Institute (TTI) has shown that the Surface Free Energy (SFE) of aggregates and binders are related to stripping mechanisms and can be used to predict the moisture-induced damage potential of HMA (Cheng et al., 2002).

The objective of this project is to demonstrate whether the SFE concept reported by Cheng et al. (2002) can be utilized to characterize the moisture-induced damage potential of selected asphalt binders and aggregates that are widely used in Oklahoma. The SFE components of two selected asphalt binders, namely PG 64-22 and PG 70-28 from Ardmore, Oklahoma, were determined separately from measurements of advancing contact angles by Dynamic Wilhelmy Plate Method. PG 70-28 used in this study is modified with the polymer Elvaloy® RET. Two amine-based liquid anti-strip additives, namely AD-Here HP Plus from Arr-Maz, Florida and Redicote E-6 from Akzo-Nobel, Chicago, were used. Three selected amounts (0.25%, 0.75% and 1.50%) of these additives were added to both the binders.

Many researchers have reported that liquid anti-strip additives reduce the SFE of asphalt binders and therefore, increase the wetability of binders to the aggregate (Aksoy et al., 2004; Roberts et al., 1996; Tunnicliff and Root, 1984). In this study, it was found that the surfactants (liquid anti-strip additives) do not decrease the SFE of an asphalt binder. Rather, it increases the SFE.

Asphalt is a continuous phase of non-polar materials (Robertson, 1991). Non-polar solvents have received far less attention than the polar solvents (e.g., water) with respect to the surfactant-action phenomenon. Surfactants of all kinds decrease surface tension of water (polar solvent) as the hydrocarbon tail groups are directed outward. In case of non-polar solvent, asphalt binder in this case, the polar head groups are directed outward. This actually results in an increase in surface tension (Myers, 1992; Rosen, 1978) in asphalt binder.

A general trend observed in this study is that the total SFE increases with an increase in percent of additive, Redicote E-6 performing better than AD-Here HP Plus. Both the additives are more effective in PG 64-22 than PG 70-28 with respect to increase in the total SFE. 1.5% AD-Here HP Plus and 1.5% Redicote E-6 increased the total SFE of PG 64-22 by 67% and 208%.

Acid-Base characteristics of asphalt binders, with and without anti-strip additives, were evaluated in this study, focusing on the moisture-induced damage potential of acidic aggregates using SFE method. Asphalt binders are acidic in nature. The acid component of the SFE of PG 64-22 and PG 70-28 are 2.9 dyne/cm^2 and 2.5 dyne/cm^2, respectively, whereas, the corresponding base components are 0.4 dyne/cm^2 for both. Basic chemical compounds such as amines, in the form of anti-strip additives, are found to reduce the acid component and increase the base component of asphalt binders, thereby improving the adhesion between acidic asphalt binder and highly acidic aggregate. With the addition of 0.75% AD-Here HP Plus and 0.75% Redicote E-6 in PG 64-22, the acid component is reduced as much as 67% and 65%, respectively. The corresponding increases in base components are 86% and 105%. Again, with the addition of 1.5% Redicote E-6 in PG 64-22, the acid component reduces by 92% and base component increases by 1141%. A similar trend is observed with respect to the acid-base characteristics of PG 70-28.

The SFE components of an aggregate can be measured using a Universal Sorption Device (USD), as performed by Cheng et al. (2002). A limestone aggregate was selected as basic aggregate to be included in this study. The source of the selected limestone is APAC-Oklahoma, Vinita. One hydrophilic aggregate (exhibits high silica content), namely chat was also selected. The chat used in this study was collected from Kenoyer North Chat Pile, Ottawa County, Oklahoma.

The SFE of limestone and chat are 166.6 ergs/cm^2 and 132.2 ergs/cm^2, respectively. The higher surface energy of limestone provides better adhesion strength between the limestone and the asphalt binder. The basic component of SFE of limestone and chat are 390.8 ergs/cm^2 and 219 ergs/cm^2, respectively. It is evident that limestone is more basic than chat. Comparatively, the acid component of the SFE of a highly acidic aggregate, namely the Georgia Granite as found by Cheng et al. (2002), is very high (24.1 dyne/cm^2), if compared with limestone (6.48 dyne/cm^2) and chat (2.82 dyne/cm^2) found in this study.

The free energy of adhesion (adhesion strength) between an aggregate and an asphalt binder was determined. The free energy of adhesion between chat and PG 64-22 without additive is 100.9 ergs/cm^2. The free energy of adhesion decreases with an increase in percent of AD-Here HP Plus. Likewise, the addition of Redicote E-6 decreases the adhesion strength between chat and PG 64-22. The adhesion strength between chat and PG 70-28 is 100.2 ergs/cm^2 which also decreases with the addition of each of the additives.

The limestone exhibited better adhesion strength with both PG 64-22 and PG 70-28 than the corresponding chat-asphalt HMA. Both the additives, AD-Here HP Plus and Redicote E-6, decreased the adhesion strength between limestone and asphalt binder.

This is a significant finding of this study that the adhesion strength between the asphalt binder and the limestone or the chat decreases with the addition of any of the anti-strip additives at any dosages. Therefore, it is clearly evident that anti-strip additives could be detrimental to the basic aggregates or less acidic aggregates. To this end, free energy of adhesion was calculated for the highly acidic aggregate, namely the Georgia granite. The SFE components of the Georgia granite were obtained from Cheng et al. (2002). It was observed that free energy of adhesion increases with the addition of anti-strip additives. The free energy of adhesion of the Georgia granite and PG 64-22 without any anti-strip additive is 101.1 ergs/cm^2. With the addition of 1.5% AD-Here HP Plus and 1.5% Redicote E-6 the free energy of adhesion increases to 114.1 ergs/cm^2 and 150.8 ergs/cm^2, respectively. Therefore, liquid anti-strip additives are beneficial for only highly acidic aggregates.

It is observed that in the presence of water, the free energy of adhesion between the limestone and asphalt binders (both PG 64-22 and PG 70-28) and between the chat and asphalt binders (both PG 64-22 and PG 70-28) decrease with an increase in the amount of anti-strip additives. This again concludes that both the anti-strip additives have detrimental effect on limestone and chat in this case in the presence of water. Comparatively, both the anti-strip additives have improved the free energy of adhesion in the presence of water between the Georgia granite and asphalt binders (both PG 64-22 and PG 70-28). This is due to the fact that the Georgia granite is a highly acidic aggregate.

Moisture susceptibility tests were performed on a mix design with 80% chat and 20% limestone. Samples having air voids between 7.5% and 8.5% were prepared. Three sets of samples were tested. One of the three sets had 80% chat, 20% limestone and PG 64-22 with no additive in it. The other two sets had PG 64-22 with 0.75% AD-Here HP Plus and 0.75% Redicote E-6.

It was observed that the tensile stress ratio increased with the addition of each of the anti-strip additives, AD-Here HP Plus performing better than Redicote E-6. The tensile strength ratio increased 3% with the addition of 0.75% Redicote E-6 and 7% with the addition of 0.75% AD-Here HP Plus.

It was found that the tensile strength of HMA without any anti-strip additive is 862.0 kPa. The addition of 0.75% AD-Here HP Plus and 0.75% Redicote E-6 reduces the tensile strength to 759.5 kPa and 746.9 kPa, respectively. This is in agreement with the findings from the SFE characteristics that addition of anti-strip additives are detrimental to the limestone and the chat. Therefore, liquid anti-strip additives can only improve the adhesion between highly acidic aggregate, namely granite and asphalt binders.

The results obtained in this study are very promising. It's a valid method for predicting moisture-induced damage potential of asphalt binders, aggregates and anti-strip additives. Based on this study, the authors recommend the SFE method be considered as a complemental tool for predicting moisture-induced damage potential.

1. INTRODUCTION

1.1 Background

Moisture-induced damage of asphalt pavement can lead to serious distress, reduced performance and increased maintenance of asphalt pavements. Localized bleeding, particle degradation, disintegration, potholes, shoving and structural failure of a pavement due to permanent deformation and cracking are examples of moisture-induced damage (see Figures 1.1 and 1.2[1]). One of the leading causes of such damages is the *stripping* of asphalt binder from aggregate surface and in some cases softening of the asphalt matrix (Kennedy et al., 1984).

Despite significant advances in the past two decades on understanding the behavior of Hot Mix Asphalt (HMA) and on improved design of asphalt pavements, moisture-induced damage is still one of the most common and complex problems in flexible pavements. Currently, the performance of HMA due to moisture exposure is evaluated by the retained strength test (AASHTO T283 and OHD L36). This test, however, does not directly address any mechanisms that govern stripping, and it only serves as an indicator of moisture-induced damage. A retained strength task force was formed in 1999 to address excessive retained strength failures in laboratory and field (Hobson, 2002). One of the recommendations of that task force was to investigate SFE characteristics of aggregates and binders, and their relationships to retained strength of resulting HMA specimens. Recently, Texas Transportation Institute (TTI) has shown that SFE of aggregates and binders are related to

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[1] Figures are presented at the end of each chapter

stripping mechanisms and can be used to predict the moisture-induced damage potential of HMA (Cheng et al., 2002).

Hicks (1991) attributed moisture-induced damage in asphalt pavements to the following mechanisms, among others: (i) loss of adhesion depicted in Figure 1.3(a), and (ii) loss of cohesion depicted in Figure 1.3(b). Loss of adhesion, also called *stripping*, is caused by breaking of the adhesive bond between the aggregate surface and the asphalt binder primarily due to the action of water and water vapor (Kennedy et al., 1983; Jo et al., 1997). When the bond is broken, the asphalt pavement weakens and develops various types of failure such as cracking and raveling (Fromm, 1974). Softening is a general loss of stability of a mixture due to loss of cohesion caused by the action of moisture within the asphalt binder. These two mechanisms are often interrelated, and thus moisture-induced damage in asphalt pavements may be a combined result of cohesion and adhesion losses (Hicks, 1991).

Elphingstone (1997) defined SFE of a solid (or liquid) as the work required to increase a unit area of surface of that solid under vacuum. Consequently, the *free energy of cohesion* (Figure 1.4(a)) is the work done by a unit force acting along the surface of an asphalt binder at right angle to any line of unit length against a cohesive force to create two interfaces from one (i.e., asphalt binder in this case) under vacuum. Similarly, the *free energy of adhesion* (Figure 1.4(b)) is the free energy required to create two interfaces from one interface consisting of two different phases in contact (aggregate and asphalt binder in this case).

1.2 Objectives

The objective of this project is to demonstrate whether the SFE concept reported by Cheng et al. (2002) can be utilized to characterize the moisture-induced damage potential of selected asphalt binders and aggregates that are widely used in Oklahoma. Pursuit of this objective requires measurements of surface free energies of selected binders (with and without anti-strip additives) and selected aggregates. In Phase II – Year 1, the SFE components of two selected binders, PG 64-22 and PG 70-28 from Valero Refinery, Oklahoma, were evaluated with and without anti-strip additives. Two anti-strip additives, AD-here HP Plus and Redicote C-450 from Arr-Maz, Florida and Akzo Noble, Texas, respectively, were used. Findings of Phase II – Year 1 are reported by Wasiuddin et al. (2003). The major objective of Phase II – Year 2 is to measure the SFE energy components of two selected aggregates that are widely used by the Oklahoma Department of Transportation (ODOT) to calculate the adhesion strength (in the presence and absence of water) between aggregate and asphalt binder with and without anti-strip additives.

1.3 Tasks Performed in Phase II – Year 2

The major task of Phase II – Year 2 was to measure the SFE characteristics of two selected aggregates. Pursuit of this task one acidic (hydrophilic) and one basic (hydrophobic) aggregate that are commonly used in Oklahoma were selected. In Task 2, engineering properties of the selected aggregates were evaluated according to the standards recommended by the ODOT. SFE components of the selected aggregates were determined in Task 3 using the Universal Sorption Device (USD). The adhesion strength (in the presence and absence of water) between aggregate and asphalt binder with and without anti-strip additives were also calculated in this task. Some of the results obtained in Task 3 were validated with the moisture susceptibility test (AASHTO T-283) results performed as Task 4. Finally, in Task 5 a final report was prepared which includes problem statement, theory and methodology, results, discussions on results, conclusions and recommendations.

