



Royal Institute of Technology

DEPARTMENT OF
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ON INVESTIGATION OF STRIPPING PROPENSITY OF BITUMINOUS MIXTURES

Licentiate Thesis

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Abstract

In this study, an experimental programme was designed to establish a relationship between bituminous mixture constituent material properties and their propensity to moisture induced damage in form of stripping. Six bitumen types (3 from Uganda and 3 from Sweden) with presumably varying characteristics were evaluated basing on rheology and chemistry. Eleven aggregates were used in this study. Seven were sourced from active quarries in Uganda and four were from Sweden.

Bitumen rheology was established basing on penetration, softening point, viscosity, ductility and visco-elastic parameters obtained from dynamic mechanical analysis. Bitumen chemistry was studied using Fourier Transform Infrared Spectroscopy, Gel Permeation Chromatography (GPC) and Thin Layer Chromatography (TLC).

Bituminous mixtures were reconstituted from the bitumen and aggregate combinations basing on the Swedish mix design procedure ROAD 94 using dense graded mixtures with 16mm maximum aggregate size (AG16). Mixture sensitivity to moisture was evaluated basing on Swedish FAS 446-98 specifications closely related to the modified Lottman procedure.

The investigation was done in two phases namely, (a) the effect of aggregate properties on mixture moisture sensitivity and (b) the of cross effects of bitumen and aggregates on mixture moisture sensitivity.

The results reveal chemical compositional differences in bitumens that would be considered similar basing on classical rheological properties like penetration and viscosity. Results of dynamic mechanical analysis show that binders have similar visco-elastic response around 0°C. This could be a potential phenomenon to serve as a grading scheme for bitumen as is the case with penetration and viscosity grading systems.

The results from phase I of the study show that presence of Ca-feldspars and ferromagnesian minerals in aggregates largely relates to improved resistance of mixtures to moisture damage. In addition, mixtures from aggregates with high concentrations of acid insolubles (SiO_2 and Al_2O_3) are sensitive to moisture damage.

The results of phase II of this study show that the choice of aggregate type is the dominant factor affecting moisture sensitivity of the resulting mixtures. Bitumen type seems not to be an important factor in determining moisture sensitivity of bituminous mixtures. Aggregates with Ca-feldspars and ferromagnesian minerals seemed to be the most resistant to moisture damage irrespective of the bitumen type.

Assessment of moisture sensitivity basing on absolute stiffness values of water treated mixtures seems not to be reliable. Results from this study show that mixtures with similar wet resilient moduli had varying tensile strength ratios, hence varying moisture sensitivity tendencies. Modulus of resilience ratio (MRR) and tensile strength ratio (TSR) parameters show similar trends in comparing moisture sensitivity of different mixtures. However, MRR values are generally lower than TSR values for the same mixtures.

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1 INTRODUCTION

1.1 Background

In recent years, many mileages of roadway worldwide have been replaced prematurely, due to moisture-induced damage in form of stripping. Stripping causes loss of adhesion at the bitumen-aggregate interface due to action of water (Fromm, 1974; Taylor et al., 1983; Kiggundu et al., 1988; Kandhal et al., 1989). The strength is impaired since the mix ceases to act as a coherent structural unit. Loss of adhesion also renders cohesive resistance of the interstitial bitumen body useless (Kiggundu, 1988). Water may enter the interface through diffusion across bitumen films, seepage in film microvoids, and by direct access in partially coated aggregates or may be resident in aggregate pores prior to mixing (Stuart, 1990; Fwa et al., 1994). The process of stripping is illustrated in Figure 1.1. Bitumen molecules with heteroatom containing functional groups orient and adsorb onto the aggregate adsorption sites. When water enters the interface, it interferes with the bond in some mixtures and causes bitumen to strip off from the aggregate surface.

Stripping is discerned through raveling, flushing, localized bleeding, and others. Theories and causative mechanisms of stripping are complex and still speculative. Most publications attribute stripping to variables like bitumen chemical and rheological properties, aggregate surface chemistry; morphology and adsorbed coatings, pH at the interface, traffic, construction practice; and presence and nature of antistripping additives. For quite some time, stripping effects have been reported and several research efforts have sought solutions to the problem (Rice, 1958; Brown, 1959; Majidzadeh et al., 1968; Tunncliffe et al., 1982; Petersen, 1984; Takallou, 1984; Parker et al., 1987; Jimenez, 1990, etc.). Nevertheless, the fundamental causes of stripping are poorly understood, and the problem is still persistent.

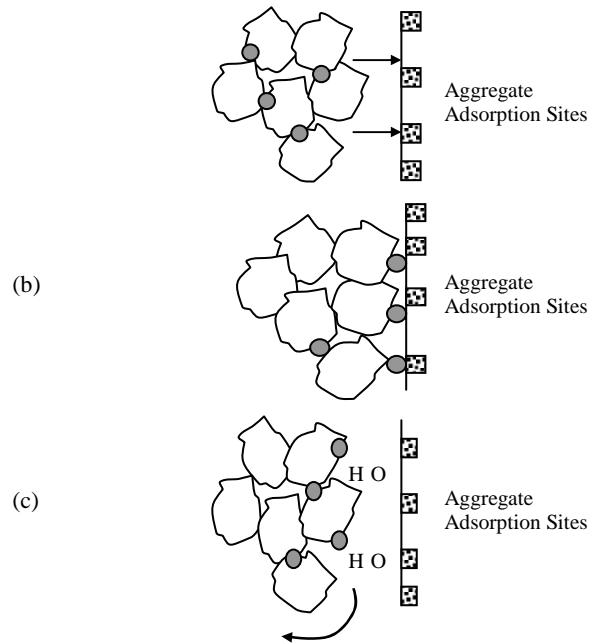


Figure 1.1: (a) Heteroatom Containing Bitumen parts move towards the Aggregate sites (b) Bitumen Adsorbed onto Aggregate (c) Stripping due to Water at the Interface

The need for perpetual and long serving pavements along with rapidly changing technology challenges the research fraternity. With the rapid infrastructural development that has occurred over the last decade in Uganda, there has been high traffic growth within and between cities around Lake Victoria region.

This region receives high rainfall for more than half of the year (average annual rainfall is 1,500mm). Many bituminous surfaces in this region always manifest rapid damage during and shortly after rainy seasons where aggregates clearly separate from bitumen (Cf. Figure 1.2). This observation raises speculation that on these roads, there is a possible link between damage and bitumen-aggregate adhesive bond weakening through stripping.



Figure 1.2: Signs of Moisture Damage in a Paved Surface Located in Kampala City, Uganda

If this explanation is true, we should observe reduced strength in bituminous mixtures obtained from component materials if they are soaked in water. In order to test this hypothesis, research was undertaken to examine the stripping propensity of bituminous mixtures used in Lake Victoria region. The said mixtures were made from bitumen got from several sources and aggregates from active quarries around the region. In addition, four aggregates from Sweden were included to strengthen directional effects and widen variability in characteristics. Bitumen was characterized basing on mechanical and chemical properties. The aggregates were characterized basing on their mineralogy and chemical composition. After reconstitution of bituminous mixtures from these component materials, possible loss of strength (tensile strength and resilient modulus) due to water conditioning was evaluated to establish their moisture sensitivity.

1.2 Research Objectives

The major aim of this research effort was to investigate pavement performance through studying the stripping propensity of bituminous roads around Lake Victoria in Uganda. Specifically, the study aimed at achieving the following objectives:

- a) Evaluate the effects of bitumen rheology and chemistry on moisture sensitivity of mixes used around Lake Victoria in Uganda, and
- b) Study the effect of composition of aggregates (chemical and mineralogical) from active quarries around L. Victoria on moisture sensitivity of bituminous mixtures.

1.3 Significance of the Study

An understanding of chemical interactions at the bitumen-aggregate interface that are water susceptible in combination with knowledge of adsorption behavior onto aggregate helps in predicting water sensitive mixtures. Avoiding such mixtures would pave way to enhanced road performance. This study has significantly enriched the loopholes in the prevailing mass of knowledge on bituminous material composition and interrelationship during performance in Uganda. It would also form a basis for rationalism in material selection and mix design. All these targets are in line with Uganda's Ministry of Works, Housing and Communication's (MoWHC) policy of having safe and efficient roads to support government's Poverty Eradication Action Plan (PEAP) and research leading to improved inventory of local construction materials and where applicable improvement of pavement materials using synthetic additives (MoWHC's Budget Policy Statement FY 2002/2003).

2 LITERATURE REVIEW

2.1 Introduction

A review of available information was made and this section highlights the past and present research on fundamental concepts of stripping. It focuses on hot mixes although the concepts are at least equally important in cold mixes.

2.2 Properties of Bitumen

The use of bitumen is reflected in many applications and dates back to ancient times. In bituminous mixes, bitumen holds the aggregates forming a mass that supports high stresses. It is crucial that strong and durable interfacial bonds exist under all conditions. Depending on how bitumen interacts with aggregate, stripping may affect this desirable precept. Since the early 1970s, there has been a general claim that bitumen is of lessened performance quality due to increase in truck traffic, the 1973 Arab oil embargo, the 1972 Clean Air Act which increased dust coatings, increased use of vibratory rollers in lieu of pneumatic tired ones, switch to drum mixers, and use of Open Graded Friction Courses on improperly compacted dense mixes (Smith, 1992, Kandhal et al., 2001; Kandhal, 2001). To enhance moisture damage resistance, it is necessary to explore techniques of improving bitumen quality.

2.2.1. Chemical Composition

The chemistry occurring at the interface strongly relates to stripping. Bitumen chemistry previously alluded to the classical colloidal model by Nellenstyn. This model considers bitumen as a colloid of asphaltenes (n-pentane insolubles) in saturated oils under peptization by resins to preclude

coagulation. The Strategic Highway Research Program (SHRP) developed a better “microstructural model” reliant on size, polarity and number of molecular groups, which made the previous model obsolete (Jones et al., 1992; Branthaver et al., 1993). The latter considers bitumen as a single-phase homogeneous mix of molecules, which are either polar or non-polar. The non-polar molecules serve as a solvent moiety in which the polars “float” with associations occurring at the polar sites (Jones, 1992). Fundamentally, bitumen mainly consists of hydrocarbons with heteroatom containing polar functionalities as well as organometallic complexes of iron, vanadium and nickel. Inherent complex combinations exist with the basic chemical building blocks being aliphatic, alicyclic and polyaromatic moieties (Jeon et al., 1990). Examples of functionalities include polynuclear aromatics, phenolics, pyrrolics, pyridinics, 2-quinolones, sulfoxides, sulfides, ketones, anhydrides, and carboxylics (Petersen et al., 71; Petersen et al., 1974; Petersen et al., 1974, Petersen, 1975). Functionalities govern intermolecular interactions and give rise to characteristic behavior. The interactions are through hydrogen bonding, π - π bonding and Van der Waals forces, which reduce the surface area of bitumen in contact with an aggregate. Upon heating or shearing, these interactions are destroyed enabling wetting of the aggregate. Analytical tools commonly used to characterize bitumen chemistry are summarized in Table 2.1.

Several studies showed that bitumen polars have different adsorption powers on aggregate active sites (Plancher et al., 1977; Ensley et al., 1984; and Curtis et al., 1990). During bonding, the polars form a layer at the interface distinct from the bulk bitumen. The bond strength depends on the relative tendency of the functional groups to adsorb at the aggregate surface, and relative desorption by water. Considerable work on this aspect is documented (Petersen et al., 1982; Curtis et al., 1991; Curtis, 93; and

Table 2.1: Analytical Methods Used in Characterizing Bitumen Chemistry

| Analytical Tool | Reported Parameter |
|--|---|
| Chemical Precipitation (Rostler and Sternberg ASTM D2006) | Asphaltenes, nitrogen bases, 1 st acidaffins, 2 nd acidaffins and paraffins. |
| Adsorption/desorption chromatography (Corbett ASTM D4124) | Asphaltenes, polar-aromatics, naphthene-aromatics and saturates. |
| Elemental Analyses | C, H, N, S, O, Trace metals (e.g. V, Ni) |
| Solvent precipitation (Schweyer and Taxler) | Asphaltics, Paraffinics, Cyclics. |
| Gel Perm. Chromatography (ASTM D2007) | Molecular weight distribution |
| Thin Layer Chromatography | Saturates, aromatics, resins, asphaltenes |
| Size Exclusion Chromatography | Separates basing on molecular size |
| Ion Exchange Chromatography | Strong acids, strong bases, weak acids, weak bases, and neutral fraction (amphoterics) |
| Infrared Spectroscopy | Functional groups |
| Ultraviolet-visible Spectroscopy | Characterization of generic fractions |
| Gas Chromatography | Volatile fractions |
| Supercritical fluid chromatography | Nonpolar fraction |
| X-ray diffraction | Crystalline fractions |
| Nuclear Magnetic Resonance | Saturate/aromatic carbon ratio, content of carboxylics, phenol & benzylic fractions and generic compositions. |
| High pressure liquid chromatography | Fractions related to moving phase |

Petersen et al., 1998). A summary of ranking of polars' affinity to adsorb onto and desorb from dry and wet mineral surfaces respectively is extracted from results of previous studies and summarized in Table 2.2. These studies used model functionalities similar in behaviour to bitumen polars and model surfaces similar in behaviour to aggregates.

Table 2.2: Adsorptive/Desorptive Behavioral Rankings of Bitumen Polars from Various Studies.

| Researcher /year | Rankings of Relative Adsorptions onto Dry Aggregate Surface by Bitumen Polar Groups | | | | | | | | | |
|-----------------------|--|-----------|-------------|-----------|----------|----------|--------|--------|--|--|
| | -COOH | Anhydride | 2-Quinolone | Sulfoxide | Pyridine | Pyrrolic | Ketone | Phenol | | |
| Plancher et al., 1977 | 1 | 2 | 3 | 4 | 5.5 | 5.5 | 7 | NT | | |
| Petersen et al., 1982 | 2 | 3 | 4 | 6 | 1 | 8 | 7 | 5 | | |
| Petersen J. C., 1986 | 1 | 2 | 3 | 5.5 | 8 | 7 | 5.5 | 4 | | |
| Curtis et al., 1990 | 2 | NT | NT | 1 | 3 | 6 | 5 | 4 | | |
| Curtis et al., 1993 | 2 | NT | NT | 1 | 3 | 6 | 5 | 4 | | |
| Researcher /year | Rankings of Relative Water Displacement From Aggregate Surface of Bitumen Polar Groups | | | | | | | | | |
| | -COOH | Anhydride | 2-Quinolone | Sulfoxide | Pyridine | Pyrrolic | Ketone | Phenol | | |
| Plancher et al., 1977 | 1 | 2 | 6 | 3 | 4.5 | 4.5 | 7 | NT | | |
| Petersen et al., 1982 | 1 | 2 | 4 | 3 | NT | 6 | 5 | 7 | | |
| Petersen J. C., 1986 | 1 | 2 | 3 | 4 | NT | 6 | 5 | 7 | | |
| Curtis et al., 1990 | 2 | 2 | NT | 1 | 5 | 3 | 4 | 6 | | |
| Curtis et al., 1993 | 2 | 2 | NT | 1 | 5 | 3 | 4 | 6 | | |

NT = Note tested by the respective researcher (s)
Ranking of bitumen polars for each researcher refers to giving the groups an order depending on the ease of adsorption onto and desorption from aggregate surfaces.

W equals one for perfect agreement and zero for total mismatch between rankings. Similar rankings of bitumen polar functionalities are averaged.

$$W = \frac{S}{\frac{1}{12} K^2 (N^3 - N)} \quad \text{where} \quad S = \sum_{j=1}^N \left(R_j - \frac{\sum R_j}{N} \right)^2 \dots\dots\dots(2.1)$$

K = Number of rankings, N = Number of functional groups, and R_j = Sum of ranks for the jth functional group.

A statistical analysis of these rankings gives W = 0.502 for dry adsorption and 0.560 for wet desorption of the polars. These values show a slightly above average correlation between the rankings. Thus, there is much need for continued research using better tools until a more accurate polar ranking is attained. It is noted that the most strongly adsorbed polars (carboxylics, anhydrides and sulfoxides) are the most sensitive to water. Highest resistance to stripping seems to be associated with nitrogen bases (especially pyridinics), phenolics and ketones. Water has stronger hydrogen bonding with some aggregate surfaces compared to the carboxylics. This may be the reason why the latter are easily desorbed. Carboxylics also interfere with bonding of nitrogen bases with aggregate. The Western Research Institute at Laramie, Wyoming, USA, is developing a system to simulate displacement of polars by water. Caustic treatment of crude oil is reported to give bitumen that is prone to stripping (Petersen, 1986). This alludes to formation of acid salts that concentrate at the interface and for some aggregates, adhesive bond weakening becomes imminent.

2.2.2. Rheological Properties

Proper adhesion at the interface requires good control of bitumen rheological properties during mixing and appropriately maintaining them during service. Of particular interest is viscosity-temperature susceptibility during the

mixing, placement and compaction operations. High viscosity is associated with poor bitumen wettability of the aggregate. Viscosity measures molecular mobility and magnitude of intermolecular attractive forces in bitumen. Shell recommends a viscosity range of 0.2-0.5 Pa.s for proper coating and absence of drain-off during storage and transportation (Whiteoak, 1991). During service, high viscosity offers more resistance to moisture damage than the converse (Majidzadeh et al., 1968, Hicks, 1991). A high concentration of polars is associated with high viscosity, hence increased resistance to moisture damage.

2.3. Properties of Aggregates

Many studies have authenticated reliance of stripping on aggregate chemistry, mineralogy and surface morphology (Kiggundu, 1986; Dukatz, 1989, Kandhal, 1998). These properties affect surface energy and chemical reactivity, and hence the positions and amounts of bonding sites (metal ions or charged species). Aggregates show chemical inhomogeneity resulting from oxidation, coatings, adsorbed films, ledges, kinks, dislocations and crystallographic anisotropy. The charged aggregate surface attracts and orients bitumen polar molecules.

2.3.1. Mineralogy

Mineralogical composition is a natural precursor of complex processes at the aggregate surface and affects relative affinity for water and bitumen. Aggregate minerals induce surface charge and a material that better satisfies the ensuing energy demand adheres more tenaciously. Aggregates are composed of numerous minerals and each has a definite chemical composition and crystalline structure. Natural aggregate minerals can be put

under five broad categories. These minerals and their relations to stripping are summarized in Table 2.3.

