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**Functional Durability-related Bitumen  
Specification (FunDBitS)**

**Correlations between bitumen and asphalt  
properties**

**Binder/aggregate interaction (water sensitivity)**

Deliverable D.2e  
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# **CEDR Call 2013: Energy Efficiency – Materials and Technology**

## **FunDBitS Functional Durability-related Bitumen Specification**

### **Correlations between bitumen and asphalt properties**

Binder/aggregate interaction (water sensitivity)

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## Executive summary

In the FunDBitS project, the data that has become internationally available since the BitVal project are being reviewed in order to develop performance-based bitumen characteristics which may be introduced into bitumen specification standards EN 12591, EN 14023 and EN 13924.

The relevant information available in the literature was already reviewed and possible correlations between the bitumen and asphalt properties were identified. For this, the following five main asphalt properties were considered: permanent deformation (rutting); stiffness; low temperature cracking; fatigue cracking and binder/aggregate interaction. As a result of the work performed, the interim report of the FunDBitS project, deliverable D.1, presents a description on identified correlations between bitumen and the referred five asphalt properties.

Later on, possible correlations between the bitumen and asphalt properties were reviewed in terms of the extent to which the bitumen affects the asphalt, in particularly its durability and service life, with due consideration for the reliability of the test methods and presence of other factors on the asphalt properties. Deliverable D.2 of the FunDBitS project presents the review of the correlations between the referred five asphalt properties and bitumen tests/properties.

The presented report is a part of deliverable D.2, which deals specifically with the correlations between the water sensitivity of asphalt mixtures and bitumen tests/properties related to the interactions between bitumen and aggregate or adhesion. However, in contrast with the previous chapters, adhesion phenomena are more complex as they involve at least two materials (binder and aggregate) or even three if one considers the effect of water. Furthermore, in the case of asphalt mixture the interpretation of test results may be further hampered by other types of mixture characteristics such as cohesive properties or mix design. Additionally, the lack of adhesion (e.g. in case of stripping) is also known to be a demonstration of interfacial tension between bitumen and aggregate in the presence of water.

Taking into account all elements and their complexity related to binder/aggregate interaction and the water sensitivity of asphalt mixtures, the presented report discusses the literature findings accordingly to different levels which can be designated as follows:

Level 1: mixture components addressing both bituminous binders as well as aggregates (fundamental) physicochemical properties (e.g. surface energy).

Level 1-2: loose mixture of bitumen and aggregate (coated aggregate) conditioned with water (e.g. stripping tests).

Level 2: compacted asphalt mixture conditioned with water (e.g. water sensitivity tests).

Level 3: field experience allowing validation of test results as obtained in the laboratory.

While writing up this report, it was the objective to focus on the existence of possible correlations between results acquired during testing at the different levels. In this way, it was possible to formulate conclusions and/or recommendation regarding the evaluation of bitumen/aggregate interactions.

Finally, whenever possible special attention was also paid to both the impact of ageing of bituminous binders as well as overall uncertainty (precision) issues.

## 1 Introduction

Moisture damage is an important failure mechanism in asphalt pavements. In very general terms, moisture damage has been defined as the deterioration of the properties of an asphalt mixture due to the exposure to and the action of water (paper 613: Little et al., 2003). During the service life of HMA water can interact in the liquid state, as vapour and also in the solid state. Moisture damage will lead to stripping and aggregate loss and to a decrease in the structural strength and durability of HMA.

In paper 614 (Terrel et al., 1994) identified three mechanisms of moisture damage in asphalt pavements. Moisture damage can occur because of a loss of adhesion between the aggregate and the binder interface, referred to as adhesive failure; this will result in clean aggregate surfaces after failure. Moisture can also weaken the binder and mastic phase leading to a failure inside the binder or mastic film. In this case after failure the aggregates will still be covered with bitumen. In this respect, a failure mechanism related to the formation of a weak interface has also been postulated in literature (paper 615: Jeon et al., 1990). Authors stated that surfaces of aggregates exhibiting high porosity can act as molecular sieves separating high and low molecular bitumen fractions. If such absorption occurs the bitumen remaining on the outside could become hard and brittle (paper 616: Curtis et al. 1993) and prone to fracture. But the authors could not find evidence of such a selective absorption. Finally, a third possibility has been identified in which damage is caused by the fracture of aggregates, particularly when the mixture is subjected to freezing. In general, it is obvious that the critical material property that needs to be controlled to avoid or reduce moisture damage depends on the type of failure; increasing binder/aggregate adhesion would not be beneficial if the failure mode is cohesive.

In general to get good adhesion between an adhesive and a substrate, the adhesive must be able to wet the substrate, meaning that the adhesive must have the ability to spread itself out into a film that covers the substrate surface. In order for this to happen the adhesive must have a low enough viscosity so that it can flow. Another factor that affects wetting is the relative strengths of cohesive forces (between like molecules) and those of adhesive forces (between unlike molecules such as an adhesive molecule and a substrate molecule). If the cohesive forces are weaker than the adhesive forces between the adhesive molecules and the substrate surface, then the adhesive molecules will spread out over the substrate and wet its surface. An adhesive that has a relatively low viscosity and is able to wet the substrate surface will flow into any tiny cracks or pores on the substrate surface, thus promoting what is known as mechanical bonding. Mechanical bonding increases the strength of an adhesive bond.

For adhesion between bitumen and aggregate several mechanisms are identified in the literature. Most of these mechanisms are based on physiochemical interactions between the bitumen and the aggregate and can be classified into the following three broad categories: 1) mechanical adhesion 2) physical adhesion and 3) chemical bonding (paper 614: Terrel et al., 1994). In the case of mechanical adhesion, the adhesion relies on the penetration of the binder into surface irregularities like pores and cavities on the stone surface. This adhesion depends on the “mechanical interlocking” between the substrate and the binder implying that rough surfaces provide higher adhesion compared to smooth surfaces (paper 591: Bhasin, 2006). However, in a rough surface there is also a chance that air or even water is entrapped within the pores, and if this happens the roughness will have a negative effect on the water sensitivity (paper 588: Hefer, 2004). Regarding cohesion, this can be considered as the deformation resistance under load occurring in the asphalt film surrounding aggregate particles but at a distance from the aggregate surface, beyond the influence of mechanical interlock and molecular orientation. It has been observed that adhesive failure is more likely

to occur if the asphalt binder film is very thin while cohesive failure is more likely if binder films are thick as stated in paper 592 (Little et al., 2006).