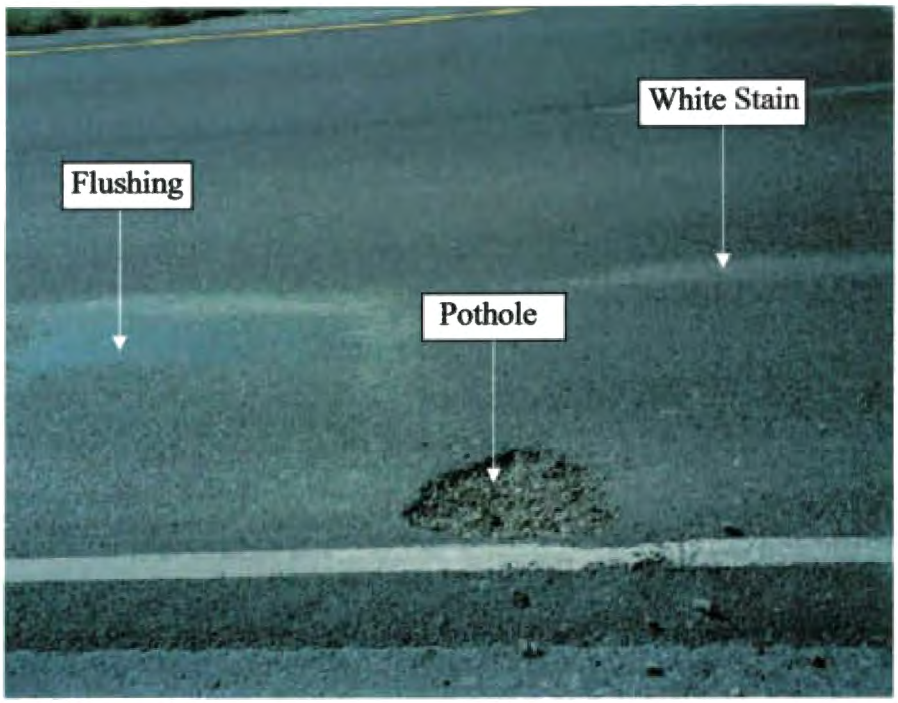


Figure 1.1 Three Stages of Stripping: White Stains, Flushing and Pothole (I-40, Oklahoma)

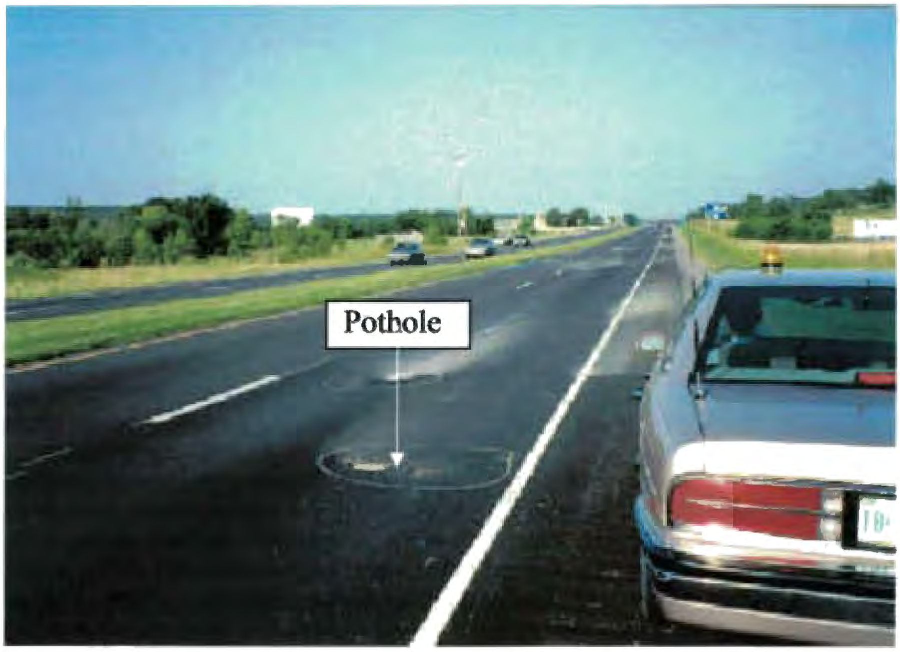


Figure 1.2 Potholing in the Inside Wheel Track of Slow Lane (Will Rogers Parkway, Oklahoma)

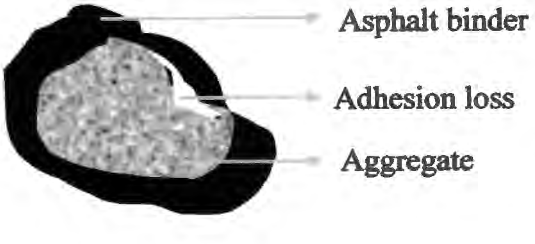


Figure 1.3(a): Loss of Adhesion

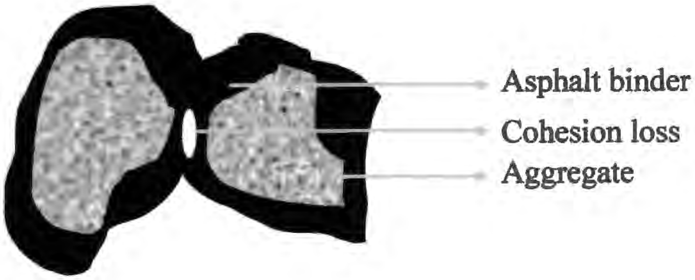


Figure 1.3(b): Loss of Cohesion

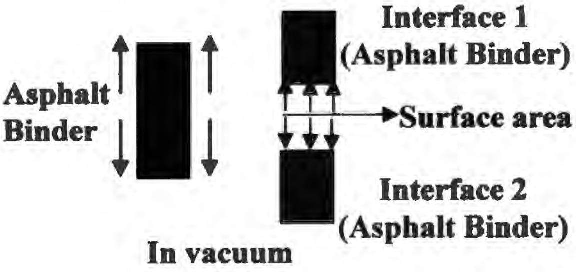


Figure 1.4(a) Free Energy of Cohesion

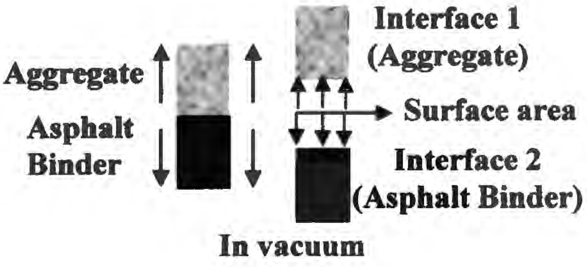


Figure 1.4(b) Free Energy of Adhesion

2. SURFACE FREE ENERGY (SFE) OF ASPHALT BINDER

2.1 SFE of Asphalt Binder

The SFE of a solid (or liquid) is defined as the work required to increase a unit area of surface of that solid under vacuum. Consequently, the *free energy of cohesion* (Figure 1.4 (a)) is the work done by a unit force acting along the surface of an asphalt binder at right angle to any line of unit length against a cohesive force to create two interfaces from one (i.e., asphalt binder) under vacuum. Similarly, the *free energy of adhesion* (Figure 1.4 (b)) is the free energy required to create two interfaces from one interface consisting of two different phases in contact (aggregate and asphalt binder in this case).

The SFE of an asphalt binder mainly comprises of an apolar component (also called Lifshitz-van der Waals component) and an acid-base component, as shown in the following equation. According to Good's postulation (1992), the acid-base term can be decomposed to a Lewis acidic surface parameter and a Lewis basic surface parameter as follows:

$$\Gamma = \Gamma^{LW} + \Gamma^{AB} \tag{2.1}$$

where,

Γ = SFE of the asphalt binder,

Γ^{LW} = Lifshitz-van der Waals component of the SFE, and

Γ^{AB} = Acid-Base component of the SFE given by

$$\Gamma^{AB} = 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{2.2}$$

where,

Γ^{+} = Lewis acid component of surface interaction,

Γ^{-} = Lewis base component of surface interaction.

Dynamic contact angles for different liquids can be used, as employed in this study, to evaluate these SFE components. The Dynamic Wilhelmy Plate method was used to measure contact angles.

2.2 Dynamic Wilhelmy Plate Method (DWPM)

The measurement of dynamic contact angle by DWPM is based on kinetic force equilibrium when a thin plate is immersed or withdrawn from a liquid solvent at a very slow and constant speed. The dynamic contact angle (see Figure 2.1) between an asphalt binder and a liquid solvent measured during the immersing process is called "*Advancing Contact Angle*" (ACA), while the dynamic contact angle during the withdrawal process is called the "*Receding Contact Angle*" (RCA). As noted by Cheng et al. (2002), the ACA, which is a wetting process, is associated with the asphalt binder healing mechanism. In this study, only ACA was considered for analyses. It is difficult to measure RCA accurately as also reported by some other researchers (see e.g., Elphingstone, 1997). A microbalance measuring the change in force from tare, ΔF, during immersion and withdrawal process is utilized. These forces in combination with a buoyant force correction are used to determine the dynamic contact angle applying the kinetic equilibrium equation, as shown below.

$$\cos\theta = (\Delta F + V_{im}(\rho_L - \rho_{air})g)/(P_t \Gamma_L) \qquad (2.3)$$

where,

θ = Contact angle (degrees),

V_{im} = Volume immersed (cm^3),

ρ_L = Density of liquid solvent (gm/cm^3),

ρ_{air} = Density of air (gm/cm^3),

P_t = Perimeter of the sample (cm),

ΔF = Change in Force (dyne),

Γ_L = SFE of liquid (ergs/cm^2) or surface tension (dyne/cm).

2.3 Calculation of SFE From Dynamic Contact Angle

Young's equation, which is essentially based on an energy balance of a drop of liquid (liquid solvent in this case) spreading on a flat solid (asphalt binder in this case) in the horizontal direction, can be used to evaluate the SFE characteristics associated with cohesion. Young's equation can be expressed as follows:

$$\Gamma_{SV} = \Gamma_{SL} + \Gamma_{LV} \cos\theta_{SL} \tag{2.4}$$

where,

θ_{SL} = Contact angle between the solid and liquid measured through the liquid,

Γ_{SV} = SFE of solid in vacuum,

Γ_{SL} = SFE of solid in liquid,

Γ_{LV} = SFE of liquid in vacuum.

Dupre's equation can be used to evaluate the free energy of adhesion, which represents the energy required to create two interfaces from two different phases in contact with a third medium (Good, 1992). Dupre's equation can be written as follows:

$$\Delta G_{12}^{a} = \Gamma_1 + \Gamma_2 - \Gamma_{12} \tag{2.5}$$

where,

$\Delta G^{a}{}_{12}$ = Free energy of adhesion,

Γ_1 = SFE of phase 1 (asphalt binder in this case),

Γ_2 = SFE of phase 2 (liquid solvent in this case),

Γ_{12} = Interfacial SFE of phase 1 and phase 2.

Assuming that equilibrium film pressure is negligible for an asphalt binder, Young's equation and Dupre's equation can be combined to obtain the so called Young-Dupre equation (Good, 1992). The Young-Dupre equation can be expressed as follows:

$$\Gamma_L(1+\cos\theta) = 2\times\sqrt{\Gamma_S^{LW}\Gamma_L^{LW}} + 2\times\sqrt{\Gamma_S^{-}\Gamma_L^{+}} + 2\times\sqrt{\Gamma_S^{+}\Gamma_L^{-}} \tag{2.6}$$

where,

Γ_L^{LW}, Γ_L^{+}, and Γ_L^{-} = SFE components of liquid solvent,

Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-} = SFE components of asphalt binder,

θ = Contact angle.

In the above equation, the SFE components of an asphalt binder are given by the three unknowns (Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-}). To obtain these unknowns, dynamic contact angles must be measured in at least three different liquid solvents. The SFE characteristics of these liquid solvents must be known a priori. Water, glycerin and formamide were used here as liquid solvents because of their relatively large SFE, immiscibility with asphalt binder, and differing SFE components (Cheng et al., 2002).

2.4 Calculation of Free Energy of Adhesion From SFE

The free energy of adhesion (ΔG^A), as defined previously, has two components, Lifshitz- van der Waals or non-polar part of adhesion and acid-base or polar part of adhesion. The following equations are used to determine the non-polar and polar adhesion between an asphalt binder and an aggregate.

$$\Delta G^A = \Delta G^{aLW} + \Delta G^{aAB} = 2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} + 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} + 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{2.7}$$

where,

ΔG^{A} = Free energy of adhesion,

ΔG^{aLW} = Non-Polar or Lifshitz-van der Waals part of adhesion,

ΔG^{aAB} = Acid-base or polar part of adhesion,

Γ_L^{LW}, Γ_L^{+}, and Γ_L^{-} = SFE components of asphalt binder,

Γ_S^{LW}, Γ_S^{+}, and Γ_S^{-} = SFE components of aggregate.

2.5 Experimental Setup and Procedure

Cheng et al. (2002) evaluated the SFE of asphalt binders using DWPM and developed a testing protocol on the basis of their experience. In this study the DWPM was used with some modifications and changes in the protocol described by Cheng et al. (2002). A Dynamic Contact Angle (DCA) analyzer, manufactured by Cahn Instruments, Inc., was used for measuring both advancing and receding contact angles using a Window-based application software, WinDCA. Cover glasses (plates) from Fisher Scientific (25 mm x 50 mm) were partially coated with an asphalt binder, with or without anti-strip additives. These coated plates are refereed to as "samples" in this paper. The following experimental setup and procedure were used for sample preparation and contact angle measurements.

For cleaning, cover glass plate was placed into an oxygen flame, called flaming, horizontally along its length in a moving condition for at least three times. The flaming of a single cover glass plate did not take more than a few seconds.

For sample preparation, approximately 100 gm of the asphalt binder was taken in a tin can, and the tin can was heated in a gravity oven for two hours at 145°C. Each cover glass plate was dipped into the hot asphalt binder vertically about 2 cm from the dipping end for approximately 5 seconds. After dipping, the sample was held above the asphalt binder for approximately 5 seconds to allow dropping off of excess asphalt binder into the tin can. The sample was then kept in a sample holder with the coated end up for 2 minutes. Sample preparation was done inside a gravity oven with the help of forceps and a sample holder. The aforementioned method provided a uniform coating of at least 1 cm in length at the top end of the cover glass plate. The prepared samples were kept inside a desiccator overnight before contact angle measurement (see Figure 2.2).

For contact angle measurement, three samples were used for each of the three different solvents, namely, water, glycerin and formamide. No solvent was reused for any two samples. Both the motor and balance of the DCA analyzer were calibrated at the beginning of each day the device was used. A sample was placed in the microbalance with the help of a sample holder such that it remained freely hanging in a vertical orientation during the duration of measurements. Liquid solvent to be used for measuring contact angles was poured in a clean beaker and placed under the mounted sample. The distance between the surface of the liquid solvent and the bottom of the sample was maintained below 4 mm before the start of the test by moving the stage up and down, as desired. The stage was then allowed to move vertically upward at 80μm/s. No change in weight (force) data occurs before the sample touches the liquid solvent (see Figure 2.3). A plus symbol inside a circle shows the ZDOI (Zero Depth of Immersion) in Figure 2.3. The sample was dipped into the liquid solvent up to 6 mm from the ZDOI at the same advancing rate. The sample is then held steady for 2 min (dwelling time) before withdrawing from the liquid solvent at the same speed. The lower portion of Figure 2.3 shows the weight (force) data for advancing contact angle, while the upper portion shows the same data for receding contact angle. The weight (force) data obtained from the microbalance were saved on the computer and used for the calculation of dynamic contact angle, using a Microsoft Excel program.