Table 2.3: Mineral Types and Their Relation to Stripping

| Category | Mineral Type | Rock | Comment | Reference |
|-----------------|---|--|--|--|
| Silica | Quartz - SiO_4 | Granite Rhyolite Sandstone Quartzite | Poor adherends as water attaches due to H-bonding. | (Rice, 1958; Majidzadeh et al., 1968; Stuart, 1990) |
| Ferro-magnesian | Olivine - $(\text{MgFe})_2\text{SiO}_4$ Augite - $(\text{Ca,Mg,Fe})(\text{Si,Al})_2\text{O}_6$ Hornblende - $(\text{Ca,Na})_2\text{-}_3(\text{Mg,Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_5(\text{Al,Si})_8\text{-O}_{22}(\text{OH})_2$ Biotite - $\text{K}(\text{Mg,Fe}^{2+})_3(\text{Al,Fe}^{3+})\text{-Si}_3\text{O}_{10}(\text{OH})_2$ | Gabbro Diabase Andesite Basalt Diorite Mica | Olivine and augite form insoluble Mg and Ca salts while biotite gives soluble K salts. Hornblende is intermediary in character. | (Rice, 1958; Majidzadeh et al., 1968; Stuart, 1990) |
| Limestone | Calcite – CaCO_3 Dolomite – $\text{CaMg}(\text{CO}_3)_2$ | Limestone Chalk Dolomite | Generally good adherends but are friable. Undergo strong acid-base and electrostatic interactions with bitumen. Some have soluble salts. | (Curtis, 1990; Stuart, 1990) |
| Feldspar | Albite - $\text{NaAlSi}_3\text{O}_8$ Orthoclase - KAlSi_3O_8 Anorthite - $\text{CaAl}_2\text{Si}_2\text{O}_8$ | Rhyolite Granite Quartzite Gneiss Sandstone Diabase Gabbro | Some strip due to Na and K soluble salt formation. Anorthite forms insoluble Ca salts that are resistant to stripping. | (Scott, 1978; Stuart, 1990) |
| Clays | Illite Kaolinite Montmorillonite | Dust Baghouse fines | Fine coatings ($< 4\mu$) and readily take up water. Form stable bonds lime. | (Clough, 1961; Ishaï et al., 1972, Balghunaim, 1991, Kandhal et al., 1998) |

2.3.2. Chemical Composition

Chemical composition determines surface chemistry and morphology of aggregates. SHRP A-003B showed that adsorption of bitumen onto aggregates is influenced by aggregate chemistry. Aggregates provide electrostatic and Lewis acid/base sites for interaction with bitumen polars (Curtis et al., 1992; Jeon et al., 1990). Bonding studies have shown that bitumen adsorbing groups are mainly naphthenic acids. Basic aggregates should therefore form stronger bonds with bitumen. Fromm (1974), reported that stripping is high in mixes with acidic granites with hydroxylated SiO_4 . Table 2.4 lists dependence of pH on mineralogy for igneous rocks. With regard to stripping, Fe, Ca, Mg and Al are generally beneficial, while alkali metals are detrimental (Stuart, 1990). Bitumen acidic polars (carboxylics and phenols) form stripping prone soluble salts with alkali metals. The concept of an aggregate being either absolutely basic or acidic is non-existent. The degree of acidity or basicity is expressed as the ratio of acidic component (SiO_2) to the basic one (mainly CaO, and Al_2O_3 , Fe_2O_3 , MgO, Na_2O , plus K_2O). Scott, (1978) and Masson et al., (1998) show that aggregates affect aqueous phase pH. Carbonates and granites raise pH of water if in contact. Silica reduces pH due to release of H^+ ions by the surface silanols.

Table 2.4: Degree of Acidity of Igneous Rocks (Stuart, 1990)

| | Acidic < -----> Basic | | | |
|----------------|--------------------------------------|------------------------------|--|--|
| Quartz | > 10 | 0 - 10 | Generally <5 | Usually Absent |
| Feldspar | Orthoclase | Orthoclase Na-Plagioclase | Na-plagioclase (Albite) | Ca-plagioclase (Labradorite, Anorthite) |
| Other minerals | Biotite, Hornblende, Muscovite | Some Biotite, Hornblende | Biotite + Hornblende + Pyroxene < 40% | Biotite + Hornblende + Pyroxene + Olivine > 40% |

2.3.3. Physical Properties

Figure 2.1 presents a summary of the effects of aggregate physical properties on the resistance (level 1) and susceptibility to stripping (level 2) as well as a test for the property (level 3). These three levels are given in the dotted areas in a box under each property.

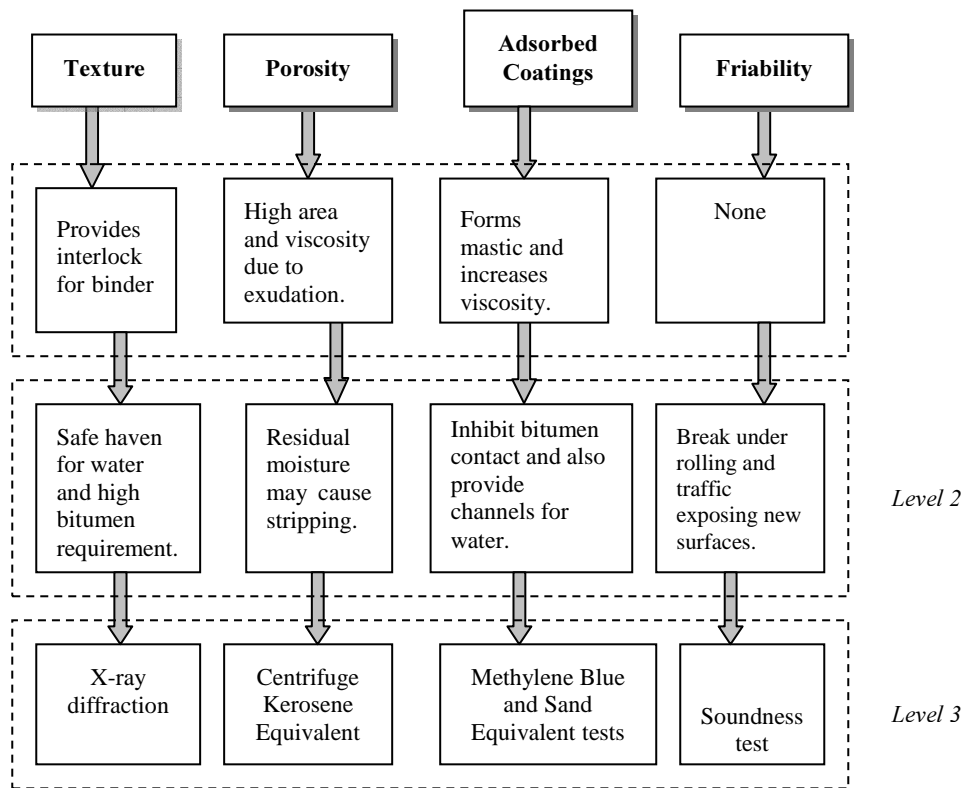


Figure 2.1: Summary of Aggregate Physical Properties and how they affect Stripping

2.4. Properties of Water

Water exhibits hydrogen bonds that affect its adhesive and cohesive characteristics. Adhesion affects capillarity while cohesion affects surface

tension. Since most aggregate surfaces have electrostatic charges, water molecules are attracted to them with stronger forces than bitumen polars to satisfy unbalanced surface charges. Adhesion is strongly affected by pH of contact water which changes with temperature (Covington et al., 1977). The pH causes a shift in angle of contact and significantly affects the wetting properties of bitumen. Weak acids affect some aggregate minerals like alkali feldspars. For example, if orthoclase (KAlSi_3O_8) comes in contact with H_2CO_3 , it forms kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, a fine insoluble residue that becomes part of the interface. The other products are soluble species which weaken the interfacial bond (Scott, 1978). Kiggundu et al., (1986) showed that interfacial tension is highest at intermediary pH values (up to 9) and drops with increase of pH to 14. The effect of water at the interface is aggregate specific. Calcareous aggregates give free Calcium ions forming strong water resistant bonds with bitumen. Siliceous aggregates (with SiO_2) form weak bonds with bitumen, which are hydrolytically unstable. Water preferentially adsorbs onto aggregates with surface hydroxyls forming $(-\text{SiOH})_n \cdots (\text{H}_2\text{O})_n$, through hydrogen bonding.

2.5. Traffic Effects

During service, there is frequent interaction between the vehicle wheel and the pavement. Traffic action increases pore water pressure in the void pockets of the mixtures, particularly in undrained conditions (pessimum voids). Traffic stresses can also directly rupture thin bitumen films, especially around sharp aggregate corners. These ruptures act as avenues for moisture into the interface. The effect of traffic is supported by the usual occurrence of stripping first in the outer traffic lanes compared to the inner lanes (Kandhal, 1992). Desirably however, traffic compaction in the early

stages of HMA reduces the air voids and permeability through densification, thereby reducing stripping propensity.

2.6. Wetting and Adsorption

Proper wetting and adsorption of bitumen onto aggregate determines the potential of stripping of a bituminous mixture. When hot bitumen contacts an aggregate, it spreads depending on the contact angle θ . Wetting is governed by the forces of attraction between bitumen and aggregate. In 1805, Thomas Young offered considerable insight into wetting phenomena. He related surface tension (γ) to the contact angle for smooth, non-deformable, insoluble homogeneous solids. The shortfalls of his efforts were inability to account for external fields, consideration of reaction kinetics between contacting species and poor modeling of ridging on aggregate surfaces. Equilibrium on rough surfaces was studied by Wenzel who improved Young's earlier work culminating in Equation 2.2 (Asthana et al., 2000).

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_w (1/r) \dots\dots\dots(2.2)$$

where r is the ratio of true ridged area to the apparent flat area, S = solid, L = liquid, V = vapor and θ_w is Wenzel contact angle. Wetting is determined by Work of Adhesion, W_a , which was formulated by Dupre in 1869 as given in Equation 2.3.

$$W_a = \gamma_{LV} [1 + \cos \theta_w (1/r)] \dots\dots\dots(2.3)$$

If a system shows low W_a , it has good tendency for bitumen to wet the aggregate. This requires low γ_{LV} and high θ_w . Experimental evaluation of surface tension, contact angle, θ , and surface energy is well documented (Taylor et al., 1952, Cheng et al., 2002).

Consider a system made of bitumen (a), aggregate (b) and an infinitesimal interface (s). After bitumen has coated the aggregate, the two exist in equilibrium and the total free energy of the system is given by $F = F_a + F_b + F_s$ (Majidzadeh et al., 1968). When a small reversible change takes place in temperature (T), pressure (p), interfacial area (A) and composition of ith material n_i , the system energy changes by $dF = dF_a + dF_b + dF_s$ (Majidzadeh et al., 1968). Mcglashan, (1979) shows that the total change in system free energy is given by Equation 2.4 below.

$$dF = -SdT + Vdp + \gamma dA + \sum_i \mu_i dn_i \dots\dots\dots(2.4)$$

where S is the entropy, V is the volume, γ is the surface tension and μ_i is the chemical potential of component i. When water enters the system, it may change the composition and area. An energy change, like the one in Equation 2.4, takes place with a shift towards a more thermodynamically stable state of minimum energy. If water has a lower free energy than bitumen, it replaces the bitumen from the aggregate. Lytton, (2002) shows that interfacial surface free energy (SFE) is divided into an apolar and an acid-base component. The apolar part is sub-divided into London dispersion forces, Debye induction forces and Keesom orientation forces. He shows that the total SFE (Γ_{Total}) is related to the apolar (Γ^{LW}) and acid (Γ^-) – base (Γ^+) components by Equation 2.5.

$$\Gamma_{Total} = \Gamma^{LW} + 2\sqrt{\Gamma^-\Gamma^+} \dots\dots\dots(2.5)$$

If the values of Γ^{LW} , Γ^- and Γ^+ for water are compared with those of bitumen under investigation, it is possible to tell whether the bitumen has a high or low stripping susceptibility.

2.7. Adhesion Mechanisms and Theories

For a bituminous mix to perform satisfactorily, there has to be strong and durable adhesion at the interface of its component materials under all climatic conditions. Several mechanisms have been used to explain the adhesion between the component materials although some seem to overlap. Ensley et al., (1984) mentioned adhesion as being poorly understood, due to bitumen internal complexity and the variety of aggregate surfaces. Initially, interaction between the bitumen polars and active aggregate surface takes place. The aggregate surface is then gradually modified and the organic binding forces within the bitumen become more dominant. Table 2.5 summarizes the important adhesion mechanisms that have been proposed.

2.8. Mechanisms of the Stripping Process

Although stripping is poorly understood, several mechanisms have been suggested to explain its occurrence. In all the mechanisms, there has to be initiation and progression of stripping (Mcglashan et al., 1984; Tarrer et al., 1991). Graf, (1986) reports that stripping in practice usually begins at the bottom of the bituminous layer, where moisture content is highest and works its way up. A review of each of the formulated mechanisms and the attendant theories is given in Table 2.6.

2.9. Moisture Sensitivity Test Methods

Most moisture sensitivity tests resulted from major research efforts in the late 1970s and during 1980s under the National Cooperative Highway Research Program (SHRP).

Table 2.5: Summary of Approaches to Adhesion of Bitumen onto Aggregate Surfaces

| Approach | Law/Theory | Probable Mechanism | References |
|------------------------------|---------------------------------------|--|---|
| <i>Mechanistic tenacity</i> | Contact mechanics theory | <ul style="list-style-type: none"> Hot bitumen fills the aggregate pores, cools and sets into a solid in contact with aggregate. The interlock and key form a strong bond. The bond strength depends on roughness and chemistry of the two, and bitumen cooling rate. | (Lee, 1936; McBain et al., 1962; Cechentinni, 1971; Kennedy et al., 1990; Zhu et al., 2000) |
| <i>Molecular orientation</i> | Electrostatic theory | <ul style="list-style-type: none"> When hot, bitumen polars dissociate and diffuse towards the interface. Induced polarization of additional bitumen parts leads to interface build-up. Electrostatic attraction between the oppositely charged species causes adhesion. | (Thelen, 1958; Ensley et al., 1984; Terrel et al., 1989; Petersen et al., 1993; Hagen et al., 1996) |
| <i>Chemical reaction</i> | Valency theory (bonding) | <ul style="list-style-type: none"> When bitumen and aggregate are in contact, reaction between the adsorbate (bitumen) polar components and the adsorbent (aggregate) reactive sites takes place leading to chemical bond formation. In general, adhesion is specific to individual bitumen-aggregate pairs. | (Winterkorn et al., 1937; Hallberg, 1950; Riedel et al., 1953; Dukatz, 1989) |
| <i>Energy change</i> | 2 nd Law of thermodynamics | <ul style="list-style-type: none"> Equilibrium shifts such that the total of Surface Free Energies of the phases involved (bitumen, air, water and asphalt) becomes minimum possible to ensure maximum stability. Adhesion process is faster if bitumen has lower surface energy (when hot or with liquid additives) or when aggregate has higher energy with respect to the enveloping medium (air or water). | (Thelen, 1958; Majidzadeh et al., 1968; Stuart, 1990; Hicks, 1991; Hagen et al., 1996) |

Table 2.6: Mechanisms of Stripping at the Bitumen-Aggregate Interface

| Process | Theory | Mechanism | References |
|----------------------------|-------------------------------------|--|--|
| Displacement | Thermodynamic and chemical reaction | Water with lower surface energy and higher dipole moment than bitumen displaces it from aggregate surfaces. | (Fromm, 1974; Mcglashan, 1984; Terrel et al., 1989; Mcgennis et al., 1995) |
| Detachment | Thermodynamic and chemical reaction | Water with lower surface energy and higher dipole moment than bitumen detaches it from the aggregate surface. | (Fromm, 1974; Terrel et al., 1989; Mcgennis et al., 1995) |
| Spontaneous emulsification | Electrostatic | Emulsion formation, due to presence of agents like clay coatings, weakens the bonding at the interface. | (Fromm, 1974; Terrel et al., 1989; Mcgennis et al., 1995) |
| Pore Pressure | Mechanical break | High pore water pressure in undrained conditions causes a break in bitumen film allowing water to enter the interface. | (Hallberg, 1950; Taylor et al., 1983; Kiggundu, 1988; Kandhal, 1994) |
| Chemical disbonding | Chemical reaction and electrostatic | Chemical and electrostatic interaction between water and some aggregates favour removal of bitumen from them. | (Scott, 1978; Edwards et al., 2000) |
| Microbial activity | Bacterial metabolism | Microbial metabolic processes at the interface give by-products that break adhesion at the interface. | (Brown et al., 1990; Parker, 1991) |
| Osmosis | Diffusion | Concentration gradient across the bitumen film causes water to be transported to the interface. | (Thunqvist, 2001) |

In the mid 1980s, the US Congress funded a SHRP program, among other efforts, to undertake binder research studies with later inclusion of the Bitumen-Aggregate Mixture Analysis System (AAMAS) in 1990. The SHRP efforts led to Superpave binder and mixture specifications and test methods (Kennedy et al., 1990; Barbour et al., 1992, Scholz et al., 1993; Terrel et al., 1993; Terrel et al., 1994). SHRP projects A-003A and A-003B

dealt with improved performance-related testing to evaluate moisture susceptibility and fundamental aspects of the bitumen-aggregate bond.

Current methods of evaluation of mix susceptibility to moisture damage base their criteria on decrease in mix properties like strength due to soaking in water. If a bitumen-aggregate mix combination fails a set criterion, it is assumed to be prone to moisture-induced damage. Table 2.7 gives selected test methods used by various agencies.

Although many test methods are available, no single test entirely correlates laboratory behavior and field performance. This means that many HMA mixtures, which might otherwise perform satisfactorily in the field, may be rejected. The converse may also arise. Another shortfall in test methods involving strength determination lies in reliance on relativity of the strengths before and after conditioning in lieu of absolute strength values. There may be cases when both dry and conditioned values are high but their ratio (e.g. TSR) is low especially after treatment with additives (Lottman et al., 1990).

In addition, most tests measure bulk properties in lieu of bond weakening by moisture. Many agencies seem to qualify the Modified Lottman test (AASHTO T283) as the most appropriate one available at the moment in detecting HMA moisture sensitivity. AASHTO T283 was included in Superpave™ mix design procedures as a promising test. A chemical conditioning stage was included in AASHTO T283 by SHRP. NCHRP Project 9-13, "*Evaluation of Water Sensitivity Tests*," completed in 1999, recommended changes to AASHTO T283 to better accommodate its use in Superpave volumetric mix design.

Table 2.7: Summary of Moisture Sensitivity Test Methods

| General Group | Examples |
|--|---|
| 1. Dynamic Immersion tests | a) Nicholson test (Majidzadeh et al., 1968 and Terrel et al., 1994) b) Dow and Tyler Wash test (Majidzadeh et al., 1968) c) Rolling Bottle test. |
| 2. Static Immersion tests | a) ASTM D-1664, AASHTO T182 (Brown et al., 1959) b) Lee test (Majidzadeh et al., 1968) c) Holmes Water Displacement test (Majidzadeh et al., 1968) d) Oberbach test (Majidzadeh et al., 1968) e) German U-37 test (Majidzadeh et al., 1968 and Thunqvist, 2001) |
| 3. Boiling tests | a) ASTM D-3625 b) Riedel and Weber test (Majidzadeh et al., 1968 and Thunqvist, 2001) |
| 4. Chemical Immersion tests | a) Riedel and Weber test (Majidzadeh et al., 1968 and Thunqvist, 2001) |
| 5. Abrasion tests | a) Cold water abrasion tests (Majidzadeh et al., 1968) b) Abrasion-Displacement tests (Majidzadeh et al., 1968) |
| 6. Simulated Traffic tests | a) English trafficking tests (Majidzadeh et al., 1968) b) Test tracks e.g. Hamburg Wheel-tracking device, Asphalt Pavement Analyzer, French Pavement rutting tester, Oregon State University, etc (Majidzadeh et al., 1968; Aschenbrener et al., 1995; and Luo et al., 2001) |
| 7. Quantitative Coating Evaluation tests | (a) Dyne Adsorption Test (Vuorinnen, 1999) (b) Mechanical Integration method (Majidzadeh et al., 1968) (c) Radioactive Isotope Tracer Technique (Majidzadeh et al., 1968) (d) Tracer – salt with flame photometer (Thunqvist, 2001) (e) Light-Reflection method (Majidzadeh et al., 1968 and Thunqvist, 2001) (f) Net Adsorption test |
| 8. Non-Destructive tests | a) Sonic tests (Majidzadeh et al., 1968 and Vuorinnen, 1999) b) Resilient Modulus tests (Stuart, 1990) |
| 9. Immersion-Mechanical tests | a) Marshall Immersion test (Stuart, 1990) b) Moisture Vapor Susceptibility test (Stuart, 1990) c) Water Susceptibility test (Stuart, 1990) d) Lottman tests (Stuart, 1990, Lottman, 1974; Lottman, 1978 and Lottman, 1982) e) Immersion-Compression ASTM-D1075 (Goldbeck, 1949) f) Freeze-Thaw pedestal tests (Kennedy, 1982 and Stuart, 1990) g) Environmental Cond. System (AASHTO TP34) h) Tunnichliff and Root test (ASTM D4867) (Parker et al., 1987) |
| 10. Miscellaneous tests | a) Detachment tests (Majidzadeh et al., 1968) b) Briquette Soaking test (Thunqvist, 2001) c) Swell tests (Majidzadeh et al., 1968 and Thunqvist, 2001) d) Stripping Coeff. measurement (Majidzadeh et al., 1968 and Khosla et al., 2000) e) Peeling test (Majidzadeh et al., 1968) |

NCHRP 9-13, Report No. 444 “*Compatibility of a Test for Moisture-induced Damage with Superpave Volumetric Mix Design*” also recommended AASHTO T283 as a suitable choice for Superpave volumetric mix design (Epps et al., 2000).