Moisture damage in asphalt can be investigated on different levels as is illustrated in figure 1-1 (papers 617: Lu, 2005 and 618: Solaimanian et al., 2003) has identified the following levels: the individual asphalt components (level 1), the loose asphalt mixtures (level 1-2), the compacted asphalt mixtures (level 2) and the in-service pavement (level 3). As indicated each level has its specific factors adding to the complexity of this phenomenon. Because of these factors any comparison between tests from different levels will need to take such parameters into account.

In field surveys water damage is recognized as stone loss, stripping or ravelling, and the formation of potholes. However, as various failure mechanisms can interact, it is often difficult to establish in a pavement survey which failure type has initiated the damage. For example, it has been shown that the formation of small fatigue cracks can initiate moisture damage as it allows water to penetrate the asphalt layer through the formation of micro cracks. On the other hand, if moisture damage weakens the asphalt layers, they in turn may become less resistant to fatigue loading conditions and initiate fatigue cracking. As a consequence, it can be difficult to even recognize moisture damage in field sites and therefore also to relate laboratory tests results to the performance of a pavement under service conditions.

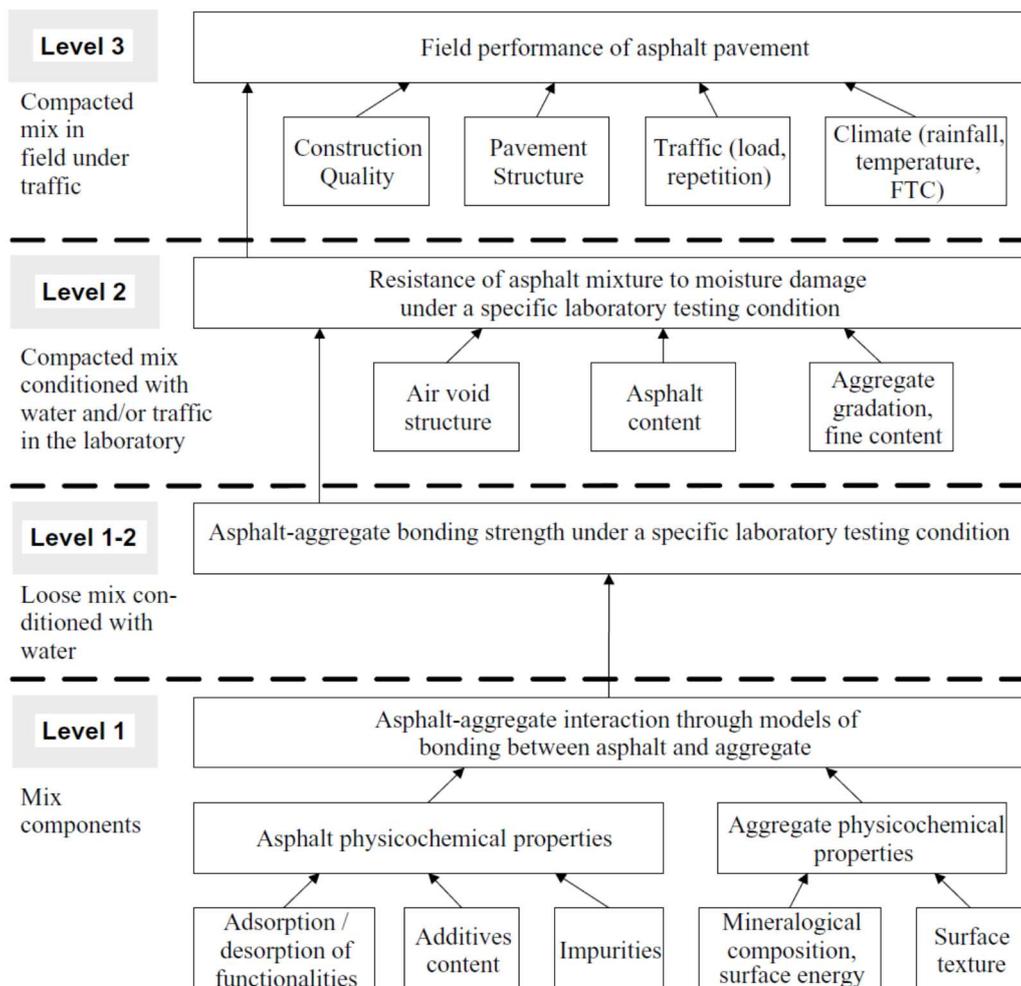


Figure 1-1: Different levels to investigate moisture damage

The objective of this report is to summarize recent literature findings where moisture damage is predicted from (fundamental) properties of the components of an asphalt mix. In the terminology of figure 1 the literature summary focussed on both level 1 as well as 1-2 tests, including a validation of level 1 or 1-2 tests with test results obtained on the other levels, especially level 2. To a minor extent, literature data originating from level 2 and 3 is also discussed whenever directly relevant to the topic of adhesion or binder/aggregate interaction. Results of the review related to level 1 are discussed in part 2 “Fundamental approaches to predict moisture damage” while part 3 “Binder/aggregate interaction – loose mix with water conditioning” deals with level 1-2. Moreover, in part 4 “Binder/aggregate interaction – tests conducted on compacted asphalt mixtures” a summary is given for paper relevant to level 2 and 3. Finally, special attention is paid to both the effect of ageing of binders as well as overall uncertainty (precision) issues in the part 5 and part 6.

## 2 Fundamental approaches to predict moisture damage (level 1)

With respect to level 1 two fundamental concepts that have been proposed to predict moisture damage based on properties from the mixture's components will be evaluated: the first one is the surface energy component concept which was first applied by Texas A&M researchers to bitumen and aggregates and who developed a methodology for the measurement of surface energies for bitumen respectively aggregates (paper 619: Cheng et al., 2002). Another concept is presented in a separate part and is based on the Hamaker equation, which was developed for materials having only Lifshitz-Vander Waals interactions (paper 620: van Oss et al., 1988). This concept has also been applied to bitumen - aggregate adhesion. Finally, a special type of contact angle measurement in which the contact between bitumen is measured in direct contact with a polished aggregate structure is also included (paper 586: Korn, 2004). This is in fact not a test method on the separate components but there are several reasons to include it; contact angle measurements are used to determine surface energies, so in fact the test procedure is very similar to the one used in the surface energy components concept. Additionally, it seems to be a rather simple test and a quite promising approach.

### 2.1 Calculation of adhesive bond strength and debonding by water from surface energy components

Researchers at Texas A&M University have applied the methodology of measuring surface energy components in order to calculate the adhesion of bitumen to an aggregate surface (paper 619: Cheng et al., 2002). They also selected and developed the most suitable test methods to determine surface energy components for bitumen and for aggregates. In this concept surface energy components of bitumen and aggregates are derived separately and the data allows calculating the interfacial work of adhesion in dry as well as in wet conditions. The concept is based on the Van Oss-Chaudhury-Good (VCG) theory of wettability and is very well explained elsewhere (papers 588: Hefer, 2004, 591: Bhasin, 2006, 592: Little et al., 2006, 620: van Oss et al., 1988); here a brief summary is given.