2.6 Test Matrix

SFE components of two selected asphalt binders, namely PG 64-22 and PG 70-28 from Ardmore, Oklahoma, were determined separately from measurements of advancing contact angles by DWPM. PG 70-28 used in this study is modified with the polymer Elvaloy® RET. Two amine-based liquid anti-strip additives, namely AD-Here HP Plus from Arr-Maz, Florida and Redicote E-6 from Akzo-Nobel, Chicago, were used. Three selected amounts (0.25%, 0.50% and 1.50%) of these additives were added to both the binders. The test matrix, including the number of samples used, for which the SFE components were evaluated is presented in Table 2.1.

2.7 Advancing Contact Angle of Asphalt Binders

Contact Angle with Water

The contact angle of the original PG 64-22, without any anti-strip additive is, 109.4° (see Table 2.2). The contact angles of the same binder with 0.25%, 0.75% and 1.5% AD-Here HP Plus are 108.0°, 107.5° and 101.6°, respectively. The corresponding contact angles of PG 64-22 with Redicote E-6 are 109.4°, 106.3° and 94.8°. It is evident that contact angle decreases with an increase in additive content; the reduction in contact angle being more dominant for Redicote E-6 than AD-Here HP Plus. The minimum contact angle of 94.8° is obtained for 1.5% Redicote E-6. This shows significant effect of Redicote E-6 at 1.5%. The standard deviations in contact angle values were between 0.2° and 1.1°.

Comparatively, the contact angle of the original PG 70-28, without any anti-strip additive is 108.1°, which is lower than the contact angle of the original PG 64-22. The contact angles decrease with an increase in additive content as found in the case of PG 64-22. The minimum contact angle is found to be 105.7°, with 1.5% AD-Here HP Plus. The standard deviations were between 0.1° and 0.9°.

Contact Angle with Glycerin

The contact angle of PG 64-22, without any anti-strip additive, is 94.1°. The contact angle for this case does not show any increasing or decreasing trend with increasing AD-Here HP Plus content. Comparatively, the contact angle decreases with an increase in the percent of Redicote E-6. The contact angle values reduced from 94.6° to 91.9° due to increasing the Redicote E-6 amount from 0.25% to 1.5%. It shows that 1.5% Redicote E-6 significantly reduces the contact angle to 91.9 °. The standard deviations in this case varied between 0.1° and 0.7 °.

The contact angle of PG 70-28, without any anti-strip additive, is 92.7° which is lower than the corresponding contact angle of PG 64-22. The contact angles are found to decrease for both additives, with increasing amount of additives. The standard deviations vary between 0.1° and 0.8°.

Contact Angle with Formamide

The contact angle of original PG 64-22 for this solvent is 91.4°. No decreasing trend is observed with an increase in the percent of AD-Here HP Plus whereas, the contact angle decreases with an increase in the percent of Redicote E-6. The minimum contact angle is found to be 82.9° with 1.5% Redicote E-6. The standard deviation was some what higher (1.4°) in this case.

For original PG 70-28, the contact angle is 89.2 which is lower than that of the original PG 64-22. A decreasing trend in contact angle was observed with an increase in additive content for both the additives. The standard deviation varies between 0.1 and 0.7.

2.8 Effect of Anti-Strip Additives on SFE of Asphalt Binders

Increase in SFE with the Addition of Anti-Strip Additives (Surfactants)

Many researchers have reported that liquid anti-strip additives reduce the SFE of asphalt binders and therefore, increase the wetability of binders to the aggregate (Aksoy et al., 2004; Roberts et al., 1996; Tunnicliff and Root, 1984). Increased wetability gives increased surface area to be wetted and promotes adhesion between the binder and the aggregate. To achieve this, surface active agents, the so-called "surfactants" are used as anti-strip additives. In this study, it was found that the surfactants (liquid anti-strip additives) do not decrease the SFE of an asphalt binder. Rather, it increases the SFE. This increased SFE increases the free energy of adhesion (adhesion strength) between the asphalt binder and the highly acidic aggregate such as granite according to Equation 2.7. The increased free energy of adhesion provides increased resistance to stripping. The more the SFE of an asphalt binder, the more the free energy of adhesion is between the highly acidic aggregate and the binder.

Reasons for Increase in SFE with the Addition of Liquid Anti-Strip Additives (Surfactants)

Asphalt is a continuous phase of non-polar materials (Robertson, 1991). Non-polar solvents have received far less attention than the polar solvents (i.e., water) with respect to the surfactant-action phenomenon. Surfactants of all kinds decrease surface tension of water (polar solvent) as the hydrocarbon tail groups are directed outward. In case of the non-polar solvent, asphalt binder in this case, the polar head groups are directed outward. This actually results in an increase in surface tension (Myers, 1992; Rosen, 1978) in asphalt binders.

Results

Table 2.3 shows the total SFE and its components obtained in this study. A general trend is that the total SFE increases with an increase in percent of additive, Redicote E-6 performing better than AD-Here HP Plus (also see Figures 2.4 and 2.5). Both the additives are more effective in PG 64-22 than PG 70-28 with respect to increase in total SFE.

PG 64-22 with AD-Here HP Plus

The total SFE of PG 64-22, without any anti-strip additive, is 9.3 dyne/cm^2. The total SFE increases to 11.4, 13.5 and 15.5 dyne/cm^2, respectively, when 0.25%, 0.75% and 1.5% AD-Here HP Plus is added. The maximum (67%) increase occurs when the additive content is 1.5%.

PG 64-22 with Redicote E-6

The total SFE of PG 64-22 increases from 9.3 dyne/cm^2 to 11.2, 14.1 and 28.6 dyne/cm^2, respectively, for 0.25%, 0.75% and 1.5% Redicote E-6, the maximum increase being 276% in case of 1.5% additive.

PG 70-28 with AD-Here HP Plus

The total of original PG 70-28 is 10.9 dyne/cm^2. The total SFE increases to 11.8, 12.4 and 13.5 dyne/cm^2, respectively, when 0.25%, 0.75% and 1.5% AD-Here HP Plus is added to the binder. The maximum increase (28%) here is much smaller than in case of PG 64-22.

PG 70-28 with Redicote E-6

The total SFE of PG 70-28 increases from 10.9 dyne/cm^2 to 11.2, 12.5 and 13.6 dyne/cm^2, respectively, for 0.25%, 0.75% and 1.5% Redicote E-6, the maximum increase being 31%.

2.9 Effect of Anti-Strip Additives on Acid-Base Characteristics of Asphalt Binders

Acid-Base Characteristics of Asphalt Binders

Asphalt binders are acidic in nature. Carboxylic acid, anhydride, phenol, pyrrole etc. are generally the acidic functional groups in asphalt binders (Petersen, 1985). In an Ion Exchange Chromatography (IEC) analysis on four SHRP core asphalts, Kim and Branthaver (1996) found that the mass fraction of strong acid varies between 3.9% and 9.55%, whereas, the mass fraction of strong base varies between 2.3% and 5.2%. Its acid value is between 0 to 4 mg KOH/g.

Acid-Base Characteristics of Aggregates

Acidic (also called hydrophilic) aggregates such as quartzite, granite and sandstone generally exhibit a high silica content. Basic (also called hydrophobic) aggregates, on the other hand, exhibit a low silica content. Carbonate rocks, such as limestone, dolomite, produce basic aggregates (Taylor and Khosla, 1983).

Interactions between Asphalt Binder and Aggregates

Basic aggregates such as limestone provides good bonding for acidic bitumen as shown in Equation 2.7. In case of acidic aggregates such as granite, their acids counteract with acids in asphalt binder. Therefore, it is very difficult to obtain a good bond between an acidic aggregate and acidic asphalt binder (Jo et al., 1997).

Acid-Base Characteristics of Anti-Strip Additives

Liquid anti-strip additives in the form of cationic surface-active agents (surfactants) are principally amines. Amines are organic compounds and are generally basic. Two major types of amine surfactants are used as anti-strip additives: fatty diamine/fattly acid salt and fattly amido-diamine/fatty acid salt.

Interaction between Aggregates and Asphalt Binders with Anti-Strip Additives

By using basic chemicals, such as amines, lime as anti-strip additives, a better adhesion can be achieved between an acidic asphalt binder and an acidic aggregate such as granite. Amines which are basic organics alter the surface of an acidic aggregate to provide better adhesion (Tunnicliff and Root, 1984).

The amines consist of a long chain hydrocarbon and amine group. The amine group reacts with the aggregate surface, and the hydrocarbon portion, which is hydrophobic, is directed into the binder. The net effect is that the long hydrocarbon chain acts as a bridge between the hydrophilic aggregate and hydrophobic bitumen surfaces thus, encouraging a strong bond between them.

Results

The SFE components of binders with and without anti-strip additives are documented in Table 2.3. A general trend is that the acid component of SFE decreases with an increase in additive percent for both the additives (see Figures 2.6 and 2.7). Another finding is that the base component decreases with an increase in additive percent for both the additives (see Figures 2.8 and 2.9). In general, Redicote E-6 performs better than AD-Here HP Plus, while both the additives are more effective in PG 64-22 with respect to decreasing the acid component and increasing the base component.

PG 64-22 with AD-Here HP Plus

The acid component of original PG 64-22 is 2.9 dyne/cm^2. The acid component decreases to 2.0, 1.0 and 0.5 dyne/cm^2, respectively, with the addition of 0.25%, 0.75% and 1.5% AD-Here HP Plus, the maximum reduction (83%) occurring for 1.5% additive content.

The base component of PG 64-22 without additive is 0.4 dyne/cm^2. The base component increases with an increase in additive amount. The maximum increase is 568% with 1.5% AD-Here HP Plus.

PG 64-22 with Redicote E-6

The acid component of PG 64-22 is reduced from 2.9 dyne/cm^2 to 1.8, 1.0 and 0.2 dyne/cm^2, respectively, with the addition of 0.25%, 0.75% and 1.5% Redicote HP Plus, the maximum reduction (93%) taking place in case of 1.5% additive content.

Redicote E-6 exhibited an excellent performance in terms of increasing the base component. The maximum increase in base component is 1142% when the additive content is 1.5%.

PG 70-28 with AD-Here HP Plus

The acid component of original PG 70-28 is 2.5 dyne/cm^2. The acid component reduces to 2.1, 1.9 and 1.8 dyne/cm^2, respectively, with the addition of 0.25%, 0.75% and 1.5% AD-Here HP Plus, the maximum decrease being 28%.

Comparatively, the component of original PG 70-28 (0.4 dyne/cm^2) increases to 0.5, 0.5 and 0.7 dyne/cm^2, respectively, for 0.25%, 0.75% and 1.5% AD-Here HP Plus.

PG 70-28 with Redicote E-6

The acid component of PG 70-28 with 0.25%, 0.75% and 1.5% Redicote E-6 are 2.5, 1.9 and 1.7 dyne/cm^2, respectively. The maximum reduction of 33% is exhibited by 1.5% Redicote E-6.

The base components of PG 70-28 are 0.5, 0.5 and 0.7 dyne/cm^2, respectively, for 0.25%, 0.75% and 1.5% Redicote E-6 with the maximum increase of 39%.

In this study, the effect of anti-strip additives has been evaluated only by the acid-base characteristics of asphalt binders with and without anti-strip additives. It should be noted that basic anti-strip additives such as amines has some other advantages besides altering the acidic aggregate surface to adhere with acidic asphalt binder. Carboxylic acid is the most strongly adsorbed functional types on most mineral surfaces; however, they were also the functional type most easily water displaced. Amine functionality has better water resistant capability than carboxylic acid functionality when adsorbed on aggregate surface (Petersen and Plancher, 1998).

2. 10 Interaction of Acidic Binder with Acidic Aggregate

Asphalt binders are acidic in nature. The acid components of PG 64-22 and PG 70-28 are 2.9 dyne/cm^2 and 2.5 dyne/cm^2, respectively, whereas the corresponding base components are 0.4 dyne/cm^2 for both. Basic chemical compounds such as amines and lime in the form of anti-strip additives reduce the acid component and increase the base component of the asphalt binder, thereby improving the adhesion between the acidic binder and the acidic aggregate. For example, with the addition of 1.5% Redicote E-6 in PG 64-22, the acid component reduces by 92% and base component increases by 1141%.

2.11 Comparison between PG 64-22 and PG 70-28

Comparison between PG 64-22 and PG 70-28 on Total SFE and SFE Components

The total SFE of PG 64-22 and PG 70-28 are 9.3 and 10.9 dyne/cm^2, respectively. The higher total SFE explains the good adhesion between aggregates and PG 70-28. The acid component of PG 70-28 is lower than PG 64-22 and the base components are equal (see Table 2.3).

Comparison between PG 64-22 and PG 70-28 on the effect of Anti-Strip Additives

1.5% AD-Here HP Plus increases the total SFE of PG 64-22 and PG 70-28 by 67% and 24%, respectively. Comparatively, 1.5% Redicote E-6 increases the corresponding SFE by 208% and 24%. Therefore, both the additives have greater influence on PG 64-22 than PG 70-28 with respect to increase in total SFE. The same trend is observed for acid component and base component.