2.10. Redress Mechanisms

There are several factors that may confound the stripping process namely air voids content in the mixture, drainage in the pavement, action of traffic, climate (rainfall, temperature, etc.), day-night temperature variations, freeze-thaw cycling, bitumen embrittlement due to aging, moisture content in the mixture, aggregate surface contamination, and others. Some of the measures recommended to offer blanket insurance against stripping include (a) careful selection or modification of bituminous materials e.g. use of antistripping agents, (b) good drainage, (c) proper control of mixing, placement and compaction, and others.

2.10.1. Anti-stripping Agents

Many practitioners have had recourse to anti-stripping agents to abate moisture damage in HMA. Several criteria are followed in selecting an anti-stripping agent like, how to determine the need for the agent, its mechanism of action (compatibility with HMA components), effective method of application, how to test for effectiveness, environmental/handling concerns, contribution to long-term performance and cost (Stroup-Cardiner et al., 1987; Roberts et al., 1991). The intent of anti-stripping agents is to modify the interfacial chemical properties, enabling active adhesion. Others prevent water at the interface from impairing the bitumen-aggregate bond thus passively promoting adhesion. The list of anti-stripping agents developed to

date is long (Coplantz et al., 1987; Lottman et al., 1990; Hicks, 1991; Selim et al., 1994, and Crossley et al., 2000).

Hydrated lime and Portland cement are probably the commonest mineral additives (Rice, 1958; Stroup-Gardiner et al., 1990; and Isacsson 1993). These additives are inorganic and do not produce volatile emissions. A detailed account of the mechanisms of their action as anti-stripping agents is given elsewhere (Bagampadde et al., 2003). Liquid additives have also been used to promote affinity between bitumen and aggregate surfaces (Chehovits et al., 1980; Dalter et al., 1982; AASHTO Report, 1994; and Won et al., 1994). Andersson et al., (1982) attributed liquid additive action to interactions between additive polar ends and aggregate surfaces. There are generally two methods of application of additives namely direct pre-blending with bitumen (either at the refinery or mixing plant) and addition during mixing in the drum or pugmill. Liquid additives are more "chemical dependent" than minerals and require more laboratory work to determine additive-aggregate match. Some of the common liquid additives used include surfactants and silane coupling agents. Other classes include Sulfur Based Additives, Polymeric Antistripping Additives, etc.

2.10.2. Other Approaches

Many field observations have showed that the majority of pavement failures due to stripping occur in surface treatments and base courses where the void content favours retention of water (Taylor et al., 1983; and Davidson et al., 1993). Unless a dense graded mix has an unfavourable air void content (pessimum range), inadequate bitumen content, or aggregate with adsorbed coatings, it is normally resistant to moisture damage. Preventive measures need to be taken to hinder the causes of stripping when placing a new pavement or overlay or even when recycling an old pavement mixture.

Prevention measures can be divided into three categories: (a) select material pairs that are resistant to stripping and properly design their mix; (b) ensure proper quality control at all stages from hot mix processing to the finished compacted mat, e.g. use of clean and dry aggregates, sticking to the job-mix formula, etc., (c) guarantee a properly designed drainage system because a pavement's resistance to moisture damage will always be as good as its drainage. The Asphalt Institute (Asphalt Institute, 1988) published a comprehensive set of guidelines to help minimize the probability of stripping.

The simplest, though expensive, alternative is to overlay the stripped pavement with a new mat by milling and placement of a stripping resistant course onto existing surface. Another curative practice involves complete removal and replacement of the stripped pavement. This is expensive and wasteful, but is the only way to ensure that all stripped and stripping-prone material is removed. An important development in the practice of stripping reduction involves the use of recycling technology (Amirkhanian et al., 1992). Some concerns have been raised as to whether the presence of stripped material in a recycled bitumen mix will accelerate stripping in the new pavement. In one study (Amirkhanian et al., 1992), it was shown that use of recycled material does not create increased risk of moisture damage in the recycled pavement.

2.11. Summary of Literature

From the foregoing review of literature, the following findings are apparent:

1. Despite a long history of research on the interfacial phenomenon of stripping, it is still obscure and no clear theory exists to explain it. A lot of research is still needed to explore it intrinsically.

2. The chemistry and composition of the constituent phases (bitumen and aggregate) are highly complex and heterogeneous. Thus, it is in principle not possible to transfer inferences on performance of bituminous mixtures from one location to another.
3. Most evaluation methods of moisture sensitivity are still under investigations by researchers in order to improve capability to predict long-term performance, and reproducibility and correlation between laboratory and field test data. Acceptable criteria need to be established. Most tests measure bulk properties like, tensile strength, in lieu of interfacial bond weakening by moisture.
4. Several remedial measures have been tried to abate stripping in mixes. However, not all are equally cost effective over a range of materials and construction practices. It is important to control the root causes of stripping before trying out antistripping agents.

3 MATERIALS AND EXPERIMENTAL METHODS

3.1 Research Steps

The research approach used to achieve the study objectives is detailed in Figure 3.1.

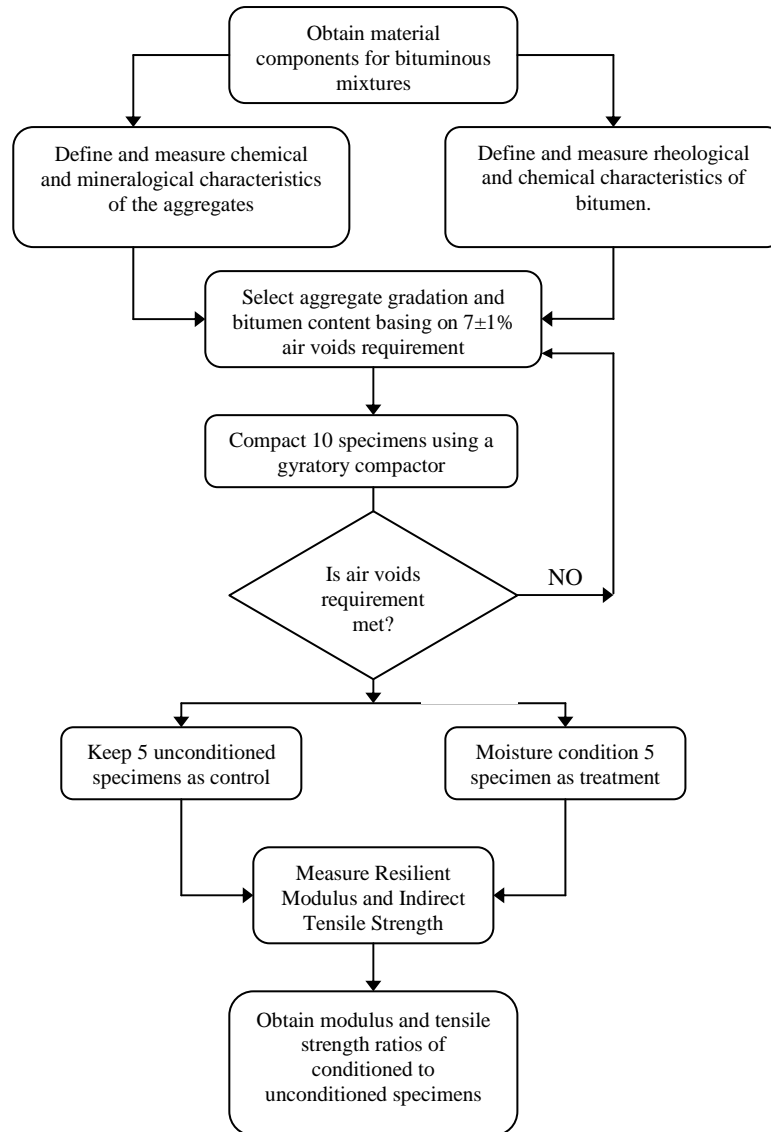


Figure 3.1: Flow Chart Illustrating the Research Steps

3.2 Materials and Tests

3.2.1 Aggregates

Eight active quarry aggregates from several districts around Lake Victoria were obtained. In addition, four aggregates from Sweden were included to strengthen directional effects and widen variability in characteristics. In this research, the aggregates were coded as AA1, AA2, AA3, AA4, AA5, AA6, AA7 and AA8 from Uganda, and AA9, AA10, AA11, and AA12 from Sweden. Later in the study, aggregate AA2 was dropped because its quarry was closed. Characterization of each of the aggregate samples for chemical composition and mineralogy was done as follows:

3.2.1.1 Chemical Composition

To determine chemical composition, the aggregate samples were analyzed for silica, alumina, potassium, sodium, total iron, magnesium, calcium and manganese. The concentrations of metallic elements are proportional to the oxides in which they naturally occur (Stuart, 1990).

- Potassium, sodium, iron, magnesium, calcium and manganese were determined by digesting aggregate samples with concentrated hydrofluoric acid (HF-40%) and hydrogen chlorate HClO_4 (70%) and the resulting solution analyzed with an atomic absorption spectrophotometer (AAS).
- Alumina was determined by a gravimetric method through precipitating Al_2O_3 with 8-hydroxyquinoline.
- Silica was determined by a spectrophotometric method where the samples were digested by fusion with sodium hydroxide and the resulting solution complexed with molybdate for analysis.

In the interest of convenient classification of aggregates in this study, the chemical composition was grouped into acid insolubles (Al_2O_3 , SiO_2) and acid solubles (CaO , MgO , Na_2O , Fe_2O_3 , K_2O , MnO_2).

3.2.1.2 Mineralogical Composition

Determining mineralogy is crucial to the understanding of the composition, occurrence, physical properties and classification of the aggregates. The aggregate samples in this study were analyzed for mineralogical composition by cutting large samples ($\geq 50\text{mm}$) into very thin sections and cleaned in readiness for macroscopic and microscopic examination. Qualitative and quantitative techniques in estimation were done under a microscope. Optical microscopy was used to determine colour, grain size and mineral crystals present. Minor phases below a detection limit of approximately 1 – 2 percent were not revealed. The minerals that were mainly observed included quartz, feldspars, mica and other oxides.

3.2.2. Bitumen

Bitumen was sourced from three suppliers commonly used in Lake Victoria region. These were coded as A, B and C in this study. One of them was of South African origin and the others were of Arabian origin. In addition, three bitumen types obtained in Sweden were included to increase variability in the composition and these were coded D, E and F. The bitumen D was from Venezuela (Laguna) while the origins of E and F were unknown. The following tests were conducted on the bitumen:

3.2.2.1 Traditional Rheological Tests

- ◆ *Penetration test (ASTM D5)*: This test measures the ability of bitumen to resist penetration by a standard needle. In this study, a standard needle loaded with 100g was set to penetrate bitumen for a duration of 5 seconds at 25°C. The depth of penetration was measured in dmm (0.1mm) at three points and the average value was taken as the penetration.
- ◆ *Softening Point Test (ASTM D36)*: This was conducted using the Ring and Ball (R&B) apparatus. Two bitumen samples were suspended in brass rings with steel balls on top and placed in a beaker with water. The system was heated at an approximately constant rate until bitumen sunk to about 25mm. The temperature at this point was read to the nearest 0.5°C and taken as the Softening Point.
- ◆ *Ductility Test (ASTM D113)*: This test measures the distance a specially prepared bitumen briquette elongates before rupture. Standard specimens were stretched at a rate of 50mm/min $\pm 5\%$ at a standard temperature of 25°C in a water bath. The distance of elongation at breaking point was measured in centimeters and taken as the ductility.
- ◆ *Brookfield Viscosity Test (ASTM D4402)*: Viscosity of the bitumen was determined using a Brookfield rotary viscometer. The measuring principle of the Brookfield viscometer bases on the application of a constant rotation speed (in rpm) to a spindle that is dipped in bitumen in a small cylindrical thermosel oven. Viscosity in mPa.s was determined at 90, 110 and 135°C by reading off the values directly from the digital screen.

3.2.2.2 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was performed using a rheometer (Rheometrics RDA II) with temperature sweeps from -30 to 80⁰C at a constant frequency of 1 rad/s. During each test, a small sample of bitumen (about 0.2g) was applied on a bottom plate of 8mm diameter covering its entire surface. The plate was mounted in the rheometer and heated until bitumen could soften. The top plate was brought into contact with the bitumen leaving a 1.5mm gap between the plates and the protruding parts of the sandwiched sample neatly trimmed. A sinusoidal strain was applied by an actuator and was set at a constant frequency. The strain and torque were input into a computer that automatically calculated the complex modulus, G^* and phase angle, δ .

3.2.2.3 Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) was used in this study to determine the relative distributions of molecular sizes in the bitumen. A solution of bitumen (5% by weight) in Tetra Hydro furan (THF) was passed through gel permeation columns having a stationary phase of a porous gel. The pores of gel filter out molecules larger than some critical size, while smaller molecules permeate the gel structure by diffusion. This makes the larger molecules elute out of the column in a shorter time compared to the smaller ones. The GPC instrument was calibrated using a broad molecular weight polystyrene standard in order to minimize bias. An automatic detector was used to measure the relative amounts of molecular sizes and input to a computer where chromatograms were obtained.

3.2.2.4 Infrared Spectroscopy

A Fourier Transform Infrared (FTIR) spectrometer was used to analyze bitumen for functional groups present. An infinity 60 AR (Mattson, resolution 0.125cm^{-1}) was used and set to give absorbances in wavenumbers ranging from 3400 to 500cm^{-1} . Bitumen solutions (5% by weight) were prepared using Carbon Disulfide (CS_2). Blank (solvent) and sample scans were performed using ATR prisms and circular sealed cells of Zinc Selenide (ZnSe) windows. The instrument was set under controlled conditions of temperature and environmental moisture in accordance with its specifications. Peaks of Infrared absorbance around 1700cm^{-1} corresponding to C=O stretch were used to characterize bitumen propensity to resist loss of adhesion due to water.

3.2.2.5 Thin Layer Chromatography

In this method, a sample of bitumen was dissolved in dichloromethane solvent (2% w/v concentration) and spotted at one end of a set of four chromarods made of quartz coated with a silica or alumina layer. The rods were then developed with a suitable solvent which caused different fractions in the bitumen (Saturates, Aromatics, Resins, Asphaltenes) to separate. The rods were scanned in an Iatroscan MK analyzer at a specified speed through a hydrogen flame. The Flame Ionization Detection (FID) signals for each fraction were amplified and recorded as separate peaks. The relative areas under the peaks were normalized and revealed the proportions of the different fractions present in the bitumen.

3.2.3 Bituminous Mixtures

Mix design and preparation was done in accordance with the Swedish FAS 446-98 specifications closely related to AASHTO T283. The process involved the following steps:

- (a) 100mm diameter and 30mm height specimens of bituminous mixtures were prepared from bitumen and aggregates basing on Swedish ROAD 94, Chapter 6 with the following properties:
 - ◆ Bitumen content by mass = 4.9%,
 - ◆ Aggregate gradation = dense graded with 16mm maximum size, AG16 (Cf. Figure 3.2),
 - ◆ Void content by volume (Gyratory compaction) = $7\pm 1\%$.
- (b) Density and voids measurement were done basing on specimen volumetric and gravimetric characteristics. The following parameters were obtained:
 - ◆ Maximum theoretical density (G_{mm}) using AASHTO T209.
 - ◆ Bulk specific gravity (G_{mb}) in accordance with AASHTO T166. The density was controlled for number of gyrations (N) and angle of gyration.
 - ◆ Air voids for each test specimen in accordance with AASHTO T269.

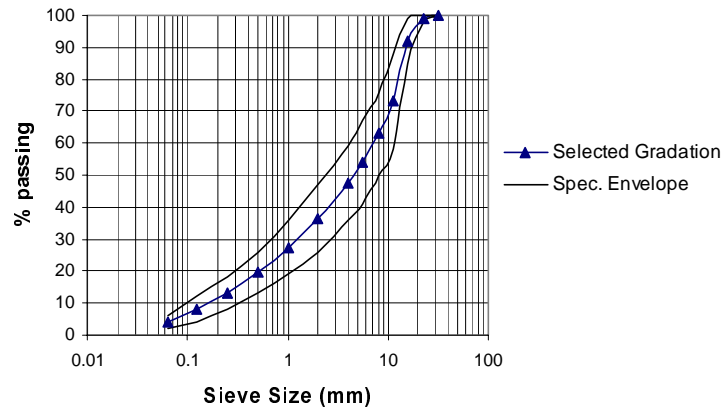


Figure 3.2: Gradation Curve that was used in the Research

- (c) A *control* sub-set of 5 test specimens was kept dry at room temperature and an *experimental* sub-set of 5 test specimens was conditioned as follows:
- ◆ The specimens were vacuum saturated with distilled water at room temperature for 3 hours using 67hPa.
 - ◆ The degree of saturation was obtained by comparing the volume of absorbed water with volume of air voids.
 - ◆ The specimens were thawed by placing them into a 40°C water bath for 7 days.
 - ◆ The specimens were then removed from the water bath and placed in a cool chamber at 10°C for 2 hours.
 - ◆ All the unconditioned and conditioned specimens were evaluated for resilient modulus and indirect tensile strength at 10°C in the MTS machine (810 Material Testing System). Resilient modulus is the ratio of applied dynamic load to the recoverable strain.

Moisture damage may reduce the non-recoverable or plastic strain after moisture conditioning more than the recoverable strain.

- ◆ Indirect tensile strength was conceptualized in evaluating bituminous mixtures by early work of T. W. Kennedy, 1977. Moisture damage probably reduces the resistance to splitting along a diametral plane of a cylindrical specimen when a relatively uniform tensile strain is induced perpendicular to the diametral plane. The tensile stresses near the edges are not well defined and are relatively high as shown in Figure 3.3.

- (d) The mixtures were evaluated for moisture sensitivity (stripping propensity) using indirect tensile strength and resilient modulus ratios, TRS and MRR.

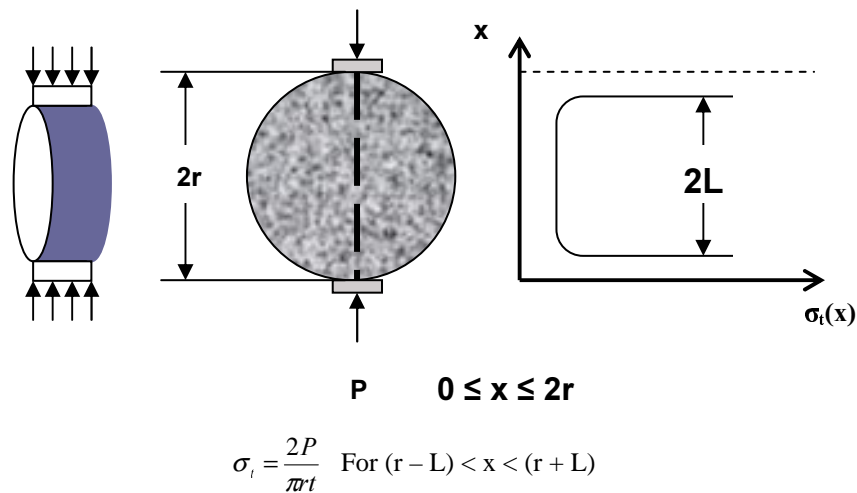


Figure 3.3: Stress Field in the Indirect Tensile Strength Test (Kennedy, 1977)

$$\text{TRS} = \frac{\text{Conditioned Tensile Strength}}{\text{Unconditioned Tensile Strength}} \times 100$$

$$\text{MRR} = \frac{\text{Conditioned Resilient Modulus}}{\text{Unconditioned Resilient Modulus}} \times 100$$

Lottman, (1978) recommends a threshold value of 70% for mixes to be stripping resistant. This was the value adopted in this study.