The surface free energy of a material is defined as the amount of work required to create a unit area of a new surface of that specific material in a vacuum. This surface energy can be divided into different parts; a first part, relating to Lifshitz-van der Waals interactions and referred to as  $\gamma^{LW}$  and a second part referring to asymmetrical polar interactions, described as acid-base interactions  $\gamma^{AB}$  or electron acceptor respectively donor parts. The Lifshitz-van der Waals component of the surface energy comprises the following interactions: Keesom (dipole-dipole interactions), Debye (dipole-induced-dipole interactions) and London dispersion forces (induced dipole-induced dipole interactions). In literature, it was shown later that the LW part should only include the London dispersive interactions, while Keesom and Debye interactions should be included in the acid-base part (paper 621: Kloubek, 1992). In this paper the notation LW part is kept, although it refers to the dispersive part only.

$$\gamma = \gamma^{LW} + \gamma^{AB} = \gamma^{LW} + 2\sqrt{\gamma^+ \gamma^-} \quad (1)$$

$\gamma$  = total surface energy

$\gamma^{LW}$  = dispersive part of the surface energy

$\gamma^{AB}$  = acid base part of the surface energy

$\gamma^+$  = Lewis acid component or electron acceptor of surface energy

$\gamma^-$  = Lewis base or electron donor component of surface energy

The interaction of two materials in vacuum or the free energy change of adhesion ( $\Delta G_{12}$ ) between two materials 1 and 2 can be formulated as a function of their respective surface

energy components as shown in equation 2. The free energy change is equal in magnitude but has the opposite sign as the work of adhesion,  $W_{12}$ .

$$\Delta G_{12} = -W_{12} = -\left(2\sqrt{\gamma_1^{LW} \gamma_2^{LW}} + 2\sqrt{\gamma_1^+ \gamma_2^-} + 2\sqrt{\gamma_1^- \gamma_2^+}\right) \quad (2)$$

The subscripts 1 and 2 refer to the respective surface energy components of two substances 1 and 2. Equation 2 shows that the interaction of two materials in vacuum is always negative, meaning there is always an attraction. Equation 2 cannot be zero since for all materials  $\gamma^{LW}$  is a finite and positive number. Based on equation (2) it is possible to calculate the surface energy components for an unknown substance by measuring the surface energy of the unknown versus at least three probe compounds of known surface energy components. From these three liquids at least two need to have (known) polar parts. Different options are available to test this experimentally and this is discussed briefly in the experimental part.

Once the surface components for bitumen and aggregates are determined, their interfacial work of adhesion, the dry bond strength, can be calculated using equation 2 where 1 or 2 is respectively aggregate and bitumen. If in this equation material 1 and 2 would be the same substance it becomes equal to two times the surface energy of this material ( $2\gamma$  in equation 1). Therefore, twice the surface energy of bitumen is related to the cohesive strength or bond energy of bitumen. Cohesive bond energy of a material is defined as the amount of work required to fracture the material to create two new surfaces of unit area each in vacuum. Numerically this is equal to twice the total surface free energy of the material. A higher magnitude of cohesive bond energy implies that more energy is required for a crack to propagate due to fracture.

$$\Delta G_{ii} = -2\gamma_i \quad (3)$$

Finally, consider a three phase system comprising of bitumen, aggregate and water represented by material 1 and 2 in medium 3 respectively. If the medium water displaces bitumen from the bitumen-aggregate interface several processes occur. The interface bitumen-aggregate is lost and this is associated with external work,  $-\gamma_{12}$ . Similarly, two new interfaces between bitumen and water and between aggregate and water are created during this process. The work done for the formation of these two new interfaces is  $\gamma_{13} + \gamma_{23}$ . Therefore, the total work needed for water to displace bitumen from the surface of the aggregate is  $\gamma_{13} + \gamma_{23} - \gamma_{12}$ . In terms of free energy, the resulting free energy of adhesion of component 1 and 2 in medium 3 can be expressed using the same relations but with opposite signs.

$$W_{132} = \gamma_{13} + \gamma_{23} - \gamma_{12} \quad (4)$$

$$\Delta G^a_{132} = \gamma_{12} - \gamma_{13} - \gamma_{23} \quad (5)$$

In order to take both the LW and polar part into account, equation 4 must be calculated as follows:

$$\Delta G^a_{132} = 2 \left[ \begin{array}{l} \sqrt{\gamma_1^{LW} \gamma_3^{LW}} + \sqrt{\gamma_2^{LW} \gamma_3^{LW}} - \sqrt{\gamma_1^{LW} \gamma_2^{LW}} - \gamma_3^{LW} + \\ \sqrt{\gamma_3^+} \left( \sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-} \right) + \sqrt{\gamma_3^-} \left( \sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+} \right) \\ - \sqrt{\gamma_1^+ \gamma_2^-} - \sqrt{\gamma_1^- \gamma_2^+} \end{array} \right] \quad (6)$$

When  $\Delta G^{a_{132}} < 0$  it indicates that there is an attraction between component 1 and 2 also when immersed in medium 3, and in this case a displacement will not happen for a system in thermodynamic equilibrium. For  $\Delta G^{a_{132}} > 0$  the interaction between 1 and 2 becomes repulsive. Latter is the driving force for phase separation of adhesives in aqueous media (8). A large negative value would indicate a good resistance to debonding while a large positive value indicates easier stripping due to water for systems in thermodynamic equilibrium. Practically for all bitumen-aggregate systems the work of debonding  $W_{132}$  is negative or  $\Delta G^{a_{132}}$  is positive indicating that debonding in the presence of water is thermodynamically favourable. The magnitude of work of debonding can differ significantly depending on the surface energy components of bitumen and aggregates. Similarly, for describing the interaction between molecules or particles of material 1 suspended in liquid 3 one can write:

$$\begin{aligned} \Delta G^{a_{131}} &= -2\gamma_{13} \\ &= -2\left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}\right)^2 - 4\left(\sqrt{\gamma_1^+ \gamma_1^-} + \sqrt{\gamma_3^+ \gamma_3^-} - \sqrt{\gamma_1^+ \gamma_3^-} - \sqrt{\gamma_1^- \gamma_3^+}\right) \end{aligned} \quad (7)$$

If the polar surface free energy component of a hydrophobic material (or two similar hydrophobic materials) is negligibly small, then the most important parameter in equation (7) is  $-4\sqrt{\gamma_3^+ \gamma_3^-}$ . This parameter represents the polar contribution to the cohesive energy of water. The value is  $-102 \text{ mJ/m}^2$  and is present in all type of interactions when immersed in water. In fact, this term is the main contributor to the interfacial attractions between non-polar materials immersed in an H-bonding material like water.