2.12 Proposed Chemical Model of Asphalt Binder

The chemical model developed in this study is based on the SFE characteristics of asphalt binder with and without anti-strip additives. This model explains all the behavioral characteristics of asphalt binder related to anti-strip additives. The model is discussed next.

An asphalt binder is a collection of polar and non-polar molecules. The polar molecules tend to associate strongly to form organized structures throughout the continuous phase of the non polar materials.

Asphalt binders are acidic in nature. Basic chemicals in the form of anti-strip additives (such as amines and lime) can reduce the acid component and increase the basic components of asphalt binders. This provides better adhesion between acidic aggregates (such as granite and quartz) and acidic asphalt binders.

When cationic surfactants (such as, amines) are added to an asphalt binder (non-polar solvent), it adsorbs onto the surface with polar head group directed outward. This actually results in an increase in surface tension of an asphalt binder which promotes the adhesion energy between acidic aggregate and binder.

2.13 Conclusions

The following conclusions can be drawn from the SFE characteristics of asphalt binders.

The total SFE of PG 64-22 and PG 70-28 increases with an increase in additive content. 1.5% AD-Here HP Plus and 1.5% Redicote E-6 increased the total SFE of PG 64-22 by 67% and 208%. The corresponding increases in total SFE of PG 70-28 are 23.6% and 24.4%, respectively.

A chemical model of asphalt binder is proposed which explains this increase in total SFE. When cationic surfactants (such as, amines) are added to an asphalt binder (non-polar solvent), it adsorbs onto the surface with polar head group directed outward. This actually results in an increase in surface tension of asphalt binder which promotes the adhesion energy between aggregate and binder.

The acid component of PG 64-22 and PG 70-28 decreases with an increase in additive content. 1.5% AD-Here HP Plus and 1.5% Redicote E-6 decreased the acid component of PG 64-22 by 83% and 92%, whereas the corresponding reduction in acid components of PG 70-28 is 28% and 33%, respectively.

Asphalt binders are acidic in nature. The acid component of PG 64-22 and PG 70-28 are 2.9 dyne/cm^2 and 2.5 dyne/cm^2, respectively whereas, the corresponding base components is 0.4 dyne/cm^2 for both. Basic chemicals in the form of anti-strip additives (such as amines and lime) can reduce the acid component and increase the basic components of asphalt binders. With the addition of 1.5% Redicote E-6 in PG 64-22, the acid component of the asphalt binder decreases by 92% and the base component increases by 1141%. This provides better adhesion between the acidic aggregate (such as granite and quartz) and the acidic asphalt binder.

The total SFE of PG 64-22 and PG 70-28 are 9.3 and 10.9 dyne/cm^2, respectively. The higher total SFE explains good adhesion between aggregates and PG 70-28. 1.5% AD-Here HP Plus increases the total SFE of PG 64-22 and PG 70-28 by 67% and 24%, respectively, whereas, 1.5% Redicote E-6 increases the corresponding SFE by 208% and 24%. Therefore, both the additives have much greater influence on PG 64-22 than PG 70-28 with respect to increase in total SFE. The same trend is observed for acid component and base component.

Finally, in this study it was found that the SFE measurements by DWPM is an excellent tool for evaluating moisture susceptibility of asphalt binders with and without anti-strip additives. Effect of short term aging, long term aging and temperature susceptibility of anti-strip additives are currently under investigation.

Table 2.1 Test Matrix

Types of Binder	Types of Anti-Strip Additives for Each Binder	Amount in Percent for Each Type of Additive	Types of Solvents for Each Percent of Additive	No. of Samples for Each Solvent
PG 64-22 PG 70-28	AD-Here HP Plus Redicote E-6	0% 0.25% 0.75% 1.5%	Water Glycerin Formamide	3

Table 2.2 Average Contact Angle with Standard Deviation

Binders	Types of Additives	Percent of Additive	Contact Angle with Water (degree)		Contact Angle with Glycerin (degree)		Contact Angle with Formamide (degree)	
			Average	St. Dev.	Average	St. Dev.	Average	St. Dev.
PG 64-22		0	109.4	0.3	94.1	0.3	91.4	0.5
	AD-Here HP Plus	0.25	108.0	0.6	93.8	0.4	90.0	0.2
		0.75	107.5	0.9	95.1	0.2	90.3	0.2
		1.5	101.6	0.6	93.9	0.2	88.8	0.7
	Redicote E-6	0.25	109.4	0.3	94.6	0.1	90.6	0.3
		0.75	106.3	0.3	93.7	0.3	88.8	0.4
		1.5	94.8	1.1	91.9	0.7	82.9	1.4
PG 70-28		0	108.1	0.1	92.7	0.1	89.2	0.3
	AD-Here HP Plus	0.25	107.5	0.1	92.7	0.1	88.8	0.1
		0.75	107.2	0.2	92.5	0.8	88.4	0.3
		1.5	105.7	0.9	91.2	0.2	86.8	0.2
	Redicote E-6	0.25	107.5	0.8	92.3	0.1	88.8	0.7
		0.75	107.4	0.2	92.2	0.3	87.9	0.0
		1.5	106.2	0.4	91.6	0.1	87.0	0.5

Table 2.3 SFE Components of Asphalt Binders with and without Additives

Binders	Types of Additives	Percent of Additive	Total SFE, Γ (dyne/cm^2)	Lifitz-van der Waal Component, Γ^{LW} (dyne/cm^2)	Acid Component, Γ^+ (dyne/cm^2)	Base Component, Γ^- (dyne/cm^2)	Acid-Base Component, Γ^{AB} (dyne/cm^2)
PG 64-22		0	9.3	7.0	2.9	0.4	2.3
	AD-Here HP Plus	0.25	11.4	9.2	2.0	0.6	2.1
		0.75	13.5	11.7	1.0	0.8	1.8
		1.5	15.5	13.1	0.5	2.9	2.4
	Redicote E-6	0.25	11.2	9.6	1.8	0.4	1.6
		0.75	14.1	12.2	1.0	0.9	1.9
		1.5	28.6	26.4	0.2	5.4	2.2
PG 70-28		0	10.9	8.8	2.5	0.4	2.1
	AD-Here HP Plus	0.25	11.8	9.7	2.1	0.5	2.1
		0.75	12.4	10.4	1.9	0.5	2.0
		1.5	13.5	11.3	1.8	0.7	2.2
	Redicote E-6	0.25	11.2	8.9	2.5	0.5	2.2
		0.75	12.5	10.7	1.9	0.4	1.8
		1.5	13.6	11.6	1.7	0.6	2.0

9.3
11.7
13.6
22.1

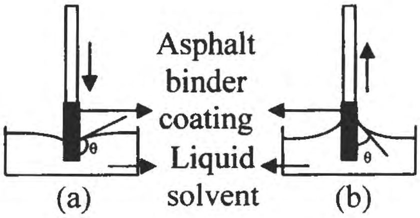


Figure 2.1 Dynamic Wilhelmy Plate Method for (a) Advancing contact angle and (b) Receding contact angle

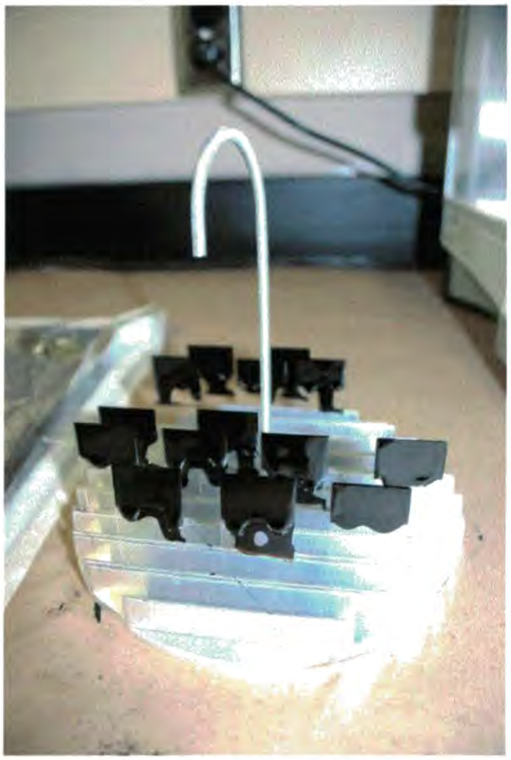
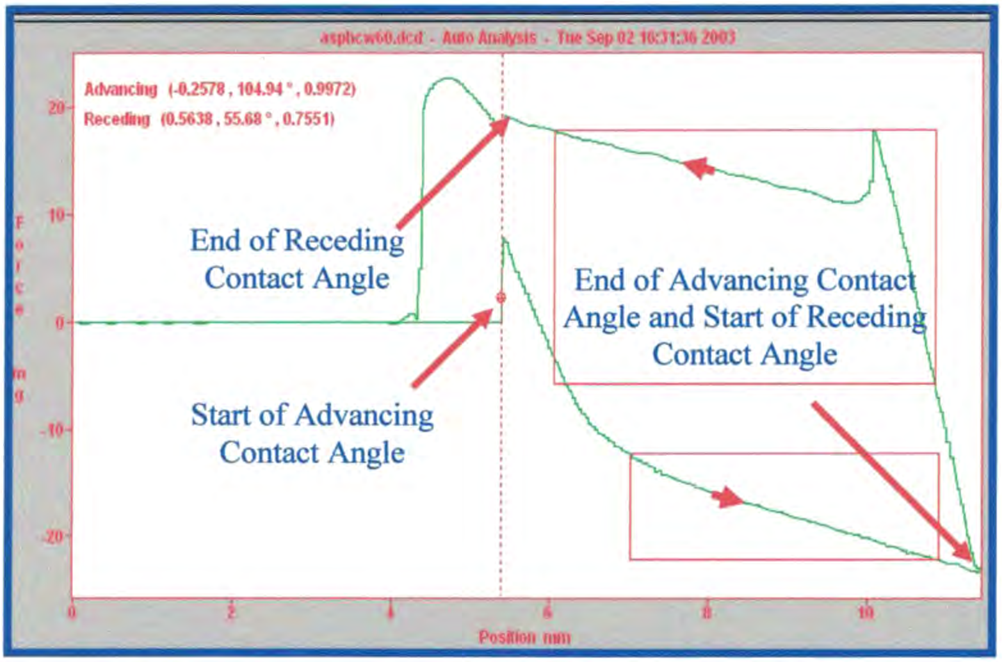


Figure 2.2 Samples in a Sample Holder



¡Figure 2.3 Wilhelmy Plate test results from DCA Analyzer for PG 64-22 with water