3.3 Experimental Programme

The following two studies on the bituminous mixtures were conducted:

3.3.1 Influence of Aggregate Properties on Bituminous Mix Stripping

Eleven aggregates were mixed with one bitumen to produce eleven mix types as shown in the matrix in Table 3.1. This was done to evaluate the effect of aggregate properties (chemistry and mineralogy) on moisture sensitivity of the bituminous mixtures. It was postulated that the choice of binder does not affect the general trend of aggregate response. Bitumen D was in largest quantity and was used in this phase of the study.

Table 3.1: Text Matrix Used to Assess the Effect Aggregate Properties

| | 7 Aggregates from Uganda | 4 Aggregates from Sweden | Total |
|-----------|--------------------------|--------------------------|-------------|
| 1 Bitumen | 7 Mixtures | 4 Mixtures | 11 Mixtures |

3.3.2 Influence of Cross Effects of Bitumen and Aggregate on Stripping

In this phase, the effects of different combinations of aggregate and bitumen properties on mixture moisture sensitivity were evaluated. The aggregates that were in largest quantities are the ones that were used in this phase. The Experimental matrix was as shown in Table 3.2.

Table 3.2: Test Matrix Used to Assess Cross Effects of Bitumens and Aggregates

| | 4 Aggregates | Total |
|--|--------------|-------|
| | | |

| | | |
|------------------|-------------|----------------------|
| 4 Binders | 16 Mixtures | Total of 16 Mixtures |
|------------------|-------------|----------------------|

3.3.3 Experimental Design

In the Experimental Design, Binder chemistry/rheology and aggregate chemistry/mineralogy are the main factors in the experimental mixtures. For each bitumen/aggregate combination, a *true experimental design* is made below to minimize possibility of type I and type II errors in hypothesis testing:

| Group | Treatment | Observations or Measures |
|--------------|------------------|---------------------------------|
| R | NT | O_{ij1} |
| R | X_1 | O_{ij2} |

R - A random sample of 5 replicate specimens from a pool of 10 that are generated in a manner that is as similar as possible. All the 10 specimens had the same aggregate, bitumen, gyratory compaction to same level of air voids, similar aggregate gradation and asphalt content.

NT - The control group without any treatment is used to explore internal validity.

X_1 - Treatment that was given to this group. It involved 3 hrs vacuum saturation at 67hPa plus 7 days of soaking in distilled water @ 40°C and 2 hours of cooling at 10°C. This test procedure is a variation of the AASHTO T283.

O_{ijk} - Observation of outcome for group k of response resilient modulus obtained through non-destructive load testing and the indirect tensile strength testing @ 10°C through destructive load testing on binder i and aggregate j. The ratio of conditioned mix strength to dry mix strength was used as a measure of stripping propensity. A cut-off ratio of 0.7 was used as threshold between poor and good performance.

This generates a combination of 10 specimens per mix type overall to be analyzed.

4 RESULTS AND DISCUSSION

4.1 Aggregates Characteristics

The results of mineralogical and chemical composition of the aggregate samples are given in this section.

4.1.1 Chemical Composition

Aggregate chemical test results are summarized in Table 4.1 as percent by weight of the various oxides. Table 4.2 and Figure 4.1 give the composition in terms of chemical percent content of the acid solubles and the acid insolubles.

Table 4.1: Percent by Weight Chemical Composition of the Aggregates

| Aggregate | | % by Weight | | | | | | | |
|-----------|------|------------------|--------------------------------|-------|-------|-------------------|------------------|--------------------------------|------------------|
| | | SiO ₂ | Al ₂ O ₃ | CaO | MgO | Na ₂ O | K ₂ O | Fe ₂ O ₃ | MnO ₂ |
| Ugandan | AA1 | 75.50 | 13.60 | 1.30 | 0.50 | 2.90 | 4.50 | 1.70 | 0.03 |
| | AA2 | 69.80 | 14.50 | 1.50 | 0.80 | 2.20 | 4.80 | 6.30 | 0.05 |
| | AA3 | 83.60 | 0.70 | 0.01 | 0.03 | 0.03 | 0.20 | 15.40 | 0.02 |
| | AA4 | 30.90 | 34.10 | 10.10 | 7.60 | 4.20 | 0.51 | 12.30 | 0.24 |
| | AA5 | 77.30 | 3.00 | 14.01 | 0.02 | 4.02 | 0.10 | 1.50 | 0.03 |
| | AA6 | 32.90 | 22.60 | 14.60 | 11.40 | 3.50 | 1.92 | 12.80 | 0.30 |
| | AA7 | 79.20 | 11.50 | 0.52 | 0.10 | 3.30 | 4.30 | 1.00 | 0.10 |
| | AA8 | 77.50 | 12.90 | 1.30 | 0.50 | 1.80 | 4.94 | 1.00 | 0.06 |
| Swedish | AA9 | 71.20 | 14.30 | 4.30 | 0.30 | 2.82 | 5.35 | 1.61 | 0.06 |
| | AA10 | 71.90 | 19.00 | 1.64 | 1.14 | 2.70 | 1.70 | 1.80 | 0.11 |
| | AA11 | 53.70 | 22.40 | 8.10 | 0.54 | 2.80 | 1.64 | 10.63 | 0.20 |
| | AA12 | 89.50 | 9.30 | 0.04 | 0.06 | 0.06 | 0.40 | 0.64 | 0.04 |

Basing on this chemical characterization, aggregates AA4 and AA6 seem to have a composition of acid solubles significantly higher than that of other aggregates at a 5% level of significance. Aggregate AA12 has a low composition of acid solubles compared to the rest of the aggregates. If the

acidic functionalities of bitumen are the ones readily adsorbed onto the aggregate adsorption sites as confirmed by Petersen et. al., 1998, then aggregates AA4 and AA6 would be good adsorbents; and AA12 would probably not properly adhere to the bitumen.

Table 4.2: Composition of Aggregates by Acid Solubles and Acid Insolubles

| | AGGREGATES UNDER STUDY | | | | | | | | | | | |
|-----------------|------------------------|------|------|------|------|------|------|------|------|------|------|------|
| | AA1 | AA2 | AA3 | AA4 | AA5 | AA6 | AA7 | AA8 | AA9 | AA10 | AA11 | AA12 |
| Acid Insolubles | 89.1 | 84.3 | 84.3 | 65.0 | 80.3 | 55.5 | 90.7 | 90.4 | 85.5 | 90.9 | 76.1 | 98.8 |
| Acid Solubles | 10.9 | 15.7 | 15.7 | 35.0 | 19.7 | 44.5 | 9.3 | 9.6 | 14.5 | 9.1 | 23.9 | 1.2 |

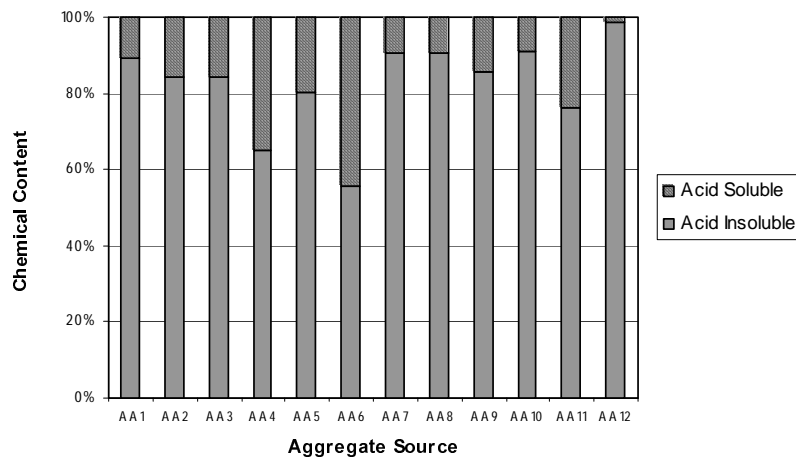


Figure 4.1: Chemical Composition of the Aggregates Used

A high concentration of acid insolubles (SiO_2 and Al_2O_3) is associated with adsorption sites with Lewis acids namely protons from surface silanols and aluminols (Vuorinen, 1999). These sites seem to poorly bond with bitumen since the acidic functionalities in the bitumen are the parts that are believed to strongly adsorb onto aggregates. The tendency for bitumen to desorb in

presence of water is even more pronounced in these aggregates. Thus, basing on chemical composition, aggregate AA12 is probably the most highly prone to stripping, followed by aggregates AA1, AA7, AA8 and AA10. Aggregates AA2, AA3, AA5, AA9 and AA11 seem to have a lower tendency to strip than the first two groups above. It is probable that aggregates AA4 and AA6 have the least propensity to stripping.

4.1.2 Mineralogical Composition

Minerals occur as aggregates of crystals. Mineralogical composition determines the surface chemistry of the aggregate and may account for the nature and type of adsorption sites for bitumen polar functionalities (Kiggundu et al., 1986). Mineralogical composition of the aggregates under study was determined and the results are given in Table 4.3. It was possible to identify the rock names of the aggregates basing the procedure by Strekeisen, (1978). Different percentages of quartz, feldspars and mica were determined for the aggregates.

Ferromagnesian minerals were identified in aggregates AA4 and AA6 and were the dominant ones. Aggregate AA11 also had some augite ferromagnesian mineral. Aggregate AA4 contains hornblende – calcium-iron-magnesium silicate and some Plagioclase feldspar (Anorthite - $\text{CaAl}_2\text{Si}_2\text{O}_8$). Aggregate AA6 is an igneous rock poor in silica and alkalis but with a ferromagnesian silicate olivine $(\text{Mg,Fe})_2\text{SiO}_4$ and melilite $(\text{Ca,Na})_2(\text{Al,Mg,Fe}^{++})(\text{Si,Al})_2\text{O}_7$. When bitumen comes into contact with the aggregates, these minerals probably react with bitumen acidic parts forming insoluble salts of calcium and magnesium at the interface. The resulting interfacial bonds may be stripping resistant because these salts cannot be diluted by water.

Table 4.3: Mineralogical Composition of the Aggregates

| Aggregate | Rock Type | Quartz | Feldspar | Mica | Ferro-magnesian | Notes |
|-----------|--------------------|---------|----------|---------|-----------------|--|
| AA1 | Granite Gneiss | 20 - 30 | 55 | 15 - 20 | - | Alkali feldspars (Orthoclase – $KAlSi_3O_8$, Albite – $NaAlSi_3O_8$), and Mica (Biotite – Black Mica, Muscovite – White Mica). |
| AA2 | Biotite Gneiss | 15 – 25 | 40 - 50 | 30 - 40 | - | Alkali feldspars (Orthoclase – $KAlSi_3O_8$, Albite – $NaAlSi_3O_8$), some Anorthite $CaAl_2Si_2O_8$ and Mica (Biotite – Black Mica, Muscovite – White Mica). |
| AA3 | Quartzite | 60 – 80 | - | - | - | Made of purely quartz of fine to medium size and some iron oxide in surface fissures. |
| AA4 | Amphibole | - | 15 -20 | - | 70 – 80 | Contains Hornblende – Calcium-iron-magnesium silicate with some sodium and Aluminium. Also has some Plagioclase (Anorthite - $CaAl_2Si_2O_8$). |
| AA5 | Quartzite | 75 – 80 | - | - | - | This rock was predominantly a quartzite of granitic origin and some traces of anorthite feldspar - $CaAl_2Si_2O_8$. |
| AA6 | Olivine Melilitite | - | - | - | 60 - 70 | Igneous rocks poor in silica and alkalis. It is a ferromagnesian silicate with olivine $(Mg,Fe)_2SiO_4$ and melilitite $(Ca,Na)_2(Al,Mg,Fe^{++})(Si,Al)_2O_7$. |
| AA7 | Granite | 35 – 45 | 40 - 55 | 15 - 25 | - | Mostly contains quartz and alkali feldspar (mainly albite); and Mica (Biotite – Black Mica, Muscovite – White Mica). |
| AA8 | Granite Gneiss | 20 - 25 | 60 - 70 | 5 - 10 | - | Has some quartz and mainly alkali feldspars (Orthoclase – $KAlSi_3O_8$, Albite - $NaAlSi_3O_8$), and some Mica (Biotite – Black Mica, Muscovite – White Mica). |
| AA9 | Granite Gneiss | 40 - 45 | 50 - 55 | - | - | Mostly contains quartz and plagioclase mainly - $CaAl_2Si_2O_8$ |
| AA10 | Syenogranite | 25 - 30 | 55 - 60 | - | - | Has quartz and mainly alkali feldspars (Orthoclase – $KAlSi_3O_8$, and Albite - $NaAlSi_3O_8$). |
| AA11 | Tonalite | 15 - 20 | 55 - 60 | - | 15 - 20 | Mostly plagioclase - $CaAl_2Si_2O_8$, silica SiO_2 and Clinopyroxene (Augite) |
| AA12 | Granite | 99.8 | - | - | - | Almost composed of quartz and traces of opaque with coarse texture. |

Aggregate AA12 predominantly had quartz at a 99.8% level and it is a granite rock with a coarse texture. Aggregates AA3 and AA5 also had high quartz content. Aggregate AA9 has an average amount of quartz mineral. Quartz is a silica and is probably a poor adherend to polar functionalities of bitumen in presence of water (Stuart, 1990). This may be due to water molecules forming stronger hydrogen bonds with siliceous surface silanols than the bond between bitumen polars and the Lewis acid sites.

The aggregates had varying types and amounts of feldspars. AA1, AA2, AA7, AA8 and AA10 had relatively high amounts of albite ($\text{NaAlSi}_3\text{O}_8$) and orthoclase (KAlSi_3O_8). These feldspars may cause stripping in presence of water due to sodium and potassium, which are strong alkalis and therefore form soluble salts with binder acidic functionalities. In addition, when in contact with water, these minerals form silica when exchanged with protons (Scott, 1978). The products may be highly prone to stripping.

Aggregate AA9 has an above average amount of anorthite feldspar ($\text{CaAl}_2\text{Si}_2\text{O}_8$), with calcium which forms insoluble salts with binder acidic functionalities which may make it resistant to stripping.

Some aggregates (AA1, AA2, AA7 and AA8) had mica in small amounts. Majidzadeh, et al., (1968) reported that presence of mica may be a cause for poor adhesion at the interface in presence of water.

4.2 Bitumen Characterization

Interfacial adhesion and resistance to stripping depends on both the rheological and chemical characteristics of bitumen that comes in contact with the aggregate (Majidzadeh et. al., 1968 and Petersen, 1986).

4.2.1 Traditional Rheological Test Results.

Several rheological properties of the bitumen types under study were determined in this study. In determining penetration and softening point, three readings were taken for each bitumen and if there were no significant differences in these three values at a 5% level of significance, the average was recorded. Table 4.4 gives average values of the results for penetration (in dmm at 25°C, 100g/5s), softening point (Ring and Ball, in °C), ductility and Brookfield viscosity (mPa.s). Viscosity was determined at three temperatures namely 90, 110 and 135 degrees Celcius.

Penetration has always been used to measure consistency of bitumen in an attempt to classify it into standard grades. Bitumen A has a significantly higher penetration of 147 compared to B, C, D and E. This bitumen seems to be of a different penetration grade, while B, C, D and E are of the same penetration grade of 80/100. Bitumen F has 69 penetration and is probably of 60/70 grade.

Table 4.4: Rheological Properties of the Bitumen Samples

| Characteristic | Bitumen Code | | | | | | |
|------------------------------|--------------|------|------|------|------|------|-----|
| | A | B | C | D | E | F | |
| Penetration @ 25°C (dmm) | 147 | 86 | 84 | 84 | 80 | 69 | |
| Softening Point (°C) | 40.2 | 47.4 | 48.5 | 44.5 | 47.0 | 48.9 | |
| Ductility @ 25°C (cm) | 150+ | 115 | 121 | 136 | 131 | - | |
| Brookfield Viscosity (mPa.s) | 90°C | 6812 | 7945 | 7656 | 7761 | 8456 | - |
| | 110°C | 980 | 1208 | 992 | 1180 | 1256 | - |
| | 135°C | 208 | 302 | 412 | 346 | 400 | 460 |

Basing on these results, bitumen A seems to better spread on an aggregate surface than the others at the same temperature since it is softer.

Bitumen A has a significantly lower softening point compared to bitumens B, C, D, E and F. Hence, bitumen A would have a higher tendency to wet

and spread on the aggregate at elevated temperatures in service as compared to the rest of the bitumen types.

Ductility is important as it gives a measure of internal cohesion of bitumen (Whiteoak, 1991). It shows capability of bitumen to withstand movements induced by traffic and temperature stresses. Bitumen A has significantly higher ductility (+150cm) compared to the other bitumen types. Although it is more cementitious and adherent to mineral aggregate than the rest of the bitumens, it has a low cohesion that would cause stability problems. From the point of view of ductility, bitumens B, C, D and E seem to be harder and hence less likely to lose tenacity with mineral aggregate surface.

Viscosity results are plotted against temperature as shown in Figure 4.2 on a semi-logarithmic scale. The plots show that bitumen A has a higher viscosity-temperature susceptibility (VTS) compared to the others. This implies that it would probably flow off a coated aggregate easily leaving a thinner film compared to the other bitumens during transportation and placement. Thin films are easily plasticized (softened) by water and can easily be scoured off the aggregate by traffic load associated pumping of water. Moreover, thin films are more permeable to water (Majidzadeh et al, 1968).

4.2.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) was used to study the dynamic visco-elastic response of the bitumens to periodically varying stresses. Conceptually, a periodic sinusoidal stress is applied to a bitumen sample in a rheometer resulting in a sinusoidal strain that lags the stress by a phase angle, δ . The ratio of stress amplitude to strain amplitude gives the complex modulus (G^*) measuring overall resistance to deformation.

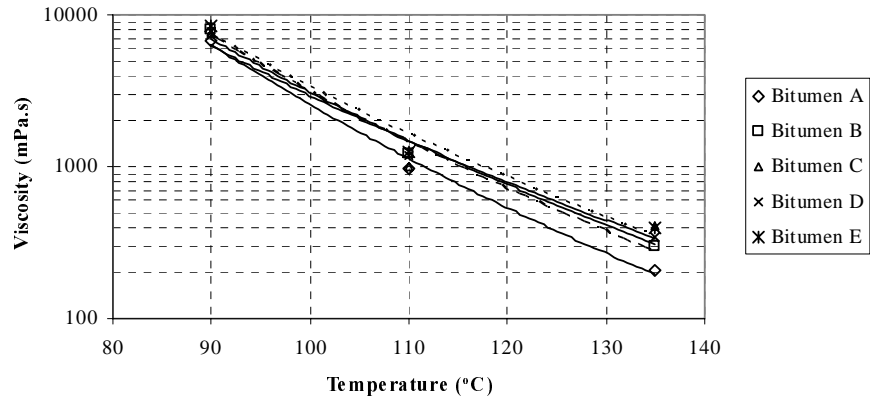


Figure 4.2: Viscosity Temperature Susceptibility of the Binders

The complex modulus gives a measure of resistance to deformation when bitumen is dynamically loaded. The component of G^* in phase with stress is called the storage modulus (G') and measures the elastic response of the bitumen. The out-of-phase with stress component is called loss modulus (G'') and gives the viscous response of the bitumen. The phase angle (δ) measures the visco-elastic behaviour of bitumen. The phase angle is 0° for a purely elastic material and 90° for a purely viscous material.