Based on three parameters: the dry adhesion, the cohesive strength of bitumen and the free energy of adhesion in the water, two related energy ratios have been proposed:  $ER_1$  and  $ER_2$  according to equation (8) and (9) respectively. In literature the ratio between the adhesive bond energy values in the dry condition and in the presence of water,  $ER_1$ , can be used to predict the moisture sensitivity of asphalt mixtures (paper 592: Little et al., 2006). Another ratio  $ER_2$  can be used; in this parameter the adhesive bond energy in the dry state is diminished with the bitumen cohesion, and this value is divided by the bitumen aggregate adhesion in the presence of water. In order to accommodate the effects of aggregate microtexture on the bitumen-aggregate bond strength in the presence of moisture both bond parameters can also be multiplied by the specific surface area of the aggregates. The procedure how to calculate these parameters is very well described in literature (ref). But is it not fully clear which of these parameters is best suited to predict moisture damage. The term  $\Delta G^{a_{12}}$  in equation (8) and (9) refers to the interfacial free energy of adhesion between bitumen and aggregate in vacuum (or air), while  $\Delta G^{a_{132}}$  refers to the wet adhesion.

$$ER_1 = \frac{\Delta G^{a_{12}}}{\Delta G^{a_{132}}} \quad (8)$$

$$ER_2 = \left| \frac{\Delta G^{a_{12}} - \Delta G_{11}}{\Delta G^{a_{132}}} \right| \quad (9)$$

In addition to the VCG method, other methods to calculate adhesion are also often used, like for example the Owens-Wendt (OW) method, also known as the Kaelble method. In the OW method SFE is a sum of two components: a dispersive (D) and a polar (P) part, where the dispersive part reflects only dispersive interactions, and the polar part is a sum of polar, hydrogen, inductive and acid–base interactions. In the OW method a minimum of two known solvents or media are needed to calculate the SFE components.

## 2.2 Calculation of adhesive bond strengths in various media based on the Hamaker equation

Recently, researchers at KTH (Royal Institute of Technology in Stockholm, Sweden) have used the Hamaker equation to estimate the interaction of bitumen and aggregate/mineral components having air or water as intervening medium (paper 610: Lyne et al., 2010). The Hamaker equation is used to estimate the van der Waals interaction, including dispersive, Keesom and Debye interactions. The Hamaker equation is composed of two parts: a first part describes the polar contribution and a second part the dispersive contribution. The Hamaker equation is shown in equation (10). In this equation, subscripts 1 and 2 refer in this case to bitumen and aggregate while subscript 3 refers to the medium, either air or water. Calculations of Hamaker's polar part require accurate dielectric data, in particular dielectric constants and for the dispersive part the refractive index of the interacting materials and the intervening medium.

$$A_{132} = \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3h\nu}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{n_1^2 + n_3^2} \sqrt{n_2^2 + n_3^2} (\sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2})} \quad (10)$$

$\varepsilon_i$  is the static dielectric constant for material/medium i

$n_i$  is the refractive index of the material/medium i, in the visible region

$h$  is Planck's constant (= 6.6261 x 10<sup>-34</sup> Js)

$k$  is Boltzmann constant (= 1.3807 x 10<sup>-23</sup> J/K)

$T$  is the absolute temperature

$\nu$  is the main electronic absorption frequency, typically  $\pm 3 \times 10^{15}$  s<sup>-1</sup>

in vacuum  $n_3=1$  and  $\varepsilon_3 = 1$

If Hamaker equation equals zero, there is no net force and the bodies are neither pulled together nor pushed apart. If the net force is positive then the bodies will adhere, if the net force is negative repulsion will occur. For most material combinations the Hamaker equation is positive and the van der Waals force is attractive. The van der Waals force is always attractive between two like surfaces and always attractive in vacuum (air). The Hamaker equation can be negative and repulsive for two different material surfaces interacting through a liquid medium ( $A_{123}$ ). Relations between the Hamaker constant and the dispersive part of the surface energy have been proposed: For example, in paper 622 (Israelachvili, 1974) has calculated the Hamaker constants of different liquids from their refractive indices. He then calculated the surface tensions of these liquids using the following equation:

$$A_{ii} = 24\pi r_{ii}^2 \gamma_i^{LW} \quad (11)$$

$r_{ii}$  is the separation distance between interacting atoms or molecules

$\gamma_i^{LW}$  is the dispersive part of the surface energy

Israelachvili found a very good agreement between the calculated surface tension of saturated hydrocarbons and the corresponding experimental values using equation (11) and  $r = 0.2054$  nm. However, this was not true for polar substances. He concluded that equation (11) may not be used to calculate the surface free energies of highly polar liquids, where short range forces other than dispersion forces (e.g. hydrogen bonds) are involved. Later on the value for  $r$  of 2 nm was corrected (by the same author) to a value of 0.165 nm.

## 2.3 Experimental studies

### 2.3.1 Surface energy approach

#### 2.3.1.1 Methods to measure surface energy

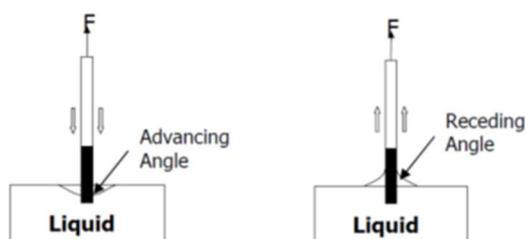
An overview of experimental methods, as was observed in the literature survey to determine the surface energy (SFE) of bitumen and aggregates or its components is presented in table 2-1. The calculation method, if applicable is indicated. In the Owens-Wendt (OW) SFE is a sum of two components: a dispersion (D) and a polar (P) part, while in the Van Oss-Chaudhury-Good (VCG) SFE is calculated based on three components a disperse, an acid and a base component. The most popular test methods include the Wilhelmy Plate Test and the Universal Sorption Device (USD) for respectively bitumen and aggregates. Because of its simplicity and because it can be used to for both bitumen and aggregates, the Sessile Drop Test is also used a lot. These three tests are briefly explained in the next paragraphs.