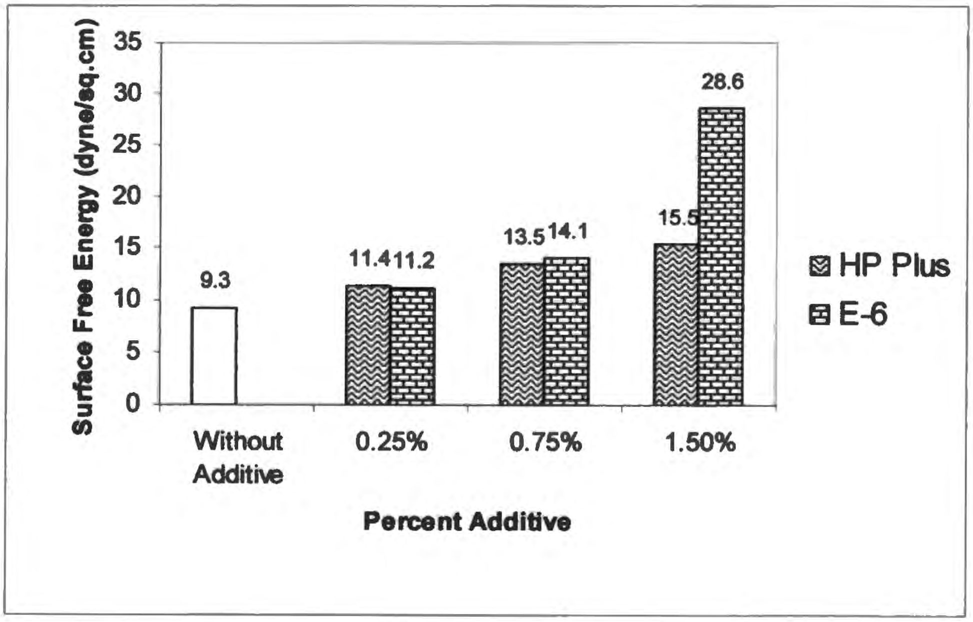


Figure 2.4 Effect of AD-Here HP Plus and Redicote E-6 on total SFE of PG 64-22

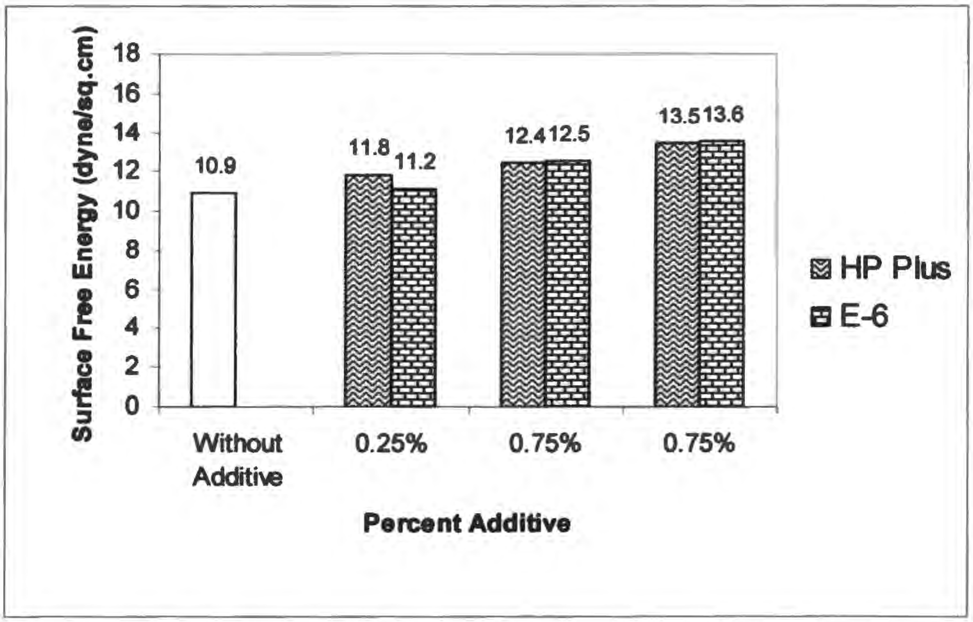


Figure 2.5 Effect of AD-Here HP Plus and Redicote E-6 on total SFE of PG 70-28

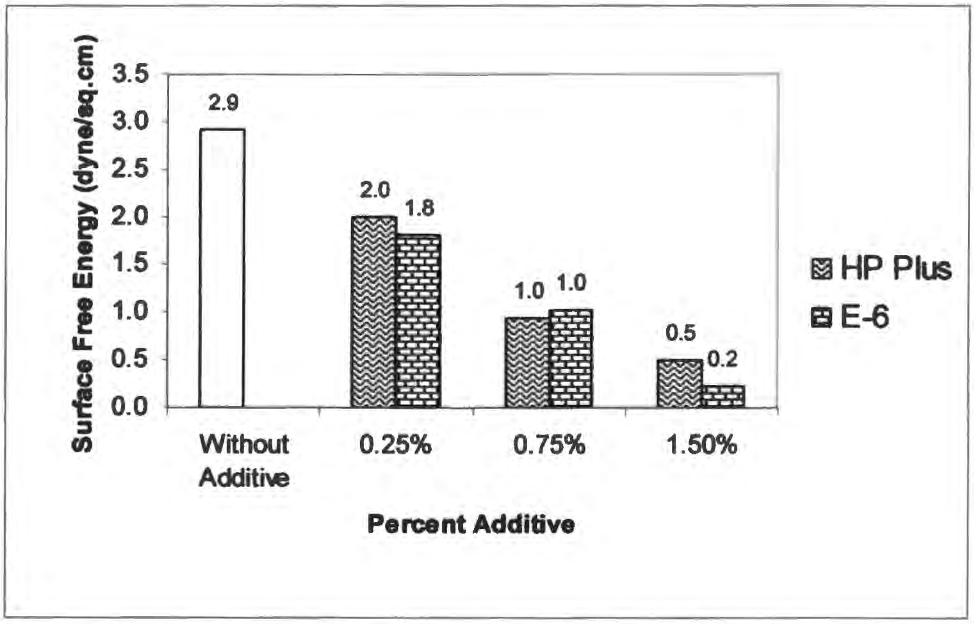


Figure 2.6 Effect of AD-Here HP Plus and Redicote E-6 on Acid Component of PG 64-22

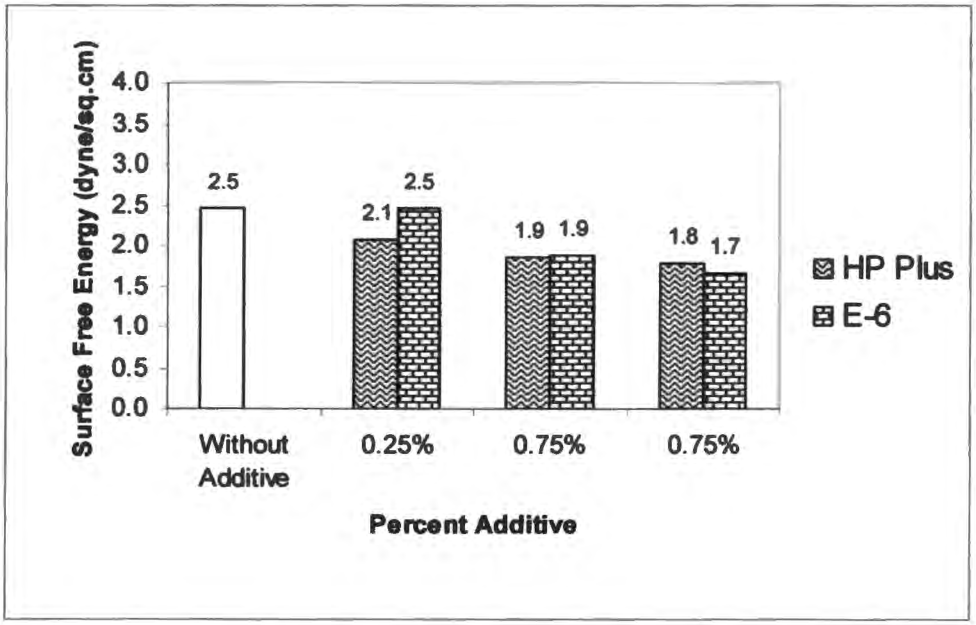


Figure 2.7 Effect of AD-Here HP Plus and Redicote E-6 on Acid Component of PG 70-28

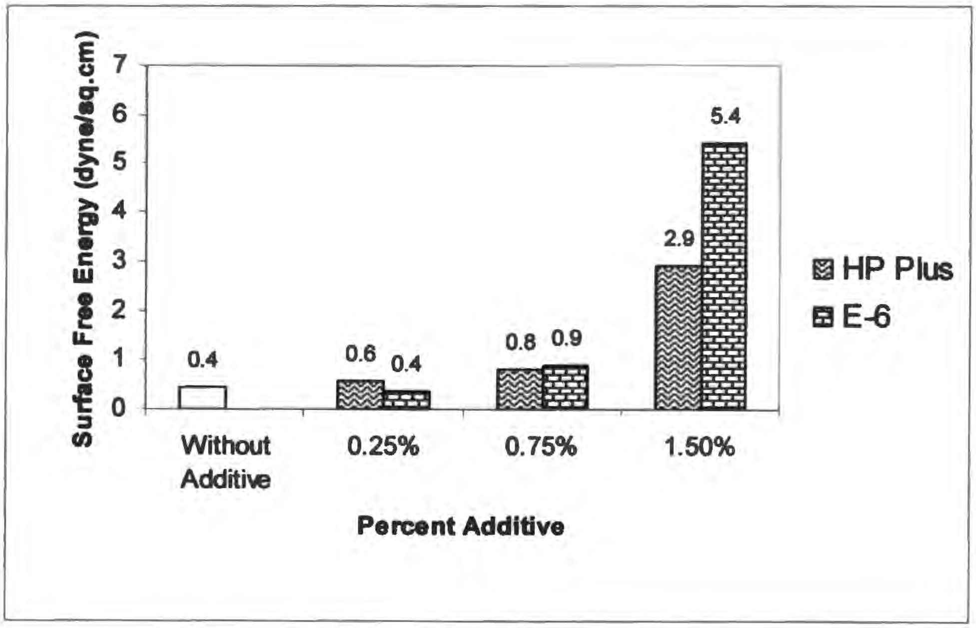


Figure 2.8 Effect of AD-Here HP Plus and Redicote E-6 on Base Component of PG 64-22

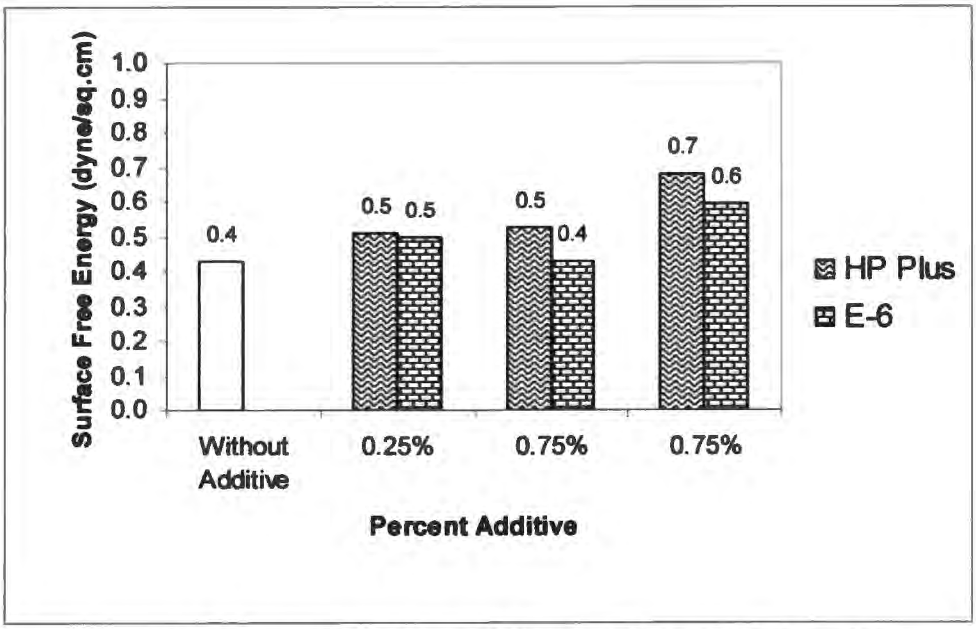


Figure 2.9 Effect of AD-Here HP Plus and Redicote E-6 on Base Component of PG 70-28

3. SFE CHARACTERISTICS OF AGGREGATES

3.1 Introduction

The SFE components of an aggregate can be measured using a Universal Sorption Device (USD), as performed by Cheng et al. (2002). In this phase, repeated trial tests were performed to determine the specific surface area of an aggregate using the USD, which is needed to calculate the spreading pressure. According to the Gibbs adsorption equation (see Equation 3.2), spreading pressure reflects a reduction in solid surface tension due to the adsorption of solvent vapor in a solid (aggregate)-vapor (solvent) system. The methodology for measuring the SFE components of an aggregate is described in the following sections.

3.2 Selection of Aggregates

A limestone aggregate was selected in cooperation with ODOT as one of the two aggregates to be included in this study. The source of the selected limestone is APAC-Oklahoma, Vinita. It is believed that hydrophobic aggregates (considered to be basic) provide better resistance to stripping of asphalt binder films than hydrophilic aggregates (considered to be acidic). Carbonate rocks, such as limestone, usually produce hydrophobic aggregates (Taylor and Khosla, 1983). One hydrophilic aggregate (exhibits high silica content), namely chat was also selected. The chat used in this study were collected from Kenoyer North Chat Pile, Ottawa County, Oklahoma.

3.3 Aggregate Properties Test

The engineering properties of limestone and chat were evaluated following the AASHTO, ASTM and OHD standards, as recommended by the Oklahoma Department of Transportation (ODOT). Table 3.1 summarizes the engineering properties, along with the test protocol followed. The L.A. abrasion values of limestone and chat were found to be 23% and 17%, respectively, which are much smaller than the maximum of 40% allowed by the ODOT. ODOT specifies a minimum aggregate durability index of 40%. In this study the aggregate durability index of limestone and chat were found to be 71% and 78%, respectively, which are much higher than the requirement. It was found that limestone and chat possess less than 5% flat or elongated particles which is less than the maximum allowed by ODOT for more than 0.3 million ESALs (see Table 3.1). The requirements for other source and consensus aggregate properties vary for surface course and base course mixes.

3.4 Principles of Operation of the USD

The main components of the USD are shown in Figures 3.1 and 3.2. A dry gas source (nitrogen), connected at the back of the unit, passes through a 2 micron filter and splits into two lines. One of the lines, called the purge line, is connected to the microbalance. The flow rate of the gas, continuously purging the microbalance, is regulated by a rotameter located on the front panel.

The second panel is connected to two normally closed solenoids valves which are provided for shutting off the flow to the mass flow controllers that are used to accurately control the flow of the dry gas. One of the streams (mass flow controller #1) flows through the humidifier (evaporator). The second mass flow controller (controller#2) provides a dry gas stream.

The purpose of the humidifier is to saturate the dry gas with water (or other solvent). It consists of a series of suspended cotton wicks packed into a stainless steel (SS) container with a water pool at the bottom. Water is injected into the bed with a syringe through a septum located on the left side of the unit. The water level is indicated by a Teflon tube located below the supply port. The gas leaving the humidifier is mixed with the dry stream via a static mixer. The dew point of the mixed stream is measured with the dew point analyzer (DPA). Two solenoid valves downstream from the DPA redirect the stream either to the aluminum block or to the vent.

The humidifier, mixer, DPA, and solenoid valves are contained in the lower compartment of the instrument. This thermostated section is normally maintained at 15°C above the sample temperature. A kapton heater provides heat and a muffin fan circulates the air through the enclosure to ensure temperature uniformity. The temperature of this section is indicated by a programmable Watlow temperature controller located on the front panel. If the controller is set for Remote Set Point, the temperature is set by the software. In Local Set Point mode, the controller can be set by an operator, overriding any automatic control.

The stream entering the aluminum block is equilibrated with the temperature of the block and is equally divided into two streams. One of the streams enters the sample compartment of the aluminum block (left side). The other stream enters the reference compartment of the block (right side). In each of the compartments, a 100 Ohm Resistance Platinum Thermometer (RTD) is provided for measuring temperature of the process stream. Based on the temperature and dew point, the relative humidity is determined.

The aluminum block is well insulated and housed in the middle section of the instrument. Temperature of the aluminum block is maintained by a constant temperature bath. The bath circulates a fluid (water, or a water/ethylene glycol mixture) through the block. The fluid enters the block at the bottom and leaves it at the top. The temperature of the bath is set by the software if the Disable/Enable switch at the back of the control unit of the bath is in the enable position. This position is indicated by the lighted LED at the word ACCESS in front of the control unit of the bath. In disable position, the temperature can be set manually.