The phase angle was plotted against temperature for the bitumens at 1rad/s as shown in Figure 4.3. The visco-elastic response of the bitumens is evidently different especially in the range of ambient temperatures (15° to 35°C) and at temperatures below 0 degrees.

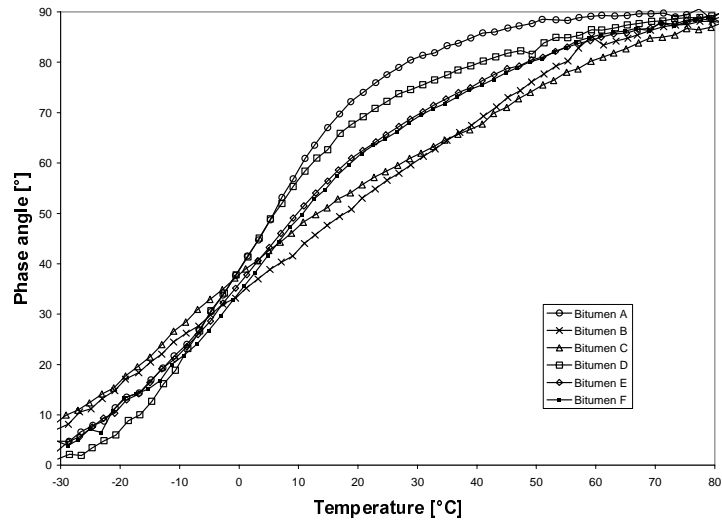


Figure 4.3: Phase Angle as a Function of Temperature

At 15°C, bitumens A and D seem to exhibit a relatively high viscous response ($\delta > 50^\circ$) compared to B, C, E and F. As temperature approaches 40°C, bitumens A, D, E and F approach a predominantly viscous behaviour where the contribution of storage modulus (G') to the complex modulus (G^*) is negligible. In a previous study, $\delta = 75^\circ$ was taken as the threshold beyond which, the bitumen would predominantly exhibit viscous response (Lu and Isacsson, 1997). Highly viscous bitumens have an internal structure characterized by weaker interactive forces between polar components. This makes movement of water molecules towards the interface easier (Majidzadeh et al., 1968). Moreover, the contribution of bitumen cohesion to mix strength is significantly reduced. A plot of T_{75} as a function of softening point is shown in Figure 4.4 with a seemingly linear relationship. The temperature (T_{75}) corresponding to $\delta = 75^\circ$ correlates well with softening point at a 5% level of significance ($R^2 = 0.8701$). Bitumens with low T_{75}

values would wet and coat an aggregate at lower temperatures than those with higher values since they soften very easily.

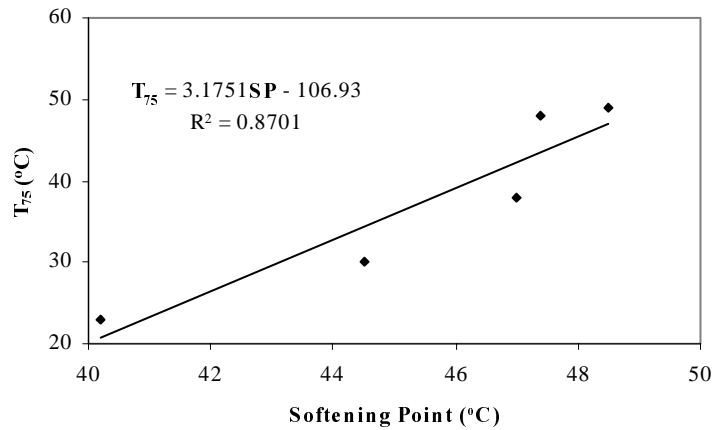


Figure 4.4: A Plot of T_{75} as a Function of Softening Point.

The results in Figure 4.3 reveal some interesting phenomenon namely, the phase angle of all the bitumens seems to be the same around 0°C . This zone of the graph is magnified as shown in Figure 4.5. The bitumens that are strongly elastic below this point become strongly viscous above the point. For example bitumens A and D that are the most elastic below 0°C become the most viscous above the same temperature. It is probably possible to grade bitumen basing on phase angle at 0°C as has been done before using other properties like viscosity at 60°C and 135°C ; and penetration at 25°C . This phenomenon has also been investigated by plotting the loss tangent (G''/G') against temperature as shown in Figure 4.6. Loss tangent measures damping of a propagated wave (or stress) and is indicative of macromolecular structure of bitumen. The loss tangent seems to be the same around 0°C for all the bitumens.

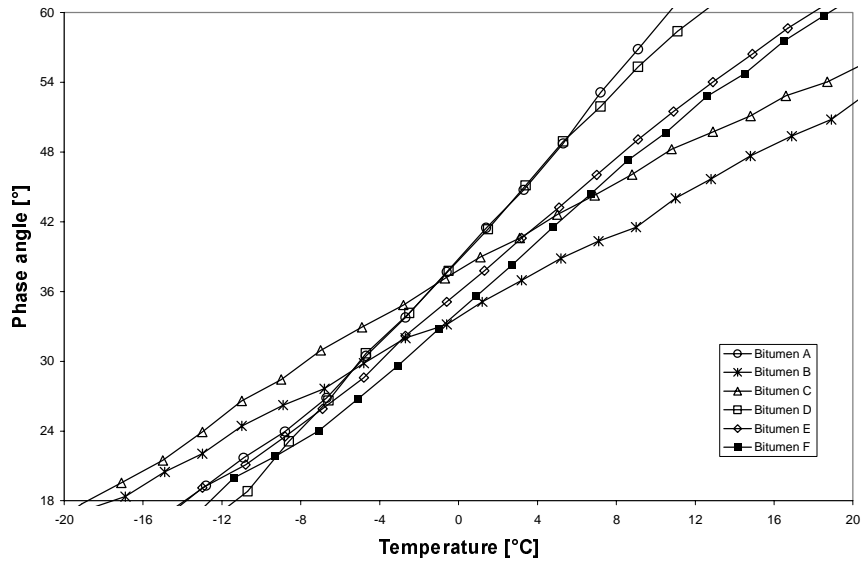


Figure 4.5: Viscoelastic Response around 0°C for the Bitumens

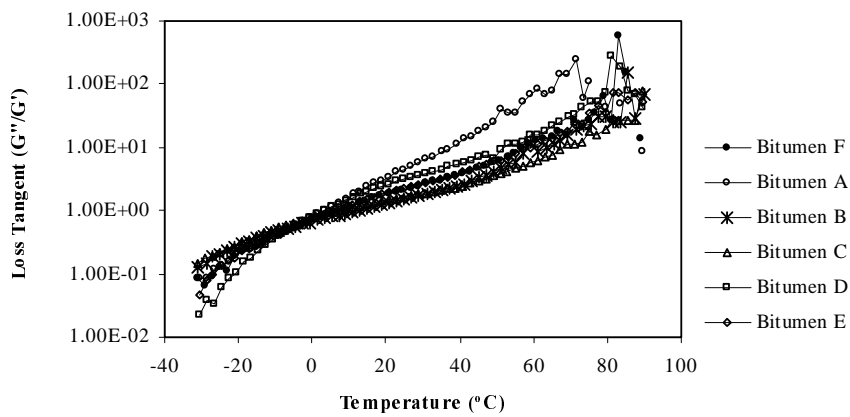


Figure 4.6: Plots of Loss Tangent as a function of Temperature

Plots of complex modulus against temperature are made for a frequency of 1 rad/s with temperature sweeps from -30°C to 80°C in Figure 4.7. For

temperatures above 20°C, bitumen A has a low complex modulus compared to the others. This bitumen would easily flow at high temperatures. It has better wetting and spreading capabilities during mixing. However, it may easily drain off the aggregate during hot mix transportation leaving thin film coating on aggregate. Mixtures with thin bitumen films around aggregates are very sensitive to moisture damage.

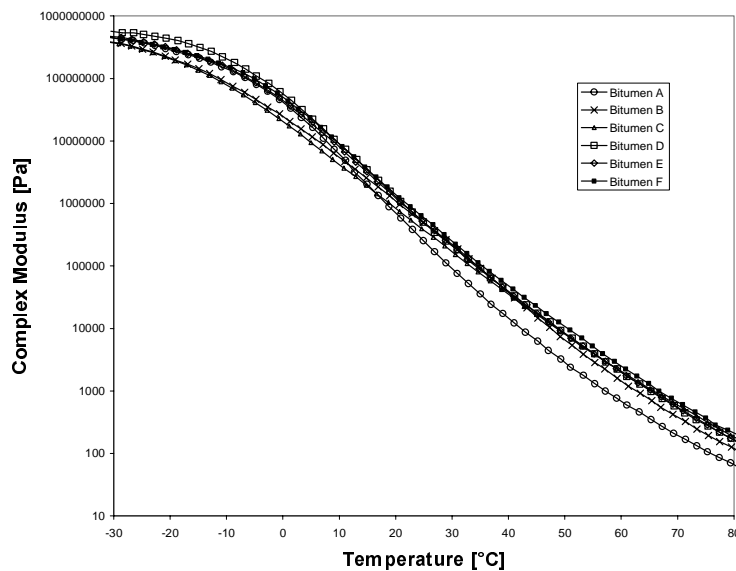


Figure 4.7: Variation of Complex Modulus with Temperature

4.2.3 Gel Permeation Chromatography (GPC)

Molecular size and structuring determines stability of adhesion at the bitumen-aggregate interface both in the dry and wet conditions. GPC was employed to characterize the bitumen types basing on molecular size by using tetra-hydrofuran (THF) as a carrier solvent. The chromatograms for the bitumens are shown in Figure 4.8. The chromatograms show that the bitumens may be different both in the large and small molecular size zones.

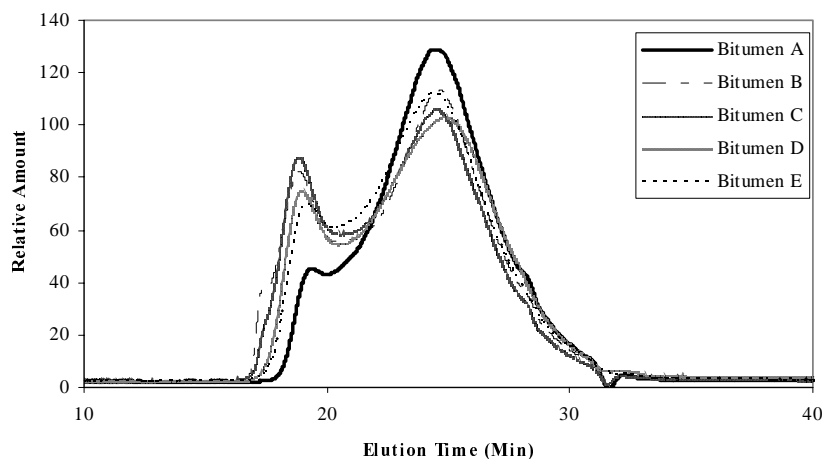


Figure 4.8: Chromatograms for the Five Bitumen types.

All the bitumens seem to exhibit an early peak (a large molecular size fraction) eluting at about the same time (≈ 18 minutes). A large, broad peak eluting at 25 minutes for all the bitumens follows. This implies that probably, the primary difference in the chromatograms is in the relative areas under the peaks. The bitumen types may therefore be qualitatively similar but quantitatively different basing on GPC results. It is important to note that bitumen B has a small distinguishable shoulder on the broad major peak. This shoulder seems to imply molecular association which may be due to high polarity. Table 4.5 gives the percentage total areas under the large molecular size (LMS) and the small molecular size (SMS) peaks for all the bitumen types. The results are graphically presented in Figure 4.9. These bitumens probably have different chemical characterization basing on relative amounts of molecular size and structuring despite many of them having almost similar rheological properties like viscosity and penetration.

Bitumen A has a significantly low concentration of LMS compared to other bitumens. It also has the highest concentration of SMS. Bitumen C seems to have the highest concentration of LMS followed by B, E, D and A in that order, all eluting at the same time. The trend is opposite for SMS.

Table 4.5: Percentage areas under Chromatograms for the bitumens

| | | Trial 1 | Trial 2 | Average Area (%) |
|------------------|-----|---------|---------|------------------|
| Bitumen A | LMS | 7.83 | 7.86 | 7.85 |
| | SMS | 92.17 | 92.14 | 92.16 |
| Bitumen B | LMS | 24.74 | 24.5 | 24.62 |
| | SMS | 75.26 | 75.5 | 75.38 |
| Bitumen C | LMS | 25.12 | 26.8 | 25.96 |
| | SMS | 74.88 | 73.2 | 74.04 |
| Bitumen D | LMS | 16.53 | 16.97 | 16.75 |
| | SMS | 83.47 | 83.03 | 83.25 |
| Bitumen E | LMS | 21.12 | 20.08 | 20.60 |
| | SMS | 78.88 | 79.92 | 79.40 |

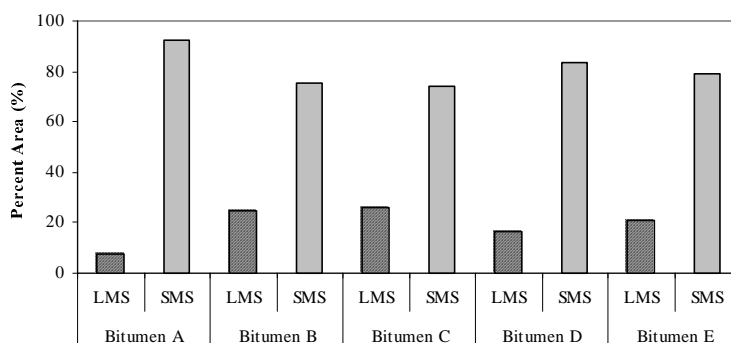


Figure 4.9: Graphical Presentation of the Areas under the Chromatograms

The LMS components are probably a highly aromatic asphaltene material which is peptized by the SMS components, the maltenes as suggested by Heithaus, (1960). It is also probable that the LMS components are due to associations by the SMS depending on polarity. Bitumen A may have its low

concentration LMS components dispersed in the SMS medium. The corresponding dispersibility of LMS in the SMS medium looks to be lower in the rest of the bitumens. This probably explains the high VTS exhibited by bitumen A compared to the other bitumen types.

4.2.4 Infrared Spectroscopy

The chemical nature and composition with respect to functional groups determines the strength of the bond at the bitumen-aggregate interface (Petersen, 1986). Infrared spectroscopy was used to examine the bitumens for functional groups using both an ATR prism and sealed cells of Zinc Selenide. Figure 4.10 shows infrared spectra for the six bitumens that were evaluated for functional groups. Peaks of infrared absorbance around 1710 to 1690 cm^{-1} corresponding to carbonyl (C=O) stretch were used to characterize bitumen propensity to resist loss of adhesion due to water.

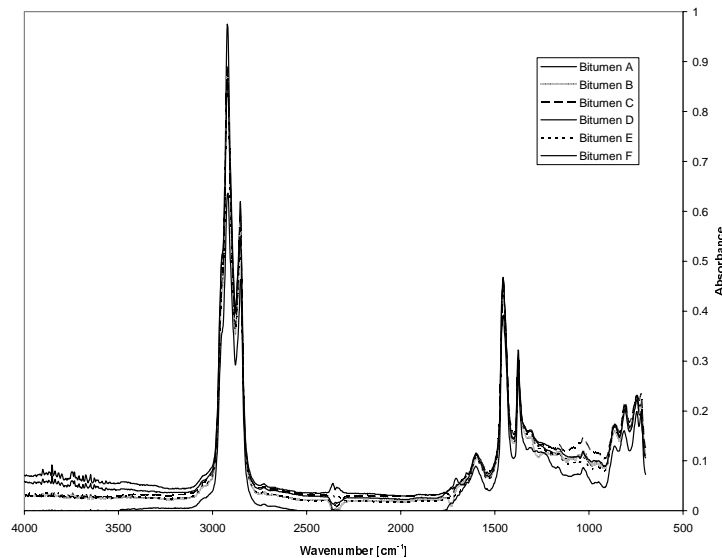


Figure 4.10: Infrared Spectra Obtained Using an ATR Prism

There are observable distinguishing features in the spectra of the different bitumens. Prominent absorption is apparent around the carbonyl region for the different bitumen types. The characteristic functional groups in this carbonyl region include carboxylic acids and 2-quinolones. Ketones and anhydrides may also exist in aged bitumens. To make the difference in the carbonyl region more discernible, this region was magnified as shown in Figure 4.11.

Bitumen D has a sharp peak around 1709cm^{-1} . The spectra for bitumens B and C show broad bands at this frequency while bitumen A has a small peak at 1705cm^{-1} . Bitumens E and F have peak at 1700cm^{-1} with differences in absorbance. In addition, bitumen B and C have troughs at 1732cm^{-1} . All the bitumens show sharp peaks around 1601cm^{-1} which may be due to presence of alternating single and double covalent bonds or minor contributions from C=N bonds at varying concentrations.

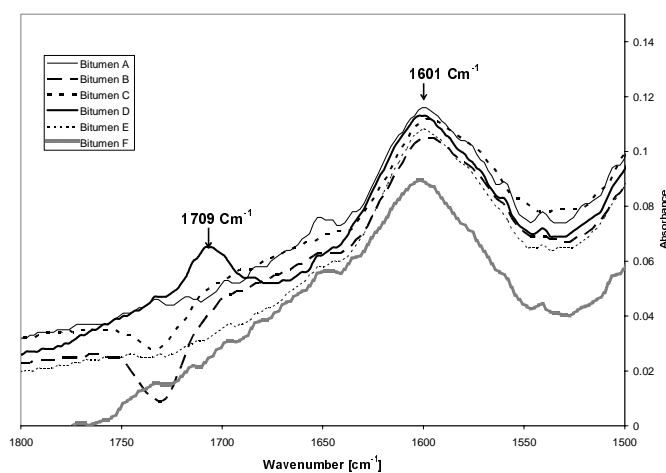


Figure 4.11: Characteristic Peaks around the C=O Stretch Regions

The results of infrared spectroscopy obtained using Zinc Selenide cells are shown in Figure 4.12. The carbonyl region was magnified as shown in Figure 4.13 to enable identify differences in the bitumen compositions around the region. Bitumen D shows a prominent sharp peak at 1707cm^{-1} . Bitumens B, C and F show small broader peaks around 1700cm^{-1} and; A and E had peaks which are lower and less broad in the carbonyl region.

To better interpret the peaks around the carbonyl region, it was decided to determine the acid numbers of all the bitumens. This was done in accordance with ASTM D 664-95 and the results are given in Table 4.6. The results of acid numbers show that bitumen D has a significantly higher acid content compared to the rest of the bitumens at a 5% level of significance.