**Table 2-1: Literature overview indicating the test methods used to determine surface energies of bitumen and aggregate**

Paper(s)	Method to determine surface energies of bituminous binders
211, 232, 221, 233, 588-595, 599, 600, 602, 603, 604,606, 609	Wilhelmy Plate Tests in probe liquids (VCG), ambient
267, 592, 600, 608	Sessile Drops of probe liquids on bitumen surface (VCG) ambient
588, 590, 592	Inverse Gas Chromatography (CVS)
586, 609	Pending drop (100°C - 140°C) combined with Sessile Drop on PTFE (OW)
596	Sessile Drops on a microtome-cut bitumen surface 20°C (OW)
600	Sessile Drops of probe liquids on bitumen surface (OW) ambient
108	Dynamic Sessile Drop measurements of probe liquids on a bitumen surface (VCG)
601	Pending Drops of bitumen (100 - 130°C) ( $\gamma$ total)
596	Pending Drops at equiviscous temperatures ( $\gamma$ total)
607	Pending Drop of bitumen at a fixed $G^*$ 209 Pa ( $\gamma$ total)
600	Wilhelmy Plate Tests in probe liquids (OW) ambient
592	Atomic force microscopy (dispersive component)
	<b>Method to determine surface energies of aggregates in asphalt applications</b>
178, 211, 221, 588, 590-594, 595, 598, 599, 602, 603, 604, 606, 609	Universal Sorption Device (CVS)
107, 608	Sessile Drops of probe liquids on flat aggregate (CVS)
596, 607, 609	Sessile Drops of probe liquids on flat aggregate (OW)
591, 592	Micro Calorimeter (CVS)
592	Inverse gas chromatography (CVS)

Legend: OW - Owens Wendt theory resulting in two SFE components: dispersive and polar; VCG: Van Oss-Chaudhury-Good theory resulting in three SFE components: dispersive, acid and base.

The Wilhelmy Plate Method also referred to as Plate Method, was proposed by researchers from Texas A&M University to investigate bitumen (papers 588 Hefer, 2004 and 590 Hefer et al., 2005 and others as referred to in table 2-1). In this test a thin bitumen coated glass plate is immersed or withdrawn from probe liquid at very slow and constant speed. The dynamic contact angles that develop between the bitumen film and the liquid are obtained, by comparing the weight of the sample slide in air to its weight in the liquid after correcting for buoyancy. The basic principle is schematically illustrated in figure 2-1. The dynamic contact angle measured during the immersion process is called the advancing contact angle (a wetting process), while the dynamic contact angle measured during the withdrawal process is called the receding contact angle (a de-wetting process). Theoretically, for a surface that does not undergo any permanent change by coming into contact with the probe liquid, the advancing and receding contact angles should be the same. However, in most cases differences are observed (paper 592 Little et al., 2006) and they have been attributed to chemical and morphological heterogeneities of the surface, or also to roughness, swelling, rearrangement, inter-diffusion and/or surface deformation. In the case of bitumen, it has been attributed to surface heterogeneities, and in bitumen, the advancing contact angles are used to determine surface energy components (paper 592 Little et al., 2006). In latter study the effect of the choice of probe liquids on the precision of the SFE determination was investigated. In principle, for the OW method it would be sufficient to determine the contact angles with two known probe liquids and for VCG calculation with three probe liquids. However, if two or more of the probe liquids have similar surface free energy components, the calculated surface free energy components of bitumen will be very sensitive to small errors in measurement of contact angles. It was advised by Texas A&M to use five probe liquids.

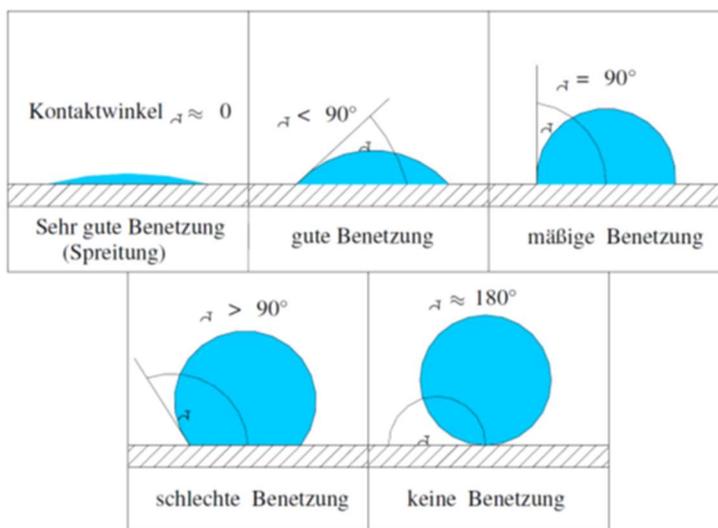


**Figure 2-1: Schematic illustration of Wilhelmy plate technique [Paper 590: Hefer et al., 2005]**

The Sessile Drop Method is based on a direct measurement of the contact angle of a known liquid on the surface of the material being tested (paper 588 Hefer, 2004). This approach is very well described in other references such as paper 586 (Korn, 2004). While the plate technique measures a dynamic contact angle in a quasi-equilibrium state, the sessile drop approach usually measures a static contact angle although it can also be used in a dynamic mode. As in the case of Wilhelmy Plate Method, the three unknown surface energy components of a solid under investigation can be calculated once the contact angles of at least three known liquids on this substrate are measured. In this test, a drop (about 2 to 3 mm in diameter) of a probe liquid is dispensed on a horizontal, flat surface of the material being tested (this can be a bitumen film or a flat stone surface), and the contact angle is measured. In figure 2-2, different contact angles are shown as a function of the degree of wetting. For a complete wetting the contact angle is zero, while for two materials that have no wetting the contact angle is 180°C. In that case the drop will roll on the surface. Instead of working with known probe liquids, it is also possible to use solid substrates with known surface energy characteristics and use sessile drop measurements to determine the SFE components of an unknown liquid.

Bitumen and aggregate can be tested using this method. In both cases, the sample needs to be flat and smooth, and aggregates are very often polished. This is not ideal, since the

surface does not represent a natural crushed state. In addition, since each measurement is made using a single drop that covers only an area of about 2 to 3 mm in diameter, the application of this test on heterogeneous aggregate surfaces will require a lot of repetitions on different locations, in order to get a reasonable average representative of the whole surface area. And, it has also been reported that non-polar liquids cannot be used on high-energy aggregate surfaces since complete wetting occurs, resulting in a zero contact angle. The quality of the drop pictures is also very important as stated in paper 601 (Wistuba et al., 2012).