The sample and the reference holders are located within the aluminum block compartments about ¼ in (0.635 mm) above the tip of RTDs or probes. The holders are attached to the microbalance arms via thin SS hangdown wires.

The microbalance together with its housing is located in the upper section of the instrument, which is thermally separated from the aluminum block. The temperature of this section is kept constant at 40°C for all experiments carried out at temperatures below or about that value. For experiments conducted at higher temperatures, this value can be raised to 50°C. The temperature controller is located inside the aluminum cabinet and is accessible by opening the back door. The temperature is set manually.

Sample weight changes during adsorption are measured with a Cahn D-200 microbalance. The microbalance is housed in an aluminum enclosure and is connected with the aluminum block via SS steel tubes of 1 in (2.54 cm) diameter. Balance control in data acquisition is accomplished through a RS-232 communicator port.

3.5 Theory and Methodology

The theory and methodology established by Cheng et al. (2002) are being followed in this research. Cheng et al. (2002) followed van Oss-Choudhury-Good (Good , 1992) postulation for the analysis of the SFE components of aggregate. The methodology and theory used for measuring the SFE components of an aggregate using the USD are as follows.

1) Three gas solvents, n-hexane (non polar), MPK (methyl propyl ketone/2-pentanone, mono-polar), and water (bi-polar) were selected whose SFE components are known.
2) The specific amount of solvent adsorbed on the surface of the absorbent (aggregate) was measured and simultaneously the vapor pressure at the surface of the aggregate was measured.
3) The specific surface area of the aggregate was calculated using the following BET (after Brunauer, Emmet and Teller) equation.

$$\frac{P}{n(P_0 - P)} = \left(\frac{c-1}{n_m c}\right)\frac{P}{P_0} + \frac{1}{n_m c} \tag{3.1}$$

where,

P = Vapor Pressure,

P_0 = Saturated Vapor Pressure of Solvent,

n = Specific amount adsorbed on the surface of the absorbent,

n_m = Specific amount adsorbed on the monolayer and

c = Constant

4) The spreading pressure at saturation vapor pressure was calculated for each solvent using the Gibbs adsorption equation as follows:

$$\pi_e = \frac{RT}{A}\int_0^{P_0} \frac{n}{P}\,dP \tag{3.2}$$

where,

π_e = Spreading pressure at saturation vapor pressure of solvent,

R = Universal gas constant,

T = Absolute temperature and

A = Specific surface area of absorbent

5) The work of adhesion of a liquid on a solid, W_A, was expressed in terms of the surface tension (surface energy) of the liquid, Γ_l, and the equilibrium spreading pressure of adsorbed vapor on the solid surface, π_e, as shown in the following equations.

$$W_A = \pi_e + 2\Gamma_l = \Delta G_{sl} \tag{3.3}$$

$$\Delta G_{sl} = \Delta G_{sl}^{LW} + \Delta G_{sl}^{AB} = 2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} + 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} + 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{3.4}$$

$$\pi_e + 2\Gamma = 2\sqrt{\Gamma_s^{LW}\Gamma_l^{LW}} + 2\sqrt{\Gamma_s^{+}\Gamma_l^{-}} + 2\sqrt{\Gamma_s^{-}\Gamma_l^{+}} \tag{3.5}$$

6) The following equation was used to calculate the non-polar component of the SFE from a non-polar solvent.

$$\Gamma_s^{LW} = \frac{(\pi_e + 2\Gamma_l)^2}{4\Gamma_l^{LW}} \tag{3.6}$$

One monopolar basic liquid vapor (subscript, m) and one known bipolar liquid vapor (subscript, b) were selected to calculate the acid-base components of the SFE using the following equations.

$$\Gamma_s^{+} = \frac{(\pi_e + 2\Gamma_{lm} - \sqrt{\Gamma_s^{LW}\Gamma_{lm}^{LW}})^2}{4\Gamma_{lm}^{-}} \tag{3.7}$$

$$\Gamma_s^{-} = \frac{(\pi_e + 2\Gamma_{lb} - 2\sqrt{\Gamma_s^{LW}\Gamma_{lb}^{LW}} - 2\sqrt{\Gamma_s^{+}\Gamma_{lb}^{-}})^2}{4\Gamma_{lb}^{+}} \tag{3.8}$$

The total SFE of the aggregate was calculated using the following equation.

$$\Gamma_s = \Gamma_s^{LW} + 2\sqrt{\Gamma^{+}\Gamma^{-}} \tag{3.9}$$

3.6 Sorption Test

The SFE components of limestone and chat were determined using the USD. Approximately 60 gm of an aggregate passing #8 sieve and retaining on #10 sieve (US Standard) was washed thoroughly with deionized water and put into the oven at 110°C for 24 hours. The sample was then put into a desiccator and used in USD test after cooling. A test program was prepared using the VTI software. The aggregate sample was put into the USD for drying at 25°C for 600 minutes as set in the program. The test started with the increment of the relative humidity from water vapor. A relative humidity step of 10% was set in the program. The relative humidity will change after the sample reaches an equilibrium condition (forms a plateau) at that relative humidity level. Two different equilibrium conditions can be set in the program. One is based on percent change in sample weight and the other on a specified time. An equilibrium condition can be set by combining the two. The USD obtains the percent change in weight data with respect to the change in relative humidity. Tables A.1-6 shows the weight data obtained in this study using water, MPK and n-hexane for limestone and chat. These tables also show the sorption of water, MPK and n-hexane on limestone. In Figure A.1, it can be seen that equilibrium (plateau) can be reached at each relative humidity step.

3.7 Specific Surface Area of Aggregates

The VTI software produces the BET curves (see Equation 3.1) from the corresponding sorption of an adsorbate (solvent) in an aggregate. The BET curves were obtained using water, MPK and n-hexane for both limestone and chat. A sample BET curve is shown in Figure A.2. Specific surface area of each of the aggregates for each of the solvents (adsorbates) were determined using Equation 3.1. Table 3.2 shows the surface area obtained for limestone and chat in this study. The specific surface areas of limestone were found to be 1.58 m^2/gm, 2.65 m^2/gm and 3.18 m^2/gm, respectively for n-hexane, MPK and water. The corresponding specific surface areas of chat were found to be 1.0 m^2/gm, 1.48 m^2/gm and 1.83 m^2/gm. It was observed that the specific surface areas of limestone are higher than those of chat.

3.8 Spreading Pressure

According to the Gibbs adsorption equation (see Equation 3.2), spreading pressure reflects a reduction in solid surface tension due to the adsorption of solvent vapor in a solid (aggregate)-vapor (solvent) system. Table 3.2 shows the spreading pressure obtained in this study for each of the solvents in each of the aggregates. The spreading pressure was used to determine the SFE components of each of the aggregates according to the Equation 3.3.

3.9 SFE Components of Aggregates

At first the non-polar component of SFE was determined using Equation 3.6. The acid component of SFE was determined following Equation 3.7 and finally, the basic component of SFE was obtained from Equation 3.8. Table 3.3 shows the values of the SFE components for limestone and chat.

The SFE of limestone and chat are 166.6 ergs/cm^2 and 132.2 ergs/cm^2, respectively. The higher surface energy of limestone provides better adhesion strength between limestone and asphalt binder as will be shown by equation in Chapter Four.

The basic component of SFE of limestone and chat are 390.8 ergs/cm^2 and 219 ergs/cm^2, respectively. It is evident that limestone is more basic than chat.

The SFE components of a highly acidic aggregate, namely the Georgia Granite are shown in Table 3.3 as found by Cheng et al. (2002). It was observed that the acid component of SFE of this aggregate is very high (24.1 dyne/cm^2) if compared with limestone (6.48 dyne/cm^2) and chat (2.82 dyne/cm^2) as found in this study.

Table 3.1 Engineering Properties of Limestone and Chat

Source Aggregate Properties	Test Protocol	Required (%)	Chat	Limestone
Los Angeles abrasion	AASHTO T 96	Max. 40	17	23
Insoluble residue	OHD L-25	Varies*	98	25
Aggregate durability index	AASHTO T 210	Min. 40	78	71
Consensus Aggregate Properties	Test Protocol	Required (%)	Chat	Limestone
Sand equivalent test	AASHTO T 176	Varies*	86	75
Flat or elongated particle	ASTM D4791	Max. 10	<5	<5
Uncompacted void content of fines	AASHTO T 304, Method A	Varies*	46	45
Percentage fractured faces	OHD L-18	Varies*	100	100

*Varies for different surface and base mixes

Table 3.2 Surface Areas and Spreading Pressures of Aggregates

Aggregates	Solvents	Surface Area (m^2/gm)	Spreading Pressure ($ergs/cm^2$)
Limestone	n-Hexane	1.58	32.9
	MPK	2.65	53.9
	Water	3.18	155.6
Chat	n-Hexane	1.01	41.1
	MPK	1.48	55.7
	Water	1.83	105.6

Table 3.3 SFE Components of Limestone and Chat

Aggregates	SFE ($dyne/cm^2$)	Non-Polar Component of SFE ($dyne/cm^2$)	Acid Component of SFE ($dyne/cm^2$)	Basic Component of SFE ($dyne/cm^2$)	Acid-Base Component of SFE ($dyne/cm^2$)
Limestone	167	65.98	6.48	391	100.6
Chat	132	82.5	2.82	219	49.68
Georgia Granite[1]	206.5	133.2	24.1	96.0	73.3

[1] The SFE components of Georgia Granite were obtained from Cheng et al. (2002)