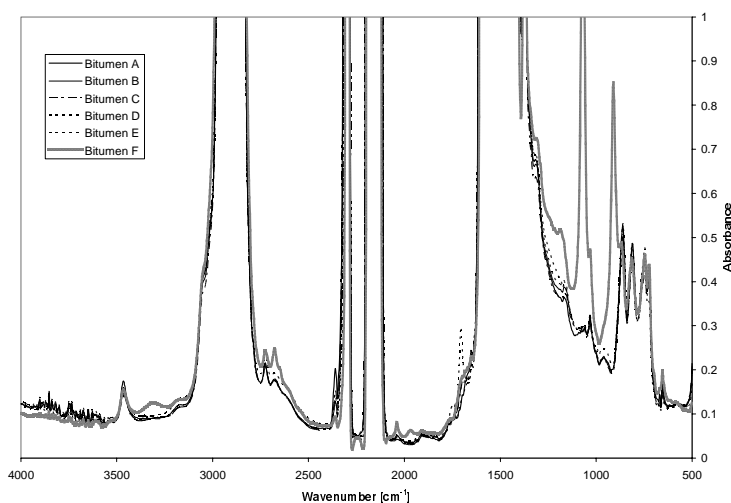


Figure 4.12: Infrared Spectra Obtained Using An Znse Sealed Cells

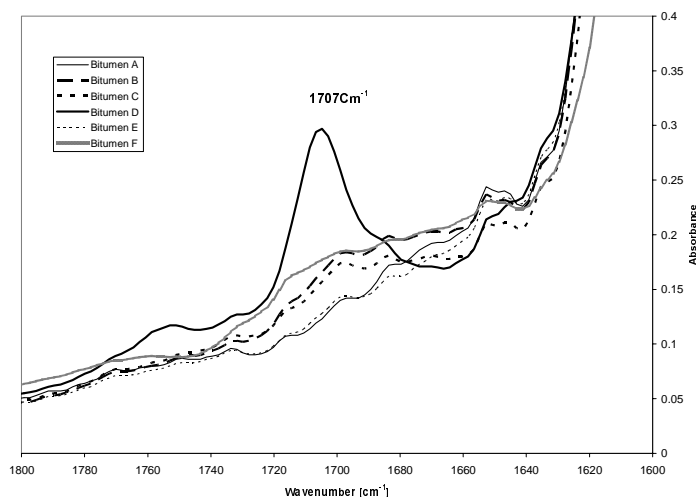


Figure 4.13: Characteristic Peaks Around The Carbonyl Region

This implies that probably the peak for bitumen D observed in the carbonyl region of the infrared spectra is due to carboxylic acids. Bitumens C and E seem to be slightly more acidic than A and B basing on the results of acid numbers.

Table 4.6: Results of Acid Numbers for the Bitumens

| Bitumen | Trial 1 (mg/g) | Trial 2 (mg/g) | Average (mg/g) |
|---------|----------------|----------------|----------------|
| A | 0.23 | 0.25 | 0.240 |
| B | 0.24 | 0.25 | 0.245 |
| C | 0.50 | 0.45 | 0.480 |
| D | 3.66 | 3.51 | 3.585 |
| E | 0.52 | 0.51 | 0.515 |

4.2.5 Thin Layer Chromatography

Thin Layer Chromatography (TLC) was used to reveal the relative amounts of generic fractions namely, saturates, aromatics, resins and asphaltenes. The

results of TLC on four bitumens are shown in Figure 4.14 and all the bitumens have almost similar quantities of asphaltenes. Bitumen F has a substantially low level of saturates compared to the other bitumens. The conception due to Nellensteyn and other researchers considers bitumen as a colloid. Bitumen consists of dispersions of micelles in oils peptized to different degrees depending on the amounts of asphaltenes and saturates. The peptizability of the asphaltenes in the oils is measured using the colloidal index (CI) defined as:

$$CI = \frac{\text{aromatics} + \text{resins}}{\text{saturates} + \text{asphaltenes}}$$

A higher CI means that the asphaltenes are more peptized by the resins in the oils based medium. Table 4.7 shows the amounts of the different fractions and the values of CI for the different bitumens. Thus, bitumen F has higher peptizability of asphaltenes in oils than bitumens B, C and D. If transport of water to the interface is across bitumen films, then the process would be easier in bitumen F compared to bitumens B, C and D.

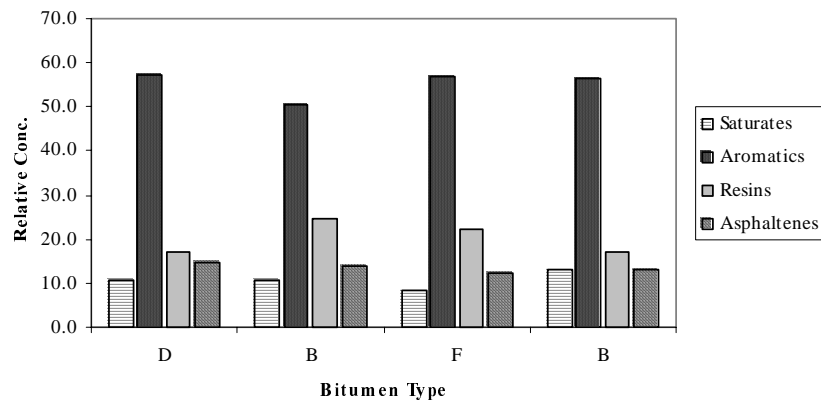


Figure 4.14: TLC Generic Fractions of Some Bitumens

Table 4.7: Chemical Characteristics of the Bitumens from TLC

| | Bitumen Code | | | |
|----------------------------|--------------|------|------|------|
| | D | C | F | B |
| Saturates | 10.9 | 10.7 | 8.5 | 13.3 |
| Aromatics | 57.4 | 50.7 | 56.8 | 56.6 |
| Resins | 16.9 | 24.6 | 22.2 | 17.0 |
| Asphaltenes | 14.7 | 14.0 | 12.5 | 13.0 |
| Colloidal Index, CI | 2.90 | 3.05 | 3.77 | 2.80 |

4.3 Bituminous Mix Results

The approach to moisture sensitivity determination in this study based on the ratios of wet-to-dry strength. The indirect tensile strength ratio (TSR) and resilient modulus ratio (MRR) were the key parameters used. To achieve the study objectives, work was divided into two phases. Phase I was devoted to the evaluation of the effect of aggregate chemical and mineralogical composition on moisture sensitivity. Phase II involved determination of cross-effects of bitumen and aggregate on moisture sensitivity. The test procedure used is a variation of the modified Lottman procedure due to a more severe conditioning stage involving a 7-day soak at 40°C.

4.3.1 Evaluation of Effect of Aggregate Properties on Moisture Sensitivity

Moisture damage through stripping is a complicated process and is believed to strongly relate to aggregate composition (chemistry and mineralogy) among other things. Some researchers speculate that mix moisture sensitivity is more dependent on the aggregate than bitumen (Decker et al., 1989).

Table 4.8 shows the test results of indirect split tensile strength (MPa) of five specimens for the mixtures both dry and conditioned. Table 4.9 gives the sample averages and coefficients of variation for each set of specimens at a particular test condition (either dry or conditioned). Most of the coefficients of variation were below 15%. This indicates a relatively good relative

preciseness between each set of values for the five specimens corresponding to each aggregate and a test condition. The TSR corresponding to mixtures from each aggregate type was obtained from the average strengths.

Table 4.8: Indirect Tensile Strength Results Before and After Conditioning

| Aggregate | FRACTURE STRENGTH (MPa) | | | | | | | | | |
|-----------|-------------------------|-------|-------|-------|-------|-----------------------|-------|-------|-------|-------|
| | Dry Specimens | | | | | Conditioned Specimens | | | | |
| AA1 | 14706 | 15751 | 16455 | 16041 | 17822 | 4850 | 5620 | 7251 | 7321 | 7077 |
| AA3 | 14984 | 15443 | 17623 | 15136 | 16210 | 6258 | 6578 | 7024 | 6452 | 6689 |
| AA4 | 14915 | 15031 | 16177 | 17044 | 16046 | 14347 | 11129 | 14330 | 13671 | 12286 |
| AA5 | 11494 | 12092 | 13387 | 11479 | 11473 | 7211 | 7341 | 8726 | 8059 | 6639 |
| AA6 | 10619 | 10511 | 10342 | 11760 | 12988 | 9899 | 10473 | 12110 | 9389 | 8951 |
| AA7 | 14883 | 15584 | 16417 | 14895 | 16225 | 6681 | 7939 | 8184 | 7549 | 7788 |
| AA8 | 15472 | 16514 | 15510 | 16157 | 16752 | 9797 | 9652 | 8288 | 8509 | 8887 |
| AA9 | 12307 | 12880 | 13254 | 12550 | 13268 | 6074 | 5968 | 4254 | 4172 | 5890 |
| AA10 | 10955 | 12654 | 14560 | 13474 | 14727 | 1982 | 2328 | 2026 | 2399 | 1864 |
| AA11 | 12009 | 9605 | 11786 | 13554 | 14103 | 7995 | 8009 | 8071 | 8001 | 8000 |
| AA12 | 10619 | 10511 | 10342 | 11760 | 12988 | 9899 | 10473 | 12110 | 9389 | 8951 |

Table 4.9: Average and Standard Deviations of Sample Groups

| Aggregate | Dry Specimen | | Conditioned Specimen | |
|-----------|--------------|-----------|----------------------|-----------|
| AA1 | mean = 16155 | cv = 7.0 | mean = 6424 | cv = 17.5 |
| AA3 | mean = 15879 | cv = 6.8 | mean = 6600 | cv = 4.3 |
| AA4 | mean = 15843 | cv = 5.6 | mean = 13153 | cv = 10.7 |
| AA5 | mean = 11985 | cv = 6.9 | mean = 7595 | cv = 10.7 |
| AA6 | mean = 11244 | cv = 10.0 | mean = 10164 | cv = 12.1 |
| AA7 | mean = 15601 | cv = 4.6 | mean = 7628 | cv = 7.6 |
| AA8 | mean = 16081 | cv = 3.6 | mean = 9027 | cv = 7.5 |
| AA9 | mean = 12852 | cv = 3.3 | mean = 5272 | cv = 18.4 |
| AA10 | mean = 13274 | cv = 11.7 | mean = 2120 | cv = 40.9 |
| AA11 | mean = 12211 | cv = 14.4 | mean = 8015 | cv = 0.4 |
| AA12 | mean = 11244 | cv = 10.0 | mean = 10164 | cv = 12.1 |

The data are summarized in Figure 4.15 showing the relative differences in the bituminous mixture strength loss due to intervention through water treatment. The losses in strength are manifest in many of the mixtures. For

example, mixtures from aggregates AA1, AA3, AA9 and AA10 show very high decrease in the strength due to water treatment.

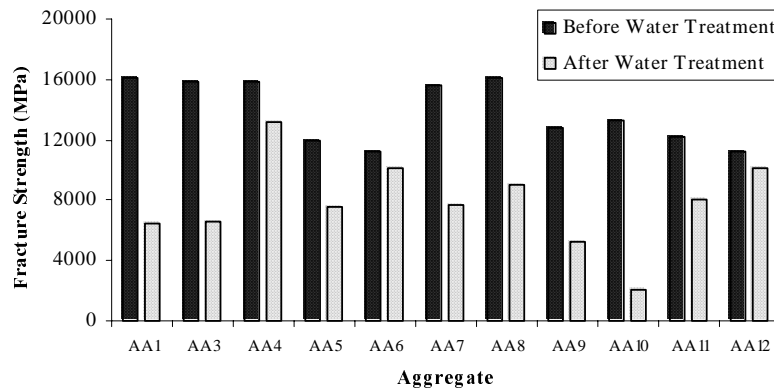


Figure 4.15: Comparison of Strength Loss Characteristics of Mixtures from the Aggregates under Study

TSR was obtained as the percentage of the average strength of conditioned specimens to that of dry specimens so that the effect of the conditioning intervention can be studied. Figure 4.16 shows the results of TSR for mixtures prepared from the eleven aggregates and bitumen D that was used in this phase. The TSR was above 70% for aggregates AA4, AA6 and AA12. Mixtures from aggregates AA5 and AA11 seem to be only slightly less than 70% though the difference may not be significant. The rest of the aggregates seem to have TSR values significantly lower than 70%.

Figure 4.17 shows a comparison of the *available* results of MRR with those of TSR parameters on the same mixtures from aggregates AA9, AA10 and AA11. The MRR results for the other aggregates are not yet complete. It is observed that the results of both parameters show the same trend.

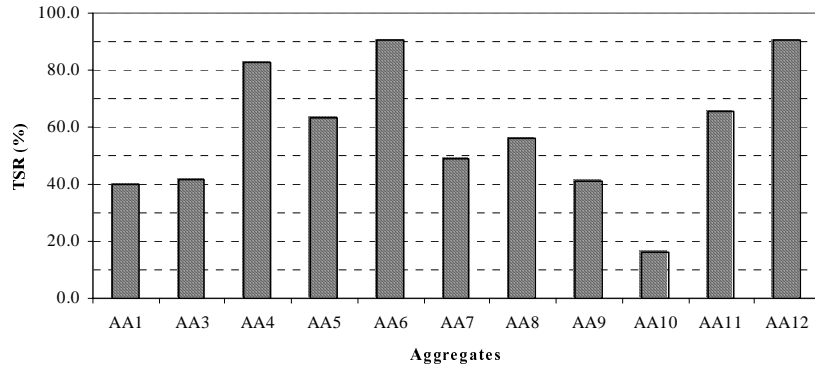


Figure 4.16: TSR Values for the Different Aggregates Under Study

Thus, the two parameters can be reliably used to compare moisture sensitivity of different aggregates. Furthermore, the ratio from resilient modulus seems to be lower than that from indirect tensile strength. Von Quintus et al., (1989) summarized the rankings of mixture properties related to pavement performance. They found out that TSR is a more dominant measure of moisture sensitivity than MRR for bituminous mixtures.

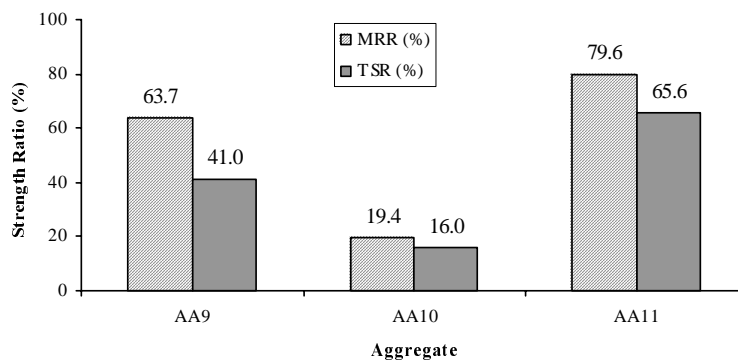


Figure 4.17: Comparison of TSR and MRR for Some Mixtures

In many test methods involving strength determination, moisture sensitivity determination relies on relativity of the strengths before and after

conditioning in lieu of absolute strength values like the minimum wet strength. There may be cases when both dry and conditioned values are high but their strength ratios are low especially after treatment with additives. For example, a plot of resilient moduli after water treatment for mixtures from all the aggregates is shown in Figure 4.18. The wet strengths of mixtures AA1, AA3, AA5, AA6, AA7, AA8 and AA11 are almost equal whereas their TSR or MRR ratios would be completely different. This is a big demerit with the method of using ratios in determining moisture sensitivity.

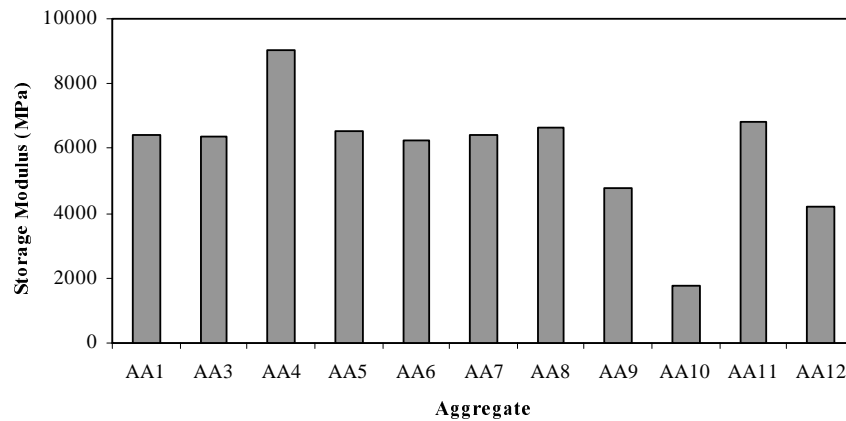


Figure 4.18: Resilient Modulus of Mixtures After Water Conditioning

4.3.2 Cross Effects of Bitumen and Aggregate Properties on Stripping

In this phase of the study, combined cross effects of bitumen and aggregate properties on moisture sensitivity was examined. Determination of tensile strength ratio (TSR) was done on mixtures from four aggregates and four bitumens. Average values of strength for 5-sized samples, in both dry and wet conditions, were obtained.

Bitumens B, C, D and F were used in this phase of study. Aggregates AA9, AA10, AA11 and AA12 were used to prepare mixtures from all the four bitumen types above and the following 4 x 4 experimental protocol designed:

| Aggregate Bitumen Code | AA9 | AA10 | AA11 | AA12 |
|---|-------------------|-------------------|-------------------|-------------------|
| B | TSR ₁₁ | TSR ₁₂ | TSR ₁₃ | TSR ₁₄ |
| C | TSR ₂₁ | TSR ₂₂ | TSR ₂₃ | TSR ₂₄ |
| D | TSR ₃₁ | TSR ₃₂ | TSR ₃₃ | TSR ₃₄ |
| F | TSR ₄₁ | TSR ₄₂ | TSR ₄₃ | TSR ₄₄ |

For each combination of bitumen and aggregate, ten mixtures were prepared. Out of these ten, five were randomly sampled and tested for strength in dry condition and the remaining five were tested after conditioning in water following a prescribed procedure (see chapter three). The bitumen types were allocated at random for each aggregate to minimize possibility of systematic errors. For each of the two 5-sized samples, the sample mean (\bar{x}), sample standard deviation (s) and coefficient of variation were obtained and the results are given in Table 4.10. The TSR for each combination of aggregate and bitumen was obtained as a percentage of the wet tensile strength to the dry tensile strength and the results are also included in the table. The coefficients of variation (CV's) for the different random samples tested are also shown. In general, the CV's are less than 15% which indicates a fairly high level of precision in testing. The TSR for each factorial combination are given in the table. The results of TSR seem to indicate a regular trend across the aggregate type.

Table 4.10: Results of TSR for Different Bitumen-Aggregate Combinations

| Binder | Aggregate | Treatment* | Mean Fracture Strength (MPa) | St. dev. (MPa) | CV (%) | TSR (%) |
|-----------|-----------|------------|------------------------------|----------------|--------|---------|
| Bitumen B | AA9 | 1 | 3190.2 | 160.5 | 5.0 | 39.7 |
| | AA9 | 0 | 8034.6 | 996.5 | 12.4 | |
| | AA10 | 1 | 1757.3 | 436.2 | 24.8 | |
| | AA10 | 0 | 7865.5 | 877.9 | 11.2 | |
| | AA11 | 1 | 4740.9 | 409.5 | 8.6 | |
| | AA11 | 0 | 7621.0 | 264.1 | 3.5 | |
| | AA12 | 1 | 7210.5 | 739.5 | 10.3 | |
| | AA12 | 0 | 7191.9 | 683.9 | 9.5 | |
| Bitumen C | AA9 | 1 | 4169.9 | 625.1 | 15.0 | 49.4 |
| | AA9 | 0 | 8446.5 | 590.7 | 7.0 | |
| | AA10 | 1 | 1671.5 | 562.8 | 33.7 | |
| | AA10 | 0 | 8119.6 | 633.9 | 7.8 | |
| | AA11 | 1 | 5062.2 | 1296.3 | 25.6 | |
| | AA11 | 0 | 7440.1 | 649.9 | 8.7 | |
| | AA12 | 1 | 7614.7 | 598.6 | 7.9 | |
| | AA12 | 0 | 7936.3 | 588.8 | 7.4 | |
| Bitumen D | AA9 | 1 | 5271.5 | 969.0 | 18.4 | 41.0 |
| | AA9 | 0 | 12851.8 | 425.3 | 3.3 | |
| | AA10 | 1 | 2119.7 | 230.5 | 10.9 | |
| | AA10 | 0 | 13274.2 | 1546.8 | 11.7 | |
| | AA11 | 1 | 8015.2 | 30.4 | 0.4 | |
| | AA11 | 0 | 12211.5 | 1760.4 | 14.4 | |
| | AA12 | 1 | 10164.3 | 1227.1 | 12.1 | |
| | AA12 | 0 | 11244.1 | 1123.3 | 10.0 | |
| Bitumen F | AA9 | 1 | 5430.7 | 1119.8 | 20.6 | 49.4 |
| | AA9 | 0 | 10994.8 | 1123.6 | 10.2 | |
| | AA10 | 1 | 2319.9 | 982.7 | 42.4 | |
| | AA10 | 0 | 10888.7 | 1605.9 | 14.7 | |
| | AA11 | 1 | 7063.2 | 1008.0 | 14.3 | |
| | AA11 | 0 | 10914.2 | 552.6 | 5.1 | |
| | AA12 | 1 | 10135.7 | 698.1 | 6.9 | |
| | AA12 | 0 | 10931.8 | 699.1 | 6.4 | |

* 1 = Conditioned Bituminous Mixtures and 0 = Mixtures without Treatment

5 ANALYSIS

An analysis of the experimental results is made in this chapter. This is aimed at providing a reliable relationship between a framework of some of the concepts that are believed to play a major role in moisture sensitivity of bituminous mixtures. A fair estimate of the precision of the procedures used in the study would evolve.