**Figure 2-2: Overview of contact angles as a function of the wetting behaviour [Paper 586: Korn, 2004]**

The Universal Sorption Device is a gravimetric sorption technique, used to measure the sorption characteristics of selected vapours on aggregate surfaces. According to literature it can be used in a static or dynamic way. Again the sorption tests need to be conducted with at least three vapours with known surface energy components in order to be able to calculate the three SFE components of an unknown aggregate. Sorption methods are particularly suitable since they can accommodate different sample sizes, irregular shapes, mineralogy compositions and surface textures associated with aggregates. In the method used by Texas A&M University an aggregate fraction passing a 4.75 mm sieve and retained on a 2.36 mm sieve is tested. The chamber, including the suspended aggregate fraction, is vacuumed and the solute is injected into the system. A highly sensitive magnetic suspension balance is used to measure the amount of solute adsorbed on the surface of the aggregate at predetermined increasing levels of relative pressure. In paper 592 (Little et al., 2006) it is noted that the specific surface area (SSA) of the aggregates is a required input to be able to compute SFE components. A method and further discussions regarding the determination of the SSA can be found in a latter paper. The methodology of using the universal sorption device is applicable only when the probe vapour molecules are adsorbed due to physical adsorption and not chemisorption (paper 592 Little et al., 2006). Experiments by Texas A&M University have confirmed that the adsorption of the selected probe vapours on typical aggregate surfaces such as granite, limestone, and gravel is mostly due to physical adsorption. But, if aggregates are coated with chemically active materials and are used for testing, it must be ensured that the probe vapours do not react with the coating. In paper 592 (Little et al., 2006) the author also shows that clean aggregates are needed and physically adsorbed impurities such as water vapour, etc., need to be removed, as they will have an effect on the SFE components. Water molecules and other impurities when adsorbed to the clean aggregate surface will lower its surface energy.

### 2.3.1.2 SFE measurements on bituminous binders

In table 2-2, values obtained for surface energy measurements on bitumen are shown. All these data are based on the Wilhelmy plate method combined with the VCG calculation procedure. There seems to be a good agreement in the total surface energy levels found. Some slight differences can be observed in the polar parts: e.g. data reported in paper 600 (Bahramian, 2012) shows slightly larger values for the polar parts as compared to other references. In general, polar parts are much smaller compared to the dispersive part. Standard deviations on the surface energy components are reported for example in papers 588 (Hefer, 2004) and 600 (Bahramian, 2012). These standard deviations are sufficient for the total and dispersive parts, but not very accurate for polar, acid and base parts. Especially the small acid and base parts have sometimes very large standard deviations.

**Table 2-2: Overview of typical values of surface energies for bituminous binders, using the Wilhelmy Plate test**

$\gamma_{\text{Total}}$	$\gamma_{\text{LW}}$	$\gamma_{\text{AB}}$	$\gamma^+$	$\gamma^-$	Paper(s)
mJ/m <sup>2</sup>	mJ/m <sup>2</sup>	mJ/m <sup>2</sup>	mJ/m <sup>2</sup>	mJ/m <sup>2</sup>	
14-32	13-32	0-3	0-1.5	0-3	211, 221, 232, 588, 590-594
26-39	18-33	6-8	4.9-6.7	1.7-2.4	600
12.1-12.5	10.6-11.2	1.3-1.5	0.7-0.8	0.6-0.7	233
15.6	13.7	1.9	1.45	0.65	599
19.1-30.6	18.8-30.6	0-0.4	0-0.34	0-5.08	604, 606, 609

Comparisons of different tests methods, using the same sample set, were reported in papers 588 (Hefer, 2004), 590 (Hefer et al., 2005), 592 (Little et al., 2006), 600 (Bahramian, 2012) and 610 (Lyne et al., 2010). For example for the comparison between the Sessile Drop Method and the Wilhelmy plate Tests, paper 592 (Little et al., 2006) reports that both test methods produce results for the LW component with adequate precision. But the correlation between LW parts of both methods was only moderate ( $R^2 = 0.59$ ), Sessile Drop measurements resulted in larger dispersive parts, attributed to differences in the test methodologies. Differences were also reported in the acid components, a larger value was obtained using the Wilhelmy Plate Method. In paper 600 (Bahramian, 2012) a similar comparison was conducted, in this case almost no differences were observed between both methods.

In paper 596 (Hirsch et al., 2009) Sessile Drop measurements of probe liquids on a bitumen surface were used to determine SFE components of bitumen (OW calculation), in this study the author reported that especially for soft binders, very small polar components were obtained. This was related to separation effects at the bitumen surface. Normally bitumen is heated, covered on a glass plate, and afterwards allowed to cool to room temperature. During this cooling the surface will optimize its surface energy by selectively placing compounds with a small surface energy at the surface. Especially, the accumulation of smaller more mobile paraffin at the surface can reduce the surface energy. The author in ref 14 could avoid this phenomenon by using a freshly microtome-cut bitumen surface instead of an air-cooled surface. Unfortunately, in the paper the comparison of both surfaces is not included, only measured data on microtome-cut surfaces are reported. These indicate rather larger polar SFE components as compared to other references. The author also expected these effects in polymer modified binders.

Effects of testing time and temperature on SFE component determination is discussed in papers 586 (Korn, 2004), 590 (Hefer et al., 2005), 596 (Hirsch et al., 2009) and 601 (Wistuba et al, 2012). A linear decrease in total surface energy with temperature has been reported,

and all binders seems to vary in a very similar way, for 30°C increase, the total surface energy decreases between 2 and 2.5 mN/m<sup>2</sup>.

In many studies, different bituminous binders show differences in the total and dispersive parts of the surface energy and also small differences in acid or base parts as reported in papers 588 (Hefer et al., 2004), 590 (Hefer et al., 2005), 592 (Little et al., 2006). However, at this moment, it is not clear how these differences relate to other bitumen parameters, and/or to the bitumen chemistry. In paper 586 (Korn, 2004) it has been reported that paraffinic binders have a larger total surface energy compared to naphthenic bitumen, but paraffinic binders have a lower polar part. In papers 596 (Hirsch et al., 2009) and 607 (Radenberg, 2014) only very little variation was observed in the total surface energies of various commercial binders, while in paper 596 (Hirsch et al., 2009) it was noted that more differences could be observed when comparing polar and dispersive parts, but the author also indicated that the errors bars on these parts are rather large. The influence of bitumen modification, anti-strip additives and ageing on the surface energy and its components is summarized in table 2-3. **In conclusion, it seems that the effect of additives like anti-strip agents is very hard to detect in SFE measurements. Also polymer or wax modification does not result in large changes, and for ageing different trends are reported.**

**Table 2-3: Overview of effect of bitumen type and bitumen modification including use of additives on surface energy and SFE components**