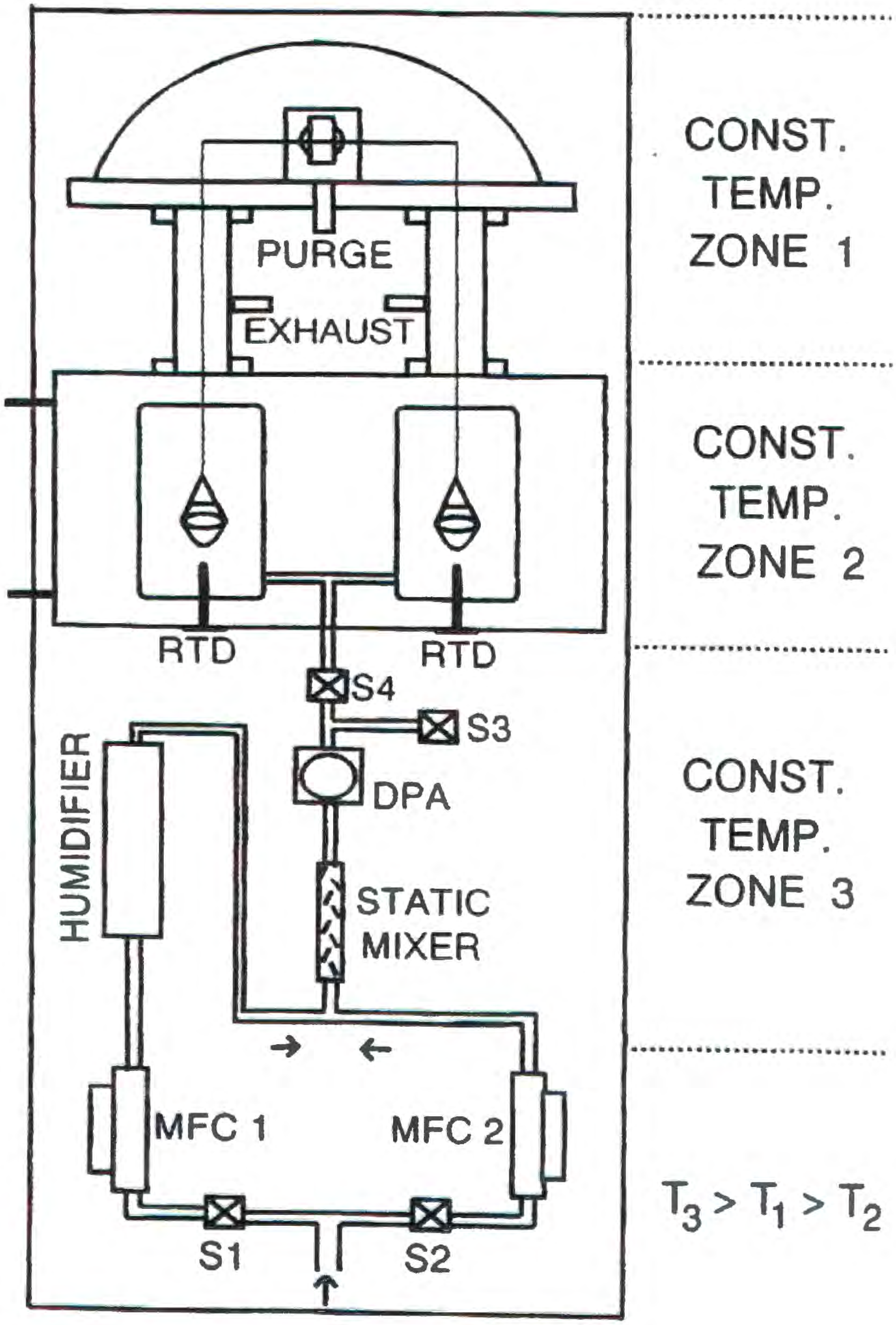


Figure 3.1 Schematic Diagram of the Universal Sorption Device

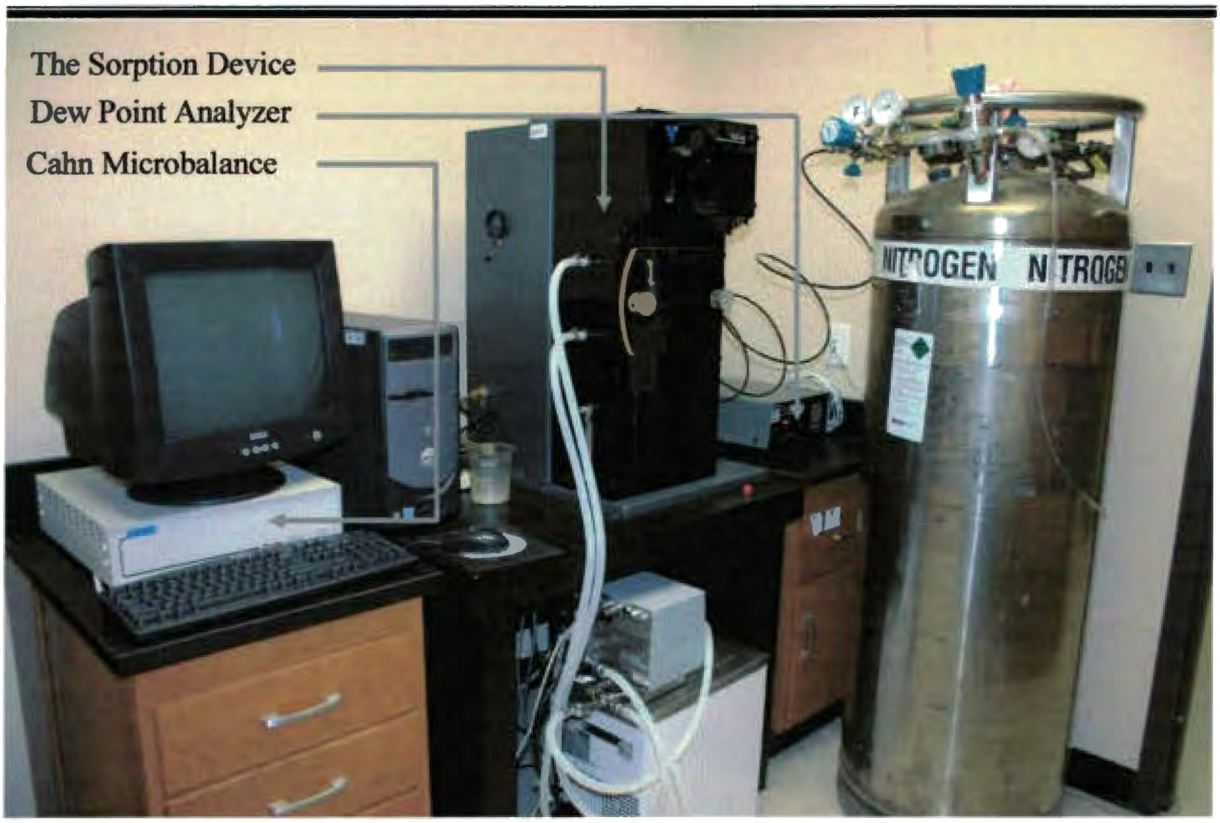


Figure 3.2 Different Components of a Universal Sorption Device

4. ASPHALT-AGGREGATE INTERACTIONS

4.1 Introduction

The adhesion strength between asphalt binder and aggregate can be determined from their SFE components. This study evaluated the effect of mineralogy of aggregate (acidic or basic) on the adhesion strength between aggregate and asphalt binder. Also, the effect of liquid anti-strip additives at different dosages on the adhesion strength between asphalt binder and aggregate were evaluated.

Currently, the retained strength test (AASHTO T-283) is used by ODOT to evaluate the moisture-induced damage potential of HMA. This study provides adhesion strength data from SFE characteristics and the tensile strength data from retained strength test.

4.2 Free Energy of Adhesion between Asphalt Binder and Aggregate

The free energy of adhesion (adhesion strength) between aggregate and asphalt binder was determined from the Equation 2.7 in Chapter Two. Table 4.1 shows the free energy of adhesion between aggregates, both acidic and basic, and asphalt binder, with and without anti-strip additives. It also shows the free energy of adhesion between a highly acidic aggregate, namely the Georgia granite and binders. The SFE components of the Georgia granite was obtained from Cheng et al. (2002).

The free energy of adhesion between chat and PG 64-22 without additive is 100.9 ergs/cm^2. The free energy of adhesion decreases with an increase in percent of AD-Here HP Plus. Likewise, the addition of Redicote E-6 decreases the adhesion strength between chat and

PG 64-22. The adhesion strength between chat and PG 70-28 is 100.2 ergs/cm^2 which also decreases with the addition of each of the additives.

Limestone exhibited better adhesion strength with both PG 64-22 and PG 70-28 than the corresponding chat-asphalt HMA. Both the additives, AD-Here HP Plus and Redicote E-6, decreased the adhesion strength between limestone and asphalt binders.

A significant finding of this study is that the adhesion strength between asphalt binders and limestone or chat decreases with the addition of any of the anti-strip additives at any dosages. Therefore, it is clearly evident that anti-strip additives could be detrimental to the basic aggregates or less acidic aggregates. To this end, the free energy of adhesion was calculated for the highly acidic aggregate, namely the Georgia granite. The SFE components of the Georgia granite were obtained from Cheng et al. (2002). It was observed that the free energy of adhesion increases with the addition of anti-strip additives (see Table 4.1). The free energy of adhesion of the Georgia granite and PG 64-22 without any anti-strip additive is 101.1 ergs/cm^2. With the addition of 1.5% AD-Here HP Plus and 1.5% Redicote E-6 the free energy of adhesion increases to 114.1 ergs/cm^2 and 150.8 ergs/cm^2, respectively. Therefore, liquid anti-strip additives are beneficial for only highly acidic aggregates.

4.3 Free Energy of Adhesion between Asphalt Binder and Aggregate in the Presence of Water

The following equation was used to calculate the adhesion of asphalt binder with aggregate in the presence of water when subscripts 1, 2 and 3 represent asphalt binder, aggregate and water, respectively. Table 4.2 shows the free energy of adhesion in the presence of water. If the value of free energy of adhesion is positive, it means the two phases of the material tend to bind together and the higher magnitude of free energy of adhesion gives the higher bonding strength.

$$\begin{aligned} Adhesion = {} & 2\Gamma_3^{LW} + 4\sqrt{\Gamma_3^+\Gamma_3^-} - 2\sqrt{\Gamma_1^{LW}\Gamma_3^{LW}} - 2\sqrt{\Gamma_1^+\Gamma_1^-} - 2\sqrt{\Gamma_1^-\Gamma_3^+} \\ & - 2\sqrt{\Gamma_2^{LW}\Gamma_3^{LW}} - 2\sqrt{\Gamma_2^+\Gamma_3^-} - 2\sqrt{\Gamma_2^-\Gamma_3^+} + 2\sqrt{\Gamma_1^{LW}\Gamma_2^{LW}} + 2\sqrt{\Gamma_1^+\Gamma_2^-} + 2\sqrt{\Gamma_1^-\Gamma_2^+} \end{aligned} \tag{4.1}$$

where,

Γ_1^{LW}, Γ_1^+, and Γ_1^- = SFE components of asphalt binder,

Γ_2^{LW}, Γ_2^+, and Γ_2^- = SFE components of aggregate,

Γ_3^{LW}, Γ_3^+, and Γ_3^- = SFE components of water.

It is observed in Table 4.2 that in the presence of water, the free energy of adhesion between the limestone and asphalt binders (both PG 64-22 and PG 70-28) and between the chat and asphalt binders (both PG 64-22 and PG 70-28) decreases with an increase in the amount of anti-strip additives. This again concludes that both the anti-strip additives have detrimental effect on limestone and chat in this case in the presence of water. Comparatively, both the anti-strip additives have improved the free energy of adhesion in the presence of water between the Georgia granite and asphalt binders (both PG 64-22 and PG 70-28). This is due to the fact that the Georgia granite is a highly acidic aggregate (see Table 3.3 for its acid-base SFE components).

4.4 Moisture Susceptibility Test (AASHTO T-283)

Moisture susceptibility tests were performed on a mix design with 80% chat and 20% limestone. Samples having air voids between 7.5% and 8.5% were prepared. Three sets of samples were tested. One of the three sets has 80% chat, 20% limestone and PG 64-22 with no additive in it. The other two sets have PG 64-22 with 0.75% AD-Here HP Plus and 0.75% Redicote E-6.

Table 4.3 shows the results of the moisture susceptibility test (AASHTO T-283). It was observed that the tensile stress ratio increased with the addition of each of the anti-strip additives, AD-Here HP Plus performing better than Redicote E-6. The tensile strength ratio increased 3% with the addition of 0.75% Redicote E-6 and 7% with the addition of 0.75% AD-Here HP Plus.

Table 4.3 shows that the tensile strength of HMA without any anti-strip additive is 862.0 kPa. The addition of 0.75% AD-Here HP Plus and 0.75% Redicote E-6 reduces the tensile strength to 759.5 kPa and 746.9 kPa, respectively. This is complemental with the findings from SFE characteristics in Section 4.2 and 4.3 that addition of anti-strip additives are detrimental to limestone and chat. Therefore, liquid anti-strip additives can only improve the adhesion between highly acidic aggregate, namely granite and asphalt binders.

Table 4.1 Free Energy of Adhesion

Binder	Additive	Percent of Additive	Limestone and Binder (ergs/cm²)	Chat and Binder (ergs/cm²)	Georgia Granite and Binder[1] (ergs/cm²)
PG 64-22	No	0	113.9	100.9	101.1
	AD-Here HP Plus	0.25	109.0 107.8	99.5 98.0	105.2 104.5
		0.75	98.8 100.2	94.1 95.4	106.9 103.4
		1.5	95.4 109.8	92.3 103.6	114.1 132.5
	Redicote E-6	0.25	106.5	98.1	103.8
		0.75	101.6	96.6	109.8
		1.5	114.2	115.3	150.8
PG 70-28	No	0	113.6	102.6	105.8
	AD-Here HP Plus	0.25	111.2	101.7	107.2
		0.75	110.0	101.4	108.4
		1.5	111.4	103.2	111.7
	Redicote E-6	0.25	114.3	103.2	106.7
		0.75	110.7	102.3	108.9
		1.5	110.0	102.4	111.3

[1]The SFE components of Georgia Granite were obtained from Cheng et al. (2002)

Table 4.2 Free Energy of Adhesion in the Presence of Water

Binder	Additive	Percent of Additive	Limestone and Binder (ergs/cm²)	Chat and Binder (ergs/cm²)	Georgia Granite and Binder[1] (ergs/cm²)
PG 64-22	No	0	-90.3	-53.3	-58.1
	AD-Here HP Plus	0.25	-96.8	-56.3	-55.6
		0.75	-107.7	-62.3	-54.4
		1.5	-118.3	-71.3	-54.5
	Redicote E-6	0.25	-97.6	-56.0	-55.3
		0.75	-106.3	-61.3	-53.1
		1.5	-117.6	-66.5	-35.9
PG 70-28	No	0	-92.2	-53.1	-54.9
	AD-Here HP Plus	0.25	-95.2	-54.7	-54.1
		0.75	-96.8	-55.3	-53.4
		1.5	-97.2	-55.4	-51.9
	Redicote E-6	0.25	-92.1	-53.2	-54.7
		0.75	-95.8	-54.3	-52.6
		1.5	-98.1	-55.6	-51.7

[1]The SFE components of Georgia Granite were obtained from Cheng et al. (2002)

Table 4.3 Tensile Strength Ratio of Different HMA Mixes

Type of HMA	Type of Conditioning	Tensile Strength (kPa)	Tensile Strength Ratio (%)
HMA without Additive	Conditioned	767.4	89
	Unconditioned	862.0	
HMA with 0.75% AD-Here HP Plus	Conditioned	727.2	96
	Unconditioned	759.5	
HMA with 0.75% Redicote E-6	Conditioned	683.6	92
	Unconditioned	746.9	

5. SFE METHOD AS A TOOL FOR MEASURING MOISTURE SUSCEPTIBILITY AND CONCLUDING REMARKS

5.1 Shortcomings of the Currently Used Moisture Susceptibility Test (AASHTO T-283)

The currently used moisture susceptibility test (AASHTO T-283) for Superpave mix design has the following shortcomings when compared with the SFE method.

(1) AASHTO T-283 cannot be performed before a mix design is completed. After performing test on a very good mix design that took at least a couple of weeks to complete, it might fail to meet the AASHTO T-283 criteria. The SFE tool can be used before even the mix design tests get started.

(2) AASHTO T-283 cannot quantitatively distinguish between the performances of two anti-strip additives irrespective to the mix design. It is possible to find the better anti-strip additives from a database.

(3) The SFE method is a better method for finding optimum amount of additive, additive mixing temperature and aging susceptibility of additives than the AASHTO T-283.

(4) AASHTO T-283 does not provide any information on the acid-base characteristics of asphalt binders with and without additives. The SFE method provides quantitative changes in acid-base characteristics after adding additives to asphalt binders.

(5) In this study it was found that different mineralogy of aggregates provides a wide range of SFE values. In AASHTO T-283, a mix design has several types of aggregates of different mineralogical types. Therefore, it is not possible to directly identify an

aggregate responsible for possible moisture-induced susceptibility using AASHTO T-283.

(6) The SFE method clearly identifies an aggregate to be acidic or basic whereas, AASHTO T-283 does not.

(7) The SFE method provides information on moisture-induced damage potential of aggregates, asphalt binders and anti-strip additives irrespective of a mix design. Therefore, a database of SFE characteristics of commonly used aggregates, asphalt binders and anti-strip additives will be able to provide information on moisture susceptibility of a mix design yet to be performed. The AASHTO T-283 comments just on a particular mix design.

(8) Finally, the SFE method is a basic and fundamental approach. It provides detailed rheological information on moisture induced damage performance whereas, AASHTO T-283 is a poorly performing performance test.