5.1 Effect of Aggregate Properties on Mixture Moisture Sensitivity

The test results of TSR for the aggregates mixed with one bitumen type (see Table 4.7) are analyzed using statistical tools. We test the claim that the tensile strength ratio (TSR) for mixes from each of the aggregates is less than 70%, i.e. the intervention through water conditioning affects the strength. Each aggregate had two random samples namely; one control of five specimens tested without water treatment and another of five specimens tested after water treatment. For each of the two 5-sized samples, the sample mean and sample standard deviation were obtained and the TSR parameter was defined as:

$$TSR = \frac{\text{Mean wet strength } (\overline{WS})}{\text{Mean dry strength } (\overline{DS})} \dots\dots\dots 5.1$$

$$TSR = \frac{\overline{WS}}{\overline{DS}}$$

$$\text{Log (TSR)} = \text{log } (\overline{WS}) - \text{log } (\overline{DS})$$

The requirement for an adequately water resistant bond between the bitumen and aggregate is a $TSR \geq 70\%$. The hypothesis below is formulated to test the above claim and the null hypothesis is taken at the limiting (minimum) TSR value of 70% since this is the worst case situation and the conclusion

drawn would hold for mixtures above that value. We therefore seek to test the hypothesis that:

$$H_0: \text{TSR} = 0.7$$

$$H_1: \text{TSR} < 0.7$$

This is equivalent to testing the hypothesis that

$$H_0: \log(\overline{wS}) - \log(\overline{dS}) = \log(0.7)$$

$$H_1: \log(\overline{wS}) - \log(\overline{dS}) < \log(0.7)$$

$\log(0.7) = -0.1549$, and in this analysis, a 5% level of significance (i.e. Type I error, $\alpha = 5\%$) was taken whereby a probability of wrongfully rejecting the null hypothesis is 0.05. Under the null hypothesis, a random variable t given by:

$$t = \frac{\log(\overline{wS}) - \log(\overline{dS}) - \log(0.7)}{S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \dots\dots\dots 5.2$$

$$\text{where } S_p^2 = \frac{(n_1 - 1)S_{\log(\overline{dS})}^2 + (n_2 - 1)S_{\log(\overline{wS})}^2}{n_1 + n_2 - 2}$$

has a t-distribution with $(n_1 + n_2 - 2)$ degrees of freedom. The samples are assumed to be drawn from a normal population. n_1 and n_2 are sample sizes which were both equal to 5. $S_{\log(\overline{dS})}$ and $S_{\log(\overline{wS})}$ are standard deviations of the logarithms of the strength values in the dry sample and wet sample respectively. If $t < -t_{n_1+n_2-2, \alpha}$, the null hypothesis is rejected since the critical region is in the left hand tail of the sampling distribution and we would assert with a 5% level of significance that on average, TSR of mixes from a particular aggregate under consideration is less than 70%.

As an example, consider the test results of aggregate AA1, the hypothesis to be tested at $\alpha = 0.05$ is:

$$H_0: \log(\bar{wS}) - \log(\bar{DS}) = \log(0.7)$$

$$H_1: \log(\bar{wS}) - \log(\bar{DS}) < \log(0.7)$$

$$\log(\bar{DS}) = \log(16155) = 4.208 \text{ and } \log(\bar{wS}) = \log(6424) = 3.808,$$

$$S_{\log(\bar{DS})} = 0.0303 \text{ and } S_{\log(\bar{wS})} = 0.0804. \text{ Also } n_1 = n_2 = 5$$

The criterion of rejecting H_0 is if $t < -t_{8, 0.05} = -1.860$. The value of S_p was obtained as:

$$S_p = \left(\frac{4 \times 0.0303^2 + 4 \times 0.0804^2}{8} \right)^{0.5} = 0.0608$$

$$t = \frac{3.808 - 4.208 + 0.1549}{0.0608 \sqrt{2/5}} = -6.374$$

Since $t = -6.374$ is less than -1.860 , the null hypothesis is rejected and it can be asserted with a 5% level of significance that on the average, the TSR for mixes from aggregate AA1 is less than 70%.

This analysis is done for mixes from all the eleven aggregates and one bitumen; and the inferences made are summarized in Table 5.1. The high TSR values for aggregates AA4 and AA6 may be attributed to presence of relatively low percentages of acid insolubles namely silica (SiO_2) and alumina (Al_2O_3). Silica and alumina surfaces form hydroxyl ions after reacting with water to form weak bonds at the interface. In addition, aggregates AA4 and AA6 had ferromagnesian minerals which are known to form insoluble salts with bitumen acidic functionalities. If these salts form at the interface, they cannot easily be diluted by water. Thus, mixtures from such aggregates would have a high resistance to stripping.

Despite having a very high level of quartz and low level of acid insolubles, aggregate AA12 has very high TSR. This high resistance to moisture damage for mixtures from aggregate AA12 cannot be easily explained basing on the chemical and mineralogical composition results obtained in this study. It may be necessary to conduct x-ray diffraction studies and probably change density distribution to unravel reasons for this observation.

Table 5.1: Statistical Inferences Regarding TSR for Mixes from the Aggregates

| Aggregate | t-value | t-critical | Reject H₀ | Conclusion at 5% level of significance |
|------------------|----------------|-------------------|-----------------------------|---|
| AA1 | -6.374 | -1.860 | YES | TSR is significantly less than 70% |
| AA3 | -14.709 | -1.860 | YES | TSR is significantly less than 70% |
| AA4 | 3.084 | -1.860 | NO | TSR is significantly greater than 70% |
| AA5 | -1.780 | -1.860 | NO | TSR is significantly greater than 70% |
| AA6 | 3.768 | -1.860 | NO | TSR is significantly greater than 70% |
| AA7 | -8.816 | -1.860 | YES | TSR is significantly less than 70% |
| AA8 | -5.967 | -1.860 | YES | TSR is significantly less than 70% |
| AA9 | -6.133 | -1.860 | YES | TSR is significantly less than 70% |
| AA10 | -20.334 | -1.860 | YES | TSR is significantly less than 70% |
| AA11 | -0.957 | -1.860 | NO | TSR is significantly greater than 70% |
| AA12 | -10.393 | -1.860 | NO | TSR is significantly greater than 70% |

Although aggregate AA5 has high percentage of acid insolubles that would lower TSR, it has some arnothite feldspar ($\text{CaAl}_2\text{Si}_2\text{O}_8$) that forms insoluble salts with bitumen acidic functionalities. This leads to water resistant bonds which probably explain the significantly high TSR values associated with this aggregate.

Aggregate AA11 has some ferromagnesian, anorthite and augite minerals which also form insoluble salts with bitumen acidic parts. This seems to cause a significantly high TSR value observed although the percentage of acid insolubles is high.

The other aggregates with low TSR values have both high levels of acid insolubles and unfavourable mineralogical composition. They have high

quartz content containing SiO₂ that is associated with weak bonds in presence of water. These aggregates also possess alkali feldspars which form soluble salts that are easily diluted by water. Some aggregates had mica which is known to impair adhesion at the interface (Majidzadeh et al., 1968). Black mica, *biotite* [K(Mg,Fe²⁺)₃(Al,Fe³⁺)Si₃O₁₀(OH)₂] and white mica, *muscovite* KAl₂(AlSi₃)O₁₀(OH)₂ are silicates with hydroxyl groups and are easily diluted when in contact with water. This seems to be the reason why aggregates containing these minerals produce bituminous mixtures that are moisture sensitive.

5.1.1 Analysis of the Effect of Aggregate Chemistry

Aggregate chemistry is one of the important concepts that possibly relates to interfacial bond weakening in presence of water. The results of aggregate chemical composition are compared with the performance of bituminous mixtures as given by the tensile strength ratio (TSR) parameter. Larger values of TSR are indicative of increased resistance to moisture damage on the bituminous mixtures. Aggregate chemistry can be assessed by studying the effect of its constituent acid insolubles on its interaction with bitumen. Table 5.2 summarizes the results of aggregate acid insolubles and TSR of bituminous mixtures from the aggregates under study.

Table 5.2: Summary of Acid Insolubles and TSR for the Aggregates under Study.

| Variable | Aggregates Under Study | | | | | | | | | | | |
|---------------------|------------------------|------|------|------|------|------|------|------|------|------|------|------|
| | AA1 | AA2 | AA3 | AA4 | AA5 | AA6 | AA7 | AA8 | AA9 | AA10 | AA11 | AA12 |
| Acid Insolubles (%) | 89.1 | 84.3 | 84.3 | 65.0 | 80.3 | 55.5 | 90.7 | 90.4 | 85.5 | 90.9 | 76.1 | 98.8 |
| TSR (%) | 39.8 | - | 41.5 | 83.0 | 63.4 | 90.1 | 48.9 | 56.1 | 41.0 | 31.0 | 65.6 | 90.4 |

A scatter plot of TSR as a function of percentage of acid insolubles (AI) is made in Figure 5.1 and a linear relationship seems to exist. Aggregate AA12

was statistically found out to be an outlier since both its TSR and level of acid insolubles are high probably due to rough texture on its surface.

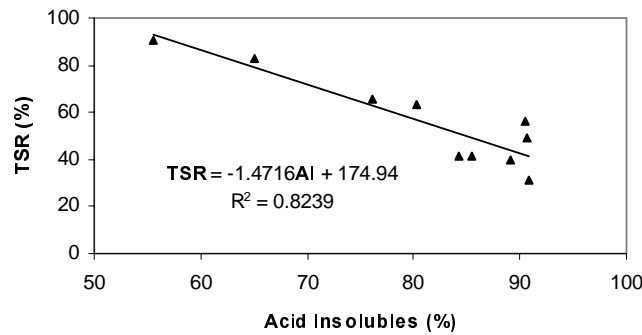


Figure 5.1: TSR as a Function of Acid Insolubles

Regression analysis was done and a least squares fit obtained as shown in the figure. Estimates of the regression coefficients imply that reduction in acid insolubles is associated with decreased moisture sensitivity. The least squares estimators are reliable since they are subjected to the least chance variations as can be shown by the *Gauss-Markov* theorem. A p-value of less than 0.05 was obtained for the slope coefficient confirming significance of acid insolubles in TSR prediction. A high coefficient of determination ($R^2 = 0.8239$) exists indicating that about 82% of variability in TSR could probably be explained by its linear relation with total percentage of acid insolubles namely SiO_2 and Al_2O_3 .

To diagnose adequacy of model fit, a standardized residuals plot against standardized predicted values is made in Figure 5.2 (a). The assumption that the samples were drawn from a normal population was checked by plotting the expected cumulative probability against observed cumulative probability of the data as shown in Figure 5.2 (b). From the plots, the assumptions of independence and normality of the random errors seem not to be violated. Thus, the fitted line model is appropriate.

Table 5.3 shows the results of TSR and the corresponding percentages of SiO₂ and Al₂O₃ contents for all the aggregates. A scatter plot of TSR as a function of SiO₂ content (SC) is shown in Figure 5.3 and depicts a linear relationship with a relatively high coefficient of determination (0.7008). The assumptions of independence and normality of the random errors were checked and no violation was apparent.

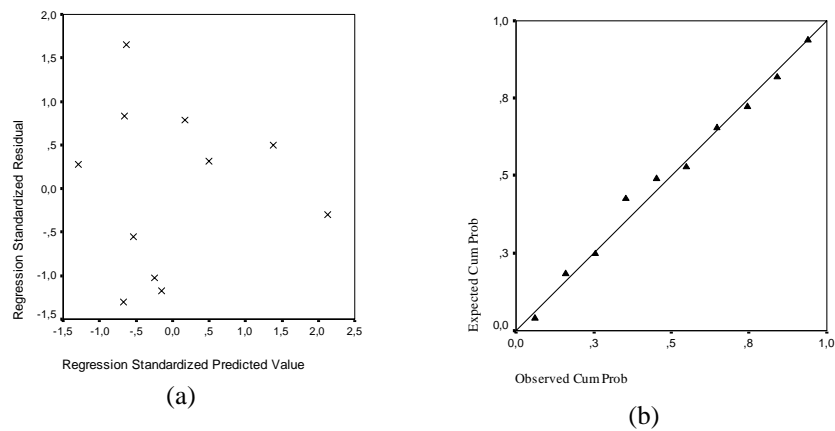


Figure 5.2: (a) Standardized residuals scatter plot (b) A Normal probability Plot of residuals

Table 5.3: Summary of TSR and SiO₂ and Al₂O₃ Contents for the Aggregates.

| Variable | Aggregates Under Study | | | | | | | | | | | |
|--|------------------------|------|------|------|------|------|------|------|------|------|------|------|
| | AA1 | AA2 | AA3 | AA4 | AA5 | AA6 | AA7 | AA8 | AA9 | AA10 | AA11 | AA12 |
| Percent SiO ₂ | 75.5 | 69.8 | 83.6 | 30.9 | 77.3 | 32.9 | 79.2 | 77.5 | 71.2 | 71.9 | 53.7 | 89.5 |
| Percent Al ₂ O ₃ | 13.6 | 14.5 | 0.7 | 34.1 | 3.0 | 22.6 | 11.5 | 12.9 | 14.3 | 19.0 | 22.4 | 9.3 |
| TSR (%) | 39.8 | - | 41.5 | 83.0 | 63.4 | 90.1 | 48.9 | 56.1 | 41.0 | 31.0 | 65.6 | 90.4 |

A stepwise regression analysis was done to assess whether the contribution of Al₂O₃ to TSR variability is significant. TSR was regressed with both SiO₂ and Al₂O₃ contents to give a multiple regression model. The relevant analytical statistics for the model with only SiO₂ content and the model with both SiO₂ and Al₂O₃ contents as regressor variables are summarized in Table

5.4. The R^2 -value for the model with only SiO_2 is 0.7008 while that of model with both SiO_2 and Al_2O_3 is 0.8239.

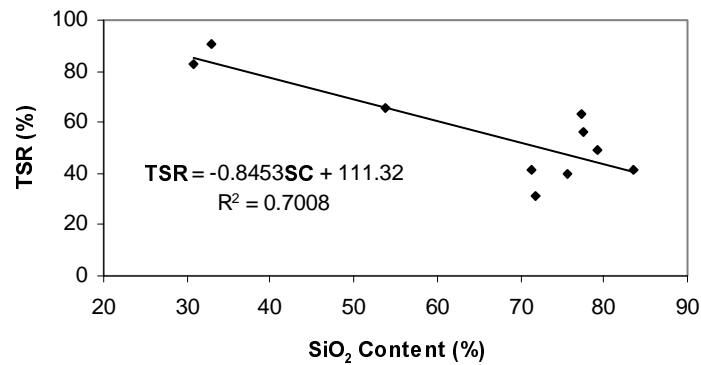


Figure 5.3: A Scatter plot of TSR against SiO_2 content

Thus, the contribution of Al_2O_3 in determining variability in TSR is 12.31%. This is probably due to the fact that the Al_2O_3 content is generally lower than SiO_2 content in all aggregates. In general, based on this study, the higher the aggregate SiO_2 and Al_2O_3 contents, the more sensitive the mixtures are to moisture damage.

Table 5.4: Summary of Stepwise regression of TSR with SiO_2 and Al_2O_3

| Model | Regressors | R^2 -value | p-value | 95% confidence interval |
|-------|---------------------|--------------|---------|--|
| 1 | SC ^a | 0.7008 | 0.003 | $-1.291 \leq B \leq -0.393^c$ |
| 2 | SC, AC ^b | 0.8239 | 0.002 | $-2.171 \leq B_1 \leq -0.697^d$ $-2.825 \leq B_2 \leq -0.095^d$ |

- SC = SiO_2 content
- SC, AC = SiO_2 and Al_2O_3 contents
- B = Regression coefficient for SC in model 1
- B_1 and B_2 are regressions coefficients for SC and AC in model 2.

The p-values obtained were much lower than 0.05 indicating that the models are very significant in predicting the TSR of mixtures. Furthermore, the 95%

confidence intervals for the model predictor coefficients do not contain zero indicating that mean TSR linearly depends on the predictor variables.

5.1.2 Analysis of the Effect of Aggregate Mineralogy

Aggregate mineralogy is also perhaps one of the important concepts that relates to interfacial bond weakening in presence of water. The results of mineralogical characterization of the aggregates were obtained and summarized (see Table 4.3). Basing on the results, the aggregates were put into five independent groups with each group having an approximately uniform mineralogy that was regarded as the treatment. The grouping is summarized in Table 5.5.

Table 5.5: Grouping of the Aggregates Basing on Mineralogy

| Group | Description of Mineralogy | Aggregates Included |
|-------|---|------------------------|
| 1 | Granitic with some quartz (15 – 45%), alkali feldspars and mica. | AA1, AA2*, AA7 and AA8 |
| 2 | Quartzites which predominantly quartz (60 – 100%) and some other minerals, | AA3 and AA5 |
| 3 | Granites that contain low to high quartz and are feldspathic. | AA9, AA10 and AA11 |
| 4 | Amphiboles/melilites with predominantly ferromagnesian minerals (60 – 80%). | AA4 and AA6 |
| 5 | Granitic with purely quartz and rough texture | AA12 |

* Note that no mixtures were prepared from Aggregate AA2 since the quarry was closed during the study

Basing on these groups, the effect of aggregate mineralogy was analyzed by testing the effect of this grouping on the TSR of the bituminous mixtures from these aggregates. The data analyzed was arranged as shown in Table 5.6. The objective was to test the hypothesis that the means of these groups are not all equal. This constituted a completely randomized design or one-way classification. The variability in TSR would be due to the effect of differences between groups (or differences in mineralogy) and random errors

or variation within groups. It was assumed that the populations from which the group data were drawn are normal with equal variances.

Table 5.6: TSR Data for the Different Mineralogical Groups

| Group | TSR (%) | | | Mean |
|-------|---------|------|------|------|
| 1 | 39.8 | 48.9 | 56.1 | 48.2 |
| 2 | 41.5 | 63.4 | | 52.5 |
| 3 | 41.0 | 31.0 | 65.5 | 45.8 |
| 4 | 83.0 | 90.1 | | 86.6 |
| 5 | 90.4 | | | 90.4 |

An analysis of variance was performed to test at a 0.05 level of significance whether differences among group means are significant. The following hypothesis was formulated for testing:

$$H_0: \mu_1 = \mu_2 = \mu_3 = \mu_4 = \mu_5$$

$$H_1: \mu_i \neq \mu_j \text{ for at least one } ij \text{ group pair.}$$

μ_k is the average for group k. The null hypothesis is rejected if $F > F_{0.05, 4, 6} = 4.53$ where F is determined by a one-way analysis of variance. The ANOVA table for the TSR data above is given as follows:

| Source | Sum of Squares | df | Mean Square | F | p-value | F_{Cr} |
|--------|----------------|----|-------------|-------|---------|----------|
| GROUP | 3412.2 | 4 | 853.05 | 5.352 | 0.035 | 4.53 |
| Error | 956.2 | 6 | 159.38 | | | |
| Total | 4368.4 | 11 | | | | |

Since $F > 4.53$, the null hypothesis is rejected and we conclude that at a 0.05 level of significance, at least two group means are different. This shows that aggregate mineralogical composition has a significant effect on the TSR.