Effect studied	Finding(s) – conclusion(s)	Paper(s)*
<b>Type of bitumen</b>	$\gamma_{total}$ paraffinic > $\gamma_{total}$ naphthenic, $\gamma_{AB}$ naphthenic > $\gamma_{AB}$ paraffinic	586
	SHRP library binders, differences were observed but did not relate to another bitumen parameter	588-592
	very little difference between binders in $\gamma_{total}$	596, 607
<b>Anti-strip agent</b> (0.4-0.5% addition)	slight increase in $\gamma_{total}$ but decrease in $\gamma_{AB}$	586
	no clear trend on surface energy and SFE components	232, 588, 590, 592
	$\gamma_{total}$ and $\gamma$ - increase slightly, only for the harder binder	604
	$\gamma_{total}$ , $\gamma_{LW}$ and $\gamma$ - increase slightly	267
<b>Hydrated lime</b>	no effect	592, 608
<b>Wax addition</b>		
3% wax addition	slight increase in $\gamma_{total}$ and $\gamma_{AB}$ due to wax	586
Sasobit (2-8%), paraffin wax (8%)	Sasobit decreases $\gamma_{total}$ , $\gamma_+$ is increased no effect on $\gamma$ - , similar effect of paraffin wax, no effect of aspha-min,	108, 233
Sasobit (0.5-8.0%), Evotherm (0.5-1.5%)	$\gamma_{total}$ , $\gamma_{LW}$ and $\gamma$ - increase slightly	267
<b>Polymer modification</b>		
Papers 586, 596, 609: SBS	no effect on $\gamma_{total}$	586
	$\gamma_{total}$ increases	596
Paper 608: SBS (3%), SBR	SBS results in an increase in $\gamma_{LW}$ , decrease in	

(3%)	$\gamma_{AB}$ , SBR almost no effect $\gamma_{total}$ increases slightly for Wilhelmy plate tests at 23°C, no effect for pendant drop tests at 120°C.	608 609
<b>Ageing</b> (RTFOT+PAV)	$\gamma_-$ increases slightly; no clear effect on $\gamma_{total}$ $\gamma_{total}$ increases, $\gamma_{LW}$ increases, $\gamma_+$ de-creases, $\gamma_-$ varies, $\gamma_{AB}$ decreases.	592 232 608
<b>Nanomaterials</b> carbon nanotubes 3%, nano-SiO <sub>2</sub> (6%), diatomite (6%)	these additives have almost no influence	608
<b>WMA additive</b> Aspha-min (1-6%)	no effect	233

\* For each reference the respective test method can be found in table 2-1.

### 2.3.1.3 SFE measurements on aggregates

Aggregates consist of an assemblage of one or more minerals, while minerals have a definite chemical composition and an ordered atomic arrangement as described in paper 588 (Hefer, 2004). Consequently, it is expected that the surface of aggregates is rather heterogeneous. In papers 586 (Korn, 2004) and 596 (Hirsch et al., 2009) aggregate types are divided into acid and basic types; acid aggregates consist mainly of quartz (silica dioxide or SiO<sub>2</sub>) and are generally considered as not so good to prevent moisture damage. The reason is that SiO<sub>2</sub> can form strong hydrogen bonds with water resulting in a strong interaction. The author also reports that on these surfaces even after heating it is very likely that a monomolecular layer of water will remain. On the other hand, basic aggregates consist mainly of calcite and are considered as good adhering aggregates. So in general terms, bad adhering aggregates may include quartz, quartzite, hornblende, biotite, orthoclase, while good adhering aggregates comprise e.g. basalt, augite and olivine. In paper (Hirsch et al., 2009), authors note that the chemical components at the stone surface with a high affinity for bitumen are in general elements such as Al, Fe, Mg and Ca, while elements with a low affinity are Na and K. The reason given is that Ca<sup>2+</sup>, and Mg<sup>2+</sup> ions form water insoluble salts, while K<sup>+</sup> and Na<sup>+</sup> form water soluble salts, with a negative effect on the bitumen stone adhesion. In paper 611 (Lyne et al., 2013), a literature overview of the effect of specific elements on the moisture sensitivity of bitumen - aggregate adhesion is reported. Minerals containing alkali metals are prone to stripping and iron compounds are considered beneficial. Magnesium and calcium are also considered advantageous. The total picture of the effect of aluminium and silica is less clear. In paper 588 (Hefer, 2004) it is noted that carbonates may result in weak boundaries, if the pH of the water drops below 6, since then the carbonates may dissolve leading to failure.

Surface energy measurements on aggregates indicate much more variation between the surface energy components compared to the values observed for various bituminous binders. In paper 592 Little et al., (2006), the authors report typically for aggregates the total surface energy is in the range of 50 up to 400 mJ/m<sup>2</sup>. The magnitude of the LW component is smaller (30 to 60 mJ/m<sup>2</sup>) compared to the magnitude of the base component (200 to 1000 mJ/m<sup>2</sup>). Most aggregates have a small magnitude of the acid component ranging from 0 up to 100 mJ/m<sup>2</sup>, so the total polar part of the surface energy is not necessarily high and can still be small depending on the acid component. In paper 596 (Hirsch et al., 2009), authors noted that differences in the total surface energy and the distribution between dispersive and polar

parts can be larger between aggregates belonging to the same class of aggregates compared to aggregates belonging to different classes. In this particular case two quartzite aggregate types showed larger differences than observed between a quartzite and a granite type.

In the collected papers, large variations between aggregates were observed, even for aggregates that differ only slightly in their mineralogical composition. For example, in papers 604 (Liu et al., 2014) and 606 (Grenfell et al., 2014) two limestone type of aggregates, consisting both for 96% of the mineral calcite, still showed a very large difference between the surface energy components. Regarding standard deviations, these are reported for example in paper 591 (Bhasin, 2006) and they are low compared to the measured values, except if an SFE component is very small.

Different test methods are available and have been used to evaluate the SFE of aggregates. **From a comparison of different methods, the following conclusions were obtained:**

- **Inverse gas chromatography is not very successful for aggregates as stated in paper 589 (Hefer et al., 2005) as the retention time measured may correspond to only the high-energy functional groups present on the surface of the material and not to an average value as reported in papers 591 (Bhasin, 2006) and 592 (Little et al., 2006);**
- **The use of contact angle methods like the Sessile Drop Method are limited as they require a flat stone surface;**
- **Static and dynamic vapour sorption measurements are very suited for aggregates with irregular shapes as concluded in paper 589 (Hefer et al., 2005). A large number of repeats as indicated in paper 596 (Hirsch et al., 2009) are needed;**
- **Atomic Force Microscopy (AFM) also requires a very flat surface and moreover only a very small area is scanned at a given time as reported in paper 589 (Hefer et al., 2005).**
- **Micro-calorimetry characterizes only the enthalpy change and could only be used if entropy would turn out to be negligible as stated in paper 589 (Hefer et al., 2005).**

In several references the effects of polishing have been discussed. In paper (Hirsch et al., 2009) authors has investigated the surface roughness after polishing and concluded that even after polishing differences in surface flatness still exists between different aggregates. In this case slight variations in the surface hardness could after polishing result in very small imperfections on the surface. The researchers tried to avoid the influence of surface irregularities by using the same sample preparation for all the aggregates, and by performing a larger number of contact angle measurements on different locations on the stone surface. The author also investigated the difference between cutting, scrubbing and polishing, when measuring contact angles with water. The polished stones gave the lowest contact angles. The author concluded that irregularities, which may be larger after cutting and scrubbing, hinder the wetting of liquids on the surface. This study also compared static and dynamic contact angles between probe liquids on stone surfaces. For some surface types differences between both contact angles were seen, while for others these were very similar. If differences were observed these could be attributed to the surface roughness. In this study the author decided to determine the SFE components of the aggregates (polar and dispersive only) using dynamic contact angles. There is still a lot of discussion on the validity of methods that measure liquid contact angles for solids which are not easily prepared into a flat plane as stated in paper 598 (Miller, 2010).

In some references the effect of using freshly cut or “aged” aggregates is discussed. In paper 586 (Korn, 2004) the author notes that after crushing, there is a reorganization of polar substances at the surface, and by adsorption of substances from the air (water molecules and dust) the surface energy of the aggregate decreases until after a few months a stable

situation has been installed. In paper 587 (Schellenberger, 2004), the author note that freshly cut aggregates have a worse moisture sensitivity behaviour compared to aggregates that have been stored for some time. In paper 588 (Hefer, 2004) possible reactions at the stone surface when water is absorbed are presented. In paper 592 (Little et al., 2006), for two aggregate types no differences due to aggregate storage could be observed. This was explained by the fact that crushed aggregates may within a few seconds after crushing accumulate surface contamination from the environment.

In both papers 598 (Miller, 2010) and 178 (Miller et al., 2012), the authors evaluated the possibility to catalogue mineral properties, with the aim to relate the mineralogy to the surface energy components and also to check if it is possible to assign surface energy values to aggregates coming from a specific quarry. This last objective can only be possible if the surface energies of aggregates are independent from when and at which point in the quarry they are taken. This last condition was however not met. Additionally, a simple relation between mineralogical composition and surface energy could not be set up because it was not always possible to draw clear correlations between surface chemistry and surface energy. The reasons for this observation are not so clear. In paper 598 (Hirsch et al., 2009), the authors report that determining the chemical and structural functional groups as active sites is useful to understand interfacial reactions, but does not explain the magnitude or strength of these sites. Additionally, measured values of organic and inorganic coatings seemed to play an important role and the influence of varying surface roughness was unclear as well.

Regarding aggregate modifications, in paper 599 (Arabani et al. 2011) the influence of a polyethylene pre-coating of three types of aggregates was evaluated. The data clearly show that PE treatment decreases the polar components of the aggregates and increases the dispersive part. However, the base component was for all aggregates higher after modification. There was no explanation for this last observation. In literature, numerous papers have evaluated the effect of hydrated lime. In papers 588 (Hefer, 2004) and 596 (Hirsch et al., 2009) it was postulated that hydrated lime ties up carboxylic acids and 2-quinolones in the bitumen, with the formation of insoluble calcium organic salts, which prevent these functionalities from reacting with a siliceous surface to form water sensitive bonds. This leaves important active sites on the siliceous surface to form strong water resistant bonds with nitrogen groups in bitumen (amines) resulting in a reduction of the water sensitivity of asphalt mixes. In paper 603 (Moghadas et al., 2013) the SFE components of the aggregates with and without hydrate lime treatment were determined, and the authors showed that hydrated lime treatment reduces the acid SFE and increases the base SFE of the two types of aggregates. However, in paper 592 (Little et al., 2006) the authors report that the methodology of using the universal sorption device is applicable only when the probe vapour molecules are adsorbed due to physical adsorption and not due to chemisorption. It is unclear if this condition is met in the case of hydrated lime.

#### 2.3.1.4 Dry and wet adhesion

Once the SFE components of bitumen and aggregate are determined, the dry and wet bond strengths can be calculated. In literature normally dry bond strengths are positive and wet bond strengths become negative as stated in paper 590 (Hefer et al., 2005) indicating an attraction between bitumen and aggregate when dry that becomes a repulsion when wet). In paper 178 (Miller et al., 2012), a large range of minerals was investigated and for some of these, free energies of adhesion between bitumen and these minerals were still negative even in the presence of water. These were typically minerals with a low acid and a low base component. So, latter minerals do not have a thermo-dynamical drive for an adhesive debonding. The fact that this was not observed for any of the aggregates studied was explained by the fact that aggregates are combinations of different minerals, resulting in

average values. In paper 606 (Grenfell et al., 2014) a limestone aggregate, which had small acid and base components, also showed a negative free energy of adhesion with bitumen. A similar observation was made in paper 609 (Porot et al., 2016). In this case all three aggregates showed a negative free energy of adhesion in the presence of water. Therefore, it is more likely that an erroneous determination of acid base components is related to this observation.

### 2.3.1.5 Paper analysis sum up including validation of test results

#### 2.3.1.1.1 Correlations between calculated bond strengths and laboratory tests indicative of moisture damage

In table 2-4, research papers investigating the validation of surface energy predictions based on laboratory tests are summarized. In some cases, the predicted and measured performance related very well as indicated in papers 591 (Bhasin, 2006), 592 (Little et al., 2006), 221 (Bhasin et al., 2007), 211 (Howson et al., 2012) and 603 (Moghadas et al., 2013), but in other cases relations were less good or even non-existent as reported in papers 596 (Hirsch et al., 2009), 604 (Liu et al., 2014) and 609 (Porot et al., 2016). It is not clear if the lack of correspondence is related to the methods used to determine surface energy or to possible errors in its experimental determination, or rather related to the type of asphalt test that is used. In this respect it seems that especially the rolling bottle test and a modulus tests in compression do not relate to SFE calculated bond strengths. On the other hand, it seems that a modulus ratio measured in tension and pull off tests conducted with a DSR relate well to the SFE calculated performance.

**Table 2-4: Overview of papers investigating relations between laboratory tests and predicted performance based on surface energy calculations**

Materials - conditioning	Lab tests	Finding(s) - conclusions	Paper