5.2 SFE Method as a Tool for Measuring Moisture-Induced Damage Susceptibility

The following paragraphs briefly describe the effectiveness of the SFE method as a tool for measuring moisture-induced damage susceptibility based on the results of this study. The results obtained in this study are very promising.

SFE of Asphalt Binder

Anti-strip additives have significant influence on the SFE of asphalt binders which can be evaluated using the SFE method. SFE increases with an increase in anti-strip additives. It was observed in this study that 1.5% AD-Here HP Plus and 1.5% Redicote E-6 increased the total

SFE of PG 64-22 by 67% and 208%, respectively, whereas, the corresponding increases in total SFE of PG 70-28 are 23.6% and 24.4%, respectively. Increased SFE promotes adhesion between asphalt binder and highly acidic aggregate against moisture-induced damage.

Acid-Base Characteristics of Asphalt Binder

Acid-Base characteristics of asphalt binders, with and without anti-strip additives were evaluated in this study, focusing on the moisture-induced damage potential of acidic aggregates using the SFE method. The acid component of SFE of PG 64-22 and PG 70-28 are 2.9 dyne/cm^2 and 2.5 dyne/cm^2, respectively, whereas, the corresponding base components are 0.4 dyne/cm^2 for both. Basic chemical compounds such as amines, in the form of anti-strip additives, are found to reduce the acid component and increase the base component of asphalt binders, thereby improving the adhesion between acidic asphalt binder and highly acidic aggregate. With the addition of 0.75% AD-Here HP Plus and 0.75% Redicote E-6 in PG 64-22, the acid component is reduced as much as 67% and 65%, respectively. The corresponding increases in base components are 86% and 105%. A similar trend is observed with respect to the acid-base characteristics of PG 70-28.

SFE of Aggregates

The SFE of limestone and chat are 166.6 ergs/cm^2 and 132.2 ergs/cm^2, respectively. The higher surface energy of limestone provides better adhesion strength between the limestone and asphalt binders than the chat and asphalt binders.

Acid-Base Characteristics of Aggregates

The basic component of SFE of the limestone and chat are 390.8 ergs/cm^2 and 219 ergs/cm^2, respectively. The higher basic component of the limestone promotes the adhesion strength between basic limestone and acidic asphalt binders.

Free Energy of Adhesion

It was found in this study that the free energy of adhesion (adhesion strength) between asphalt binders and highly acidic aggregate increases with an increase in additive content. Also, basic limestone provides better adhesion than acidic chat with acidic asphalt binder.

Free Energy of Adhesion in the Presence of Water

The free energy of adhesion in the presence of water between limestone and binder and between the chat and binders decreases with an increase in the amount of anti-strip additives. It is evident from this study that liquid anti-strip additives could be detrimental for basic or less acidic aggregates. Comparatively, liquid anti-strip additives increase the free energy of adhesion between the Georgia granite (highly acidic) and asphalt binder.

5.3 SFE Approach – An Alternate Method?

The results obtained in this study are very promising as mentioned in the above section. It is a valid method for predicting moisture-induced damage potential. Based on this study, the authors recommend the SFE method be considered as a complemental tool for predicting moisture-induced damage potential. A database should be developed consisting of the SFE components of commonly used aggregates, asphalt binders and anti-strip additives in addition to those evaluated in this study. This database will provide pre-design data on which aggregate, asphalt binders and anti-strip additives need to be used for any particular mix design. AASHTO T-283, a performance test, should be performed to check the design for moisture susceptibility.

Also, the SFE method and the SFE database should be used to find why a particular mix is failing or performing poorly. It should be used as a research tool to evaluate aggregates, asphalt binders and anti-strip additives for acid-base characteristics and moisture-induced damage potential. The main reason to consider it as only a research tool at this stage is because it needs extreme care in sample preparation, data analyses and interpretation.

5.4 Recommendations for Future Research

The following recommendations can be made based on the findings of this study.

(1) The liquid anti-strip additives are highly temperature susceptible. Therefore, additive mixing temperature and heating period should be taken into considerations for future research.

(2) Both short term aging and long term aging effects on anti-strip additives should be evaluated.

(3) Pretreatment aggregate should be evaluated in future research. Therefore, other anti-strip additives such as lime and Ultracoat should be considered for SFE evaluation.

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APPENDIX A

Table A.1 Weight Data Obtained for Limestone Using Water

Time (min.)	Weight (gm)	Weight Change (%)	Temperature (°C)	Relative Humidity (%)
600.7	40.8371	0.000	25.31	3.07
927.2	40.8472	0.025	25.31	5.20
1162.5	40.8544	0.042	25.30	9.97
1335.3	40.8652	0.069	25.31	20.01
1537.8	40.8759	0.095	25.30	29.94
1758.8	40.8863	0.120	25.30	39.79
2031.1	40.8979	0.149	25.30	49.95
2333.7	40.9117	0.183	25.30	60.18
2636.7	40.9304	0.228	25.28	69.88
2938.7	40.9560	0.291	25.30	80.36
3241.7	40.9918	0.379	25.30	90.32
3544.7	41.0223	0.453	25.31	94.94

Table A.2 Weight Data Obtained for Limestone Using MPK

Time (min.)	Weight (gm)	Weight Change (%)	Temperature (°C)	Relative Humidity (%)	Time (min.)
600.2	40.786228	0.000	25.26	38.67	10
900.3	40.829899	0.107	25.29	40.73	10
1074.6	40.839859	0.131	25.27	40.52	20
1267.2	40.848202	0.152	25.28	40.32	30
1478.1	40.855606	0.170	25.29	40.37	40
1589.7	40.861160	0.184	25.29	40.23	50
1741.6	40.866947	0.198	25.29	40.17	60
1858.1	40.872704	0.212	25.29	40.13	70
1982.6	40.877880	0.225	25.29	40.02	80

Table A.3 Weight Data Obtained for Limestone Using n-Hexane

Time (min.)	Weight (gm)	Weight Change (%)	Temperature (°C)	Relative Humidity (%)	Time (min.)
600.2	40.790359	0.000	25.28	40.50	5
900.4	40.789028	-0.003	25.30	42.36	5
946.6	40.788887	0.000	25.29	42.28	10
1031.0	40.807423	0.045	25.28	41.55	20
1200.5	40.818367	0.072	25.30	39.10	30
1226.8	40.826740	0.093	25.32	38.10	40
1250.7	40.832920	0.108	25.33	37.17	50
1354.8	40.840244	0.126	25.37	37.34	60
1571.9	40.842815	0.132	25.37	35.73	70
1719.0	40.847565	0.144	25.39	34.86	80
1808.4	40.851978	0.155	25.39	35.49	90
2108.5	40.819550	0.075	25.30	40.69	95

Table A.4 Weight Data Obtained for Chat Using Water

Time (min.)	Weight (gm)	Weight Change (%)	Temperature (°C)	Relative Humidity (%)	Time (min.)
300.7	61.0874	0.000	25.37	1.87	300.7
386.7	61.0928	0.009	25.31	9.74	386.7
467.6	61.0997	0.020	25.31	19.75	467.6
548.5	61.1065	0.031	25.31	30.03	548.5
627.2	61.1135	0.043	25.30	40.03	627.2
709.3	61.1210	0.055	25.30	49.85	709.3
807.9	61.1307	0.071	25.31	59.87	807.9
939.5	61.1446	0.094	25.30	69.76	939.5
1162.6	61.1684	0.133	25.37	80.11	1162.6
1666.3	61.2220	0.220	25.34	89.80	1666.3
2169.9	61.2723	0.303	25.35	95.12	2169.9

Table A.5 Weight Data Obtained for Chat Using MPK

Time (min.)	Weight (gm)	Weight Change (%)	Temperature (°C)	Relative Humidity (%)	Time (min.)
600.2	39.910603	0.000	25.24	38.37	10
900.4	39.934944	0.061	25.27	40.40	10
1063.2	39.940300	0.074	25.25	40.07	20
1195.6	39.944542	0.085	25.24	39.89	30
1299.1	39.948296	0.094	25.26	39.83	40
1386.6	39.951649	0.103	25.26	39.69	50
1498.8	39.955242	0.112	25.27	39.69	60
1614.4	39.959244	0.122	25.27	39.73	70
1772.2	39.963661	0.133	25.29	39.88	80

Table A.6 Weight Data Obtained for Chat Using n-Hexane

Time (min.)	Weight (gm)	Weight Change (%)	Temperature (°C)	Relative Humidity (%)	Time (min.)
300.2	61.156036	0.000	25.07	33.32	10
397.9	61.169453	0.022	25.14	34.22	10
463.5	61.177025	0.034	25.12	33.59	20
518.5	61.183285	0.045	25.21	32.86	30
545.4	61.188427	0.053	25.15	32.02	40
567.1	61.193542	0.061	25.21	31.30	50
589.1	61.198921	0.070	25.24	30.87	60
609.6	61.204556	0.079	25.19	30.49	70
627.6	61.210308	0.089	25.21	29.82	80
644.8	61.217361	0.100	25.25	29.43	90
674.4	61.222641	0.109	25.28	28.99	95

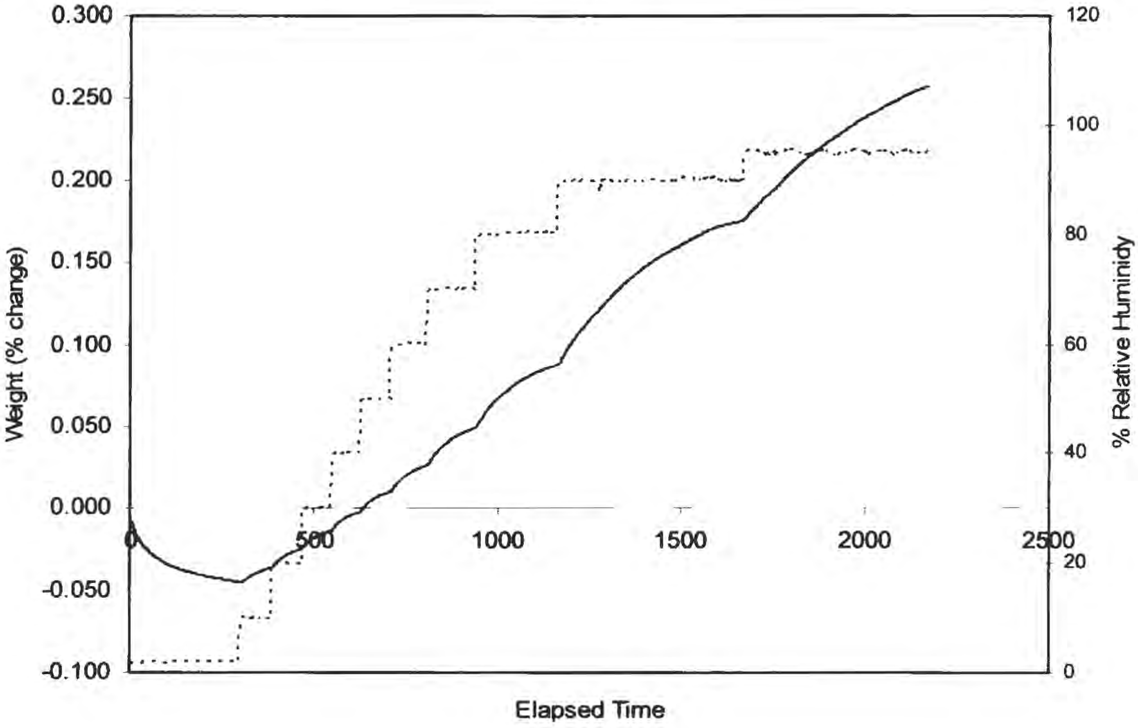

Figure A.1 Formation of Plateau (Equilibrium) at Each Relative Humidity Step

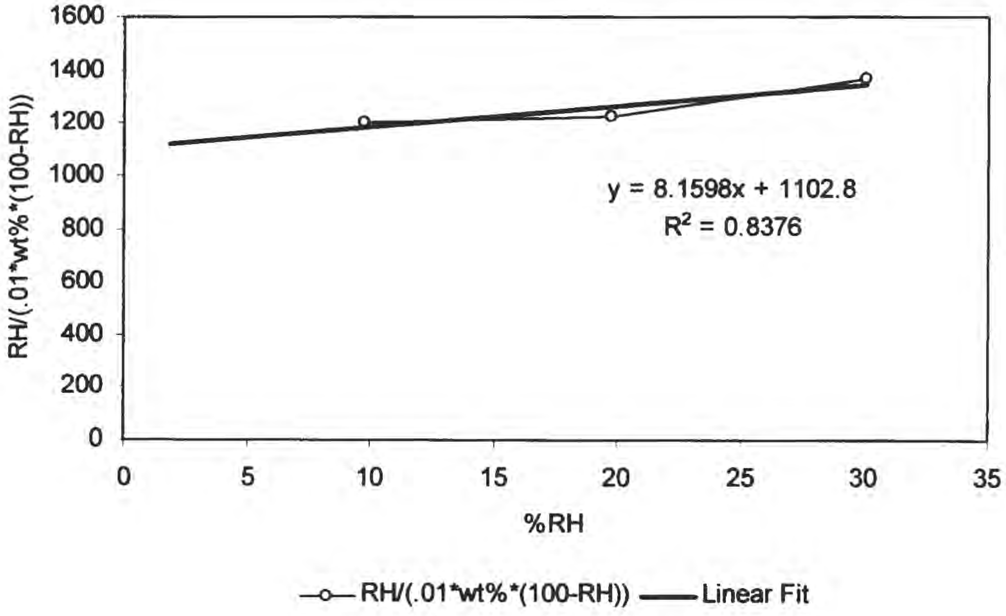

Figure A.2 BET Curve of a Sample Aggregate