The assumptions of independence and normal distribution of the errors were checked by making the plots in Figures 5.4 and 5.5 and no violation seemed to be apparent.

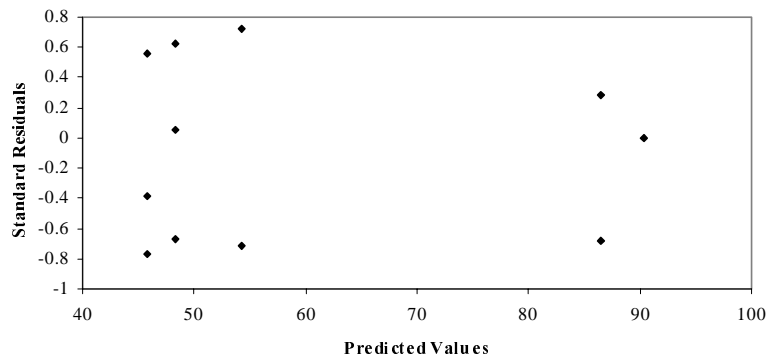


Figure 5.4: Residual Plot to Check Randomness of Errors

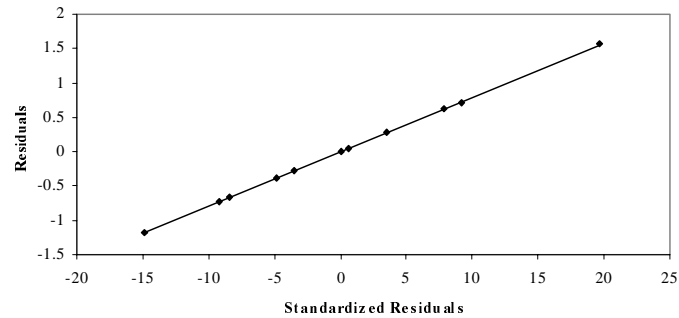


Figure 5.5: Normal Plot of the Residuals

From the analysis of the results of mineralogical composition, high resistance to moisture damage seems to be strongly favoured by ferromagnesian minerals as for example identified in aggregates AA4 and

AA6. Aggregate AA6 had a ferromagnesian silicate olivine $(\text{Mg,Fe})_2\text{SiO}_4$ and melilite $(\text{Ca,Na})_2(\text{Al,Mg,Fe}^{++})(\text{Si,Al})_2\text{O}_7$. Aggregate AA11 also had some augite ferromagnesian mineral which may account for its high TSR.

Non-alkaline feldspars are indicative low moisture sensitivity. For example, hornblende – calcium-iron-magnesium silicate and plagioclase feldspar (Anorthite - $\text{CaAl}_2\text{Si}_2\text{O}_8$) were observed to be present in aggregates with high resistance to moisture sensitivity. The high resistance to moisture damage associated with ferromagnesian minerals and non-alkaline feldspars seems to be due to formation of insoluble salts of calcium and magnesium at the interface after interaction with acidic parts of the bitumen. The resulting interfacial bonds are stripping resistant because these salts cannot be dissolved by water.

Quartz is a silica and seems to be a poor adherend to polar functionalities of bitumen in presence of water. This is due to water molecules forming stronger hydrogen bonds with siliceous surface silanols than the bond between bitumen polars and the silanols. Aggregates AA3 and AA5 for example have high quartz content and their TSR is significantly less than 70%. Aggregate AA9 has an average amount of quartz mineral and had low TSR. Although aggregate AA12 predominantly had quartz (99.8% level) and it is a granite rock, it showed very high resistance to moisture damage. One of the possible explanations may be the coarse texture on its surface which improves tenacity to the bitumen phase.

Most of the aggregates with alkaline feldspars were moisture sensitive. For example, aggregates AA1, AA2, AA7, AA8 and AA10 had relatively high amounts of albite ($\text{NaAlSi}_3\text{O}_8$) and orthoclase (KAlSi_3O_8). These feldspars are moisture sensitive because the sodium and potassium, which are strong alkalis, form soluble salts at the interface after reacting with bitumen acidic parts. The resulting bonds are easily diluted by water resulting into stripping.

Mica containing aggregates (for example AA1, AA2, AA7 and AA8) showed poor resistance to moisture damage. Biotite and muscovite micas have free potassium which interacts with bitumen to form products that are prone to moisture damage.

5.2 Analysis of Combined Effects of Bitumen and Aggregate Properties

This section presents an analysis that was done to find out (1) possibility of a significant difference in moisture sensitivity due to changing the bitumen type, and (2) whether there is a significant difference in moisture sensitivity due to changing the aggregate type. The TSR's for the different combinations of bitumen and aggregates as main factors (see Table 4.10) are summarized below.

| | Aggregate Type | | | |
|-----------|----------------|------|------|-------|
| | AA9 | AA10 | AA11 | AA12 |
| Bitumen B | 39.7 | 22.3 | 62.2 | 100.3 |
| Bitumen C | 49.4 | 20.6 | 68.0 | 95.9 |
| Bitumen D | 41.0 | 16.0 | 65.7 | 90.4 |
| Bitumen F | 49.4 | 21.3 | 64.7 | 92.7 |

The analysis to establish factor effects was done by testing the hypothesis:

H_0 : TSR is not affected by difference in bitumen and aggregates.

H_1 : Not H_0 above.

To test the above hypothesis, a 4 x 4 factorial model was formulated for the observed TSR values in terms of the grand mean of the observations and the effects of aggregate and bitumen as follows:

$$TSR_{ij} = \mu + \alpha_i + \beta_j + \varepsilon_{ij} \dots\dots\dots 5.3$$

where μ is the grand mean

α_i is the effect of the i^{th} bitumen type, $i = 1, 2, 3, 4$

β_j is the effect of the j^{th} aggregate type, $j = 1, 2, 3, 4$

ε_{ij} are random independent errors $\sim N(0, \sigma^2)$

The hypothesis to be tested is thus formulated as follows:

$H_0: \alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = 0; \beta_1 = \beta_2 = \beta_3 = \beta_4 = 0;$

$H_1: \text{The } \alpha\text{'s are not all } = 0, \text{ and the } \beta\text{'s are not all } = 0.$

Assume a 5% level of significance.

To test whether H_0 is to be rejected or not, the ratios of mean sum of squares to error sum of squares (F-ratio) are compared with critical values obtained from statistical tables. These ratios follow an F-distribution and H_0 is rejected if the observed ratios fall in the rejection region of the probability distribution. An analysis of variance was done and the results below were obtained:

Dependent Variable: TSR

| Source | Sum of Squares | df | Mean Square | F | p-value | F _{Cr} |
|-----------|----------------|----|-------------|---------|---------|-----------------|
| AGGREGATE | 12028.3 | 3 | 4009.4 | 299.210 | 0.000 | 3.86 |
| BITUMEN | 57.7 | 3 | 19.2 | 1.433 | 0.297 | 3.86 |
| Error | 121.0 | 9 | 13.4 | | | |
| Total | 12207.0 | 15 | | | | |

From the ANOVA results, conclusions are drawn (as given in Table 5.7) regarding the null hypotheses for the different factors at a 0.05 level of significance.

Table 5.7: Inferences Regarding the Tests in the Main Factors at 0.05 Level

| FACTOR | P-value | Decision Regarding H_0 | IS FACTOR SIGNIFICANT? |
|-----------|---------|--------------------------|------------------------|
| AGGREGATE | 0.000 | Reject H_0 | YES |
| BINDER | 0.297 | Not Reject H_0 | NO |

Thus, the differences among the aggregates under study seem to significantly affect the TSR. On the other hand, the differences among bitumen types do not seem to significantly affect the TSR. The means and effects of these factors are obtained and summarized in Table 5.8. Highest TSR values come from aggregate AA12 mixed with any bitumen since bitumen type is not a significant factor. Figure 5.6 shows the box plots for the means of the main factors namely bitumen and aggregate type. To check adequacy of model fit, scatter and normal plots of residuals are made (cf. Figures 5.7 and 5.8). From the plots, the assumptions of independence and normality of the random errors seem not to be violated. Thus, the fitted model is appropriate.

Table 5.8: Parameter Estimates for the Significant Factors.

| FACTOR | Effect Parameter | Mean | Effect Value |
|-------------------|------------------|--------|--------------|
| <i>Grand Mean</i> | μ | - | 56.23 |
| AGGREGATE | | | |
| AA9 | α_1 | 44,875 | -11.35 |
| AA10 | α_2 | 20,050 | -36.18 |
| AA11 | α_3 | 65,150 | 8.93 |
| AA12 | α_4 | 94,825 | 38.60 |
| BITUMEN | | | |
| B | β_1 | 56,125 | -0.10 |
| C | β_2 | 58,475 | 2.25 |
| D | β_3 | 53,275 | -2.95 |
| F | β_4 | 57,025 | 0.80 |

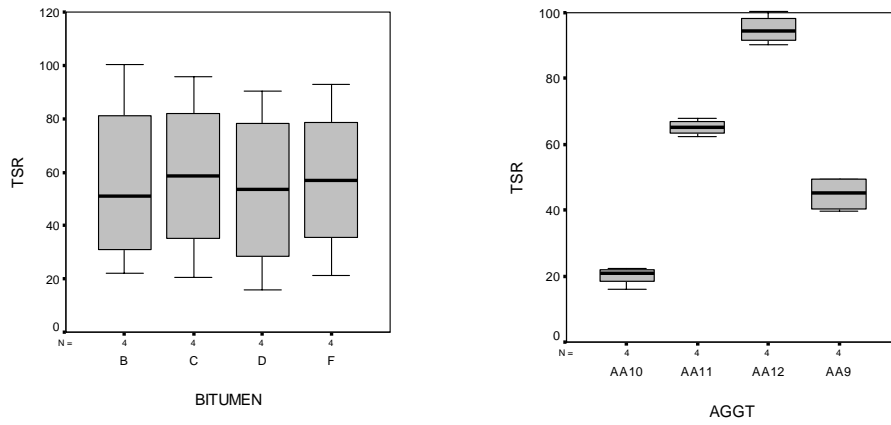


Figure 5.6: Box Plots of the Main Effects

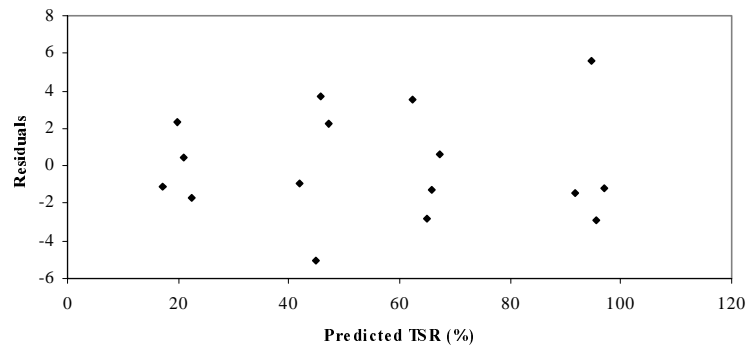


Figure 5.7: A Plot of Residuals Versus Predicted values of TSR

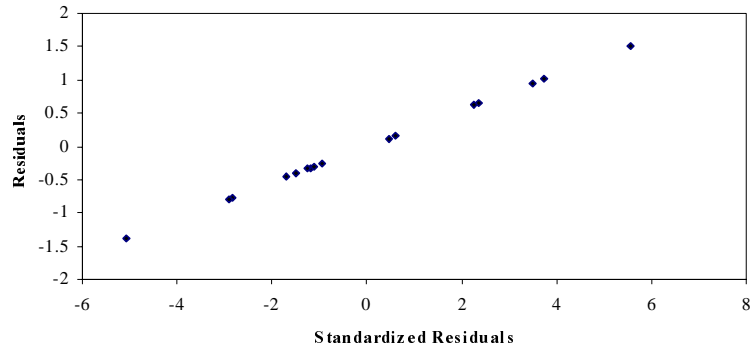


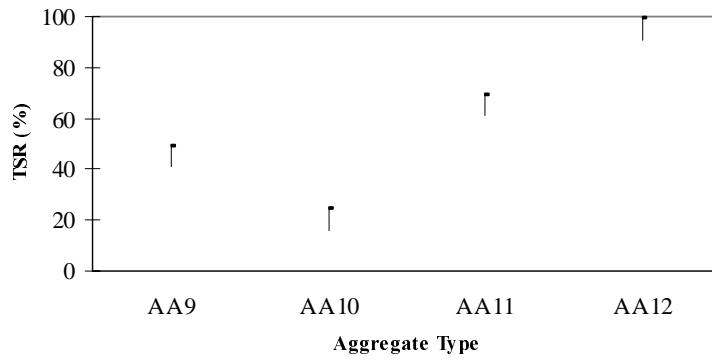
Figure 5.8: A Normal Plot of the Residuals

Figure 5.9 shows the 95% confidence intervals for TSR's of both the aggregates and the bitumens. These are intervals whereby we are 95% sure that the tensile strength ratio will fall between such intervals. These plots, as well as the box plots (Figure 5.6), show that aggregates AA11 and AA12 form bituminous mixtures that have TSR's significantly above 70%.

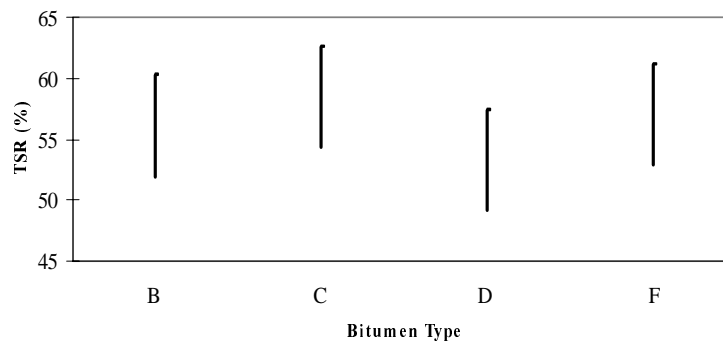
To verify the conclusions drawn above, a pairwise comparison of aggregates was run on the average TSR values using the *Bonferroni* method at a 0.05 level. The analysis resulted in the grouping shown in Table 5.9.

From the comparison, the summary below can be made between adjacent pairs of means for the aggregates after arranging them in order of corresponding magnitudes of TSR values of the bituminous mixtures.

| | | | |
|----------------|---------------|----------------|----------------|
| Aggregate AA10 | Aggregate AA9 | Aggregate AA11 | Aggregate AA12 |
| | | | |



(b) The 95% Confidence intervals for Aggregate



(b) The 95% Confidence intervals for Bitumen

Figure 5.9: The 95% Confidence Intervals for the Main Effects

An underline for any two aggregates indicates that those aggregates produce bituminous mixtures with moisture sensitivity that is significantly different. It can be seen that the aggregates used produced mixtures with mean TSR values that are different a 5% level of significance since in all cases $p < 0.05$.

Table 5.9: Results of the Bonferroni Multiple Comparison Results of Aggregates

| (I) AGGT | (J) AGGT | Mean Difference | Std. Error | p-value | 95% Confidence Interval | |
|----------|----------|-----------------|------------|---------|-------------------------|-------------|
| | | (I-J) | | | Lower Bound | Upper Bound |
| AA9 | AA10 | 24.8250* | 2.59246 | 0.000 | 16.1034 | 33.5466 |
| | AA11 | -20.2750* | 2.59246 | 0.000 | -28.9966 | -11.5534 |
| | AA12 | -49.9500* | 2.59246 | 0.000 | -58.6716 | -41.2284 |
| AA10 | AA9 | -24.8250* | 2.59246 | 0.000 | -33.5466 | -16.1034 |
| | AA11 | -45.1000* | 2.59246 | 0.000 | -53.8216 | -36.3784 |
| | AA12 | -74.7750* | 2.59246 | 0.000 | -83.4966 | -66.0534 |
| AA11 | AA9 | 20.2750* | 2.59246 | 0.000 | 11.5534 | 28.9966 |
| | AA10 | 45.1000* | 2.59246 | 0.000 | 36.3784 | 53.8216 |
| | AA12 | -29.6750* | 2.59246 | 0.000 | -38.3966 | -20.9534 |
| AA12 | AA9 | 49.9500* | 2.59246 | 0.000 | 41.2284 | 58.6716 |
| | AA10 | 74.7750* | 2.59246 | 0.000 | 66.0534 | 83.4966 |
| | AA11 | 29.6750* | 2.59246 | 0.000 | 20.9534 | 38.3966 |

* The mean difference is significant at the 0.05 level.

The bituminous mixtures from aggregate AA10 were the most sensitive to moisture damage. Aggregate AA10 is a syenogranite with 25 – 30% quartz and; potassium and sodium feldspars. The aggregate also had a high content of SiO₂ and Al₂O₃. These compounds form water sensitive bonds at the interface leading to reduced tensile strength ratio. Infact, mixtures from this aggregate mixed with aggregate D had a relatively low value of tensile strength ratio compared to the other bitumens. Bitumen D was the most acidic and therefore could not adhere tenaciously to the acidic surface of aggregate AA10 characterized by surface silanols.

Aggregate AA9 contained 40 – 45% quartz and high Ca-feldspars. Although Ca-feldspars form insoluble salts with bitumen acidic parts, the hydroxylated siliceous surface of this aggregate reduces pH and the resulting equilibrium would lead to a weak bond.

Aggregate AA11 is a tonalite and has mainly Ca-feldspars and augite ferromagnesian which are associated with strong bonds. This combination of minerals does not seem to be affected by the acidity in the bitumen.

The high resistance to moisture damage for mixtures from aggregate AA12 cannot be easily explained basing on the chemical and mineralogical composition results obtained in this study. It may be necessary to conduct x-ray diffraction studies and probably change density distribution to unravel reasons for this observation.

6. CONCLUSIONS AND POINTERS TO FURTHER RESEARCH

Basing on the moisture damage and material characterization data obtained in this study, the following conclusions are drawn:

- (a) Chemical characterization of bitumens using infrared spectroscopy, gel permeation chromatography and thin layer chromatography shows differences in bitumens, although these bitumens would be considered to be similar basing on classical rheological properties like penetration and viscosity.
- (b) Dynamic mechanical analysis results indicate that binders have similar visco-elastic response around 0°C.
- (c) Presence of Ca-feldspars and ferromagnesian minerals in aggregates largely relates to improved resistance to moisture damage of the corresponding bituminous mixtures.
- (d) Mixtures from aggregates with high concentrations of acid insolubles (SiO_2 and Al_2O_3) are sensitive to moisture damage. The contribution of Al_2O_3 to moisture damage was generally lower than that of SiO_2 possibly due to a lower content of the former compared to the latter.
- (e) The choice of aggregate type is the dominant factor affecting moisture sensitivity of the resulting mixtures. Bitumen type is not an important factor in determining moisture sensitivity of bituminous mixtures.
- (f) Assessment of moisture sensitivity basing on absolute stiffness values of water treated mixtures is not reliable. Results from this

study show that mixtures with similar wet resilient moduli had varying tensile strength ratios, hence varying moisture sensitivity tendencies.

- (g) Modulus of resilience ratio (MRR) and tensile strength ratio (TSR) parameters show similar trends in comparing moisture sensitivity of different mixtures. However, MRR values are generally lower than TSR values for the same mixtures.

The visco-elastic behaviour of binders around 0°C is an interesting phenomenon. An additional study around this area would be of great value in additional understanding of bitumen low temperature behaviour, and possibly development of a grading system similar to that for penetration and viscosity. The effect of Ca-feldspars and ferromagnesian aggregate minerals on moisture sensitivity of bituminous mixtures needs to be validated using other moisture damage evaluation methods. Additional test data is required to come up with a relationship between TSR and MRR parameters so that both can be used in the same test procedure.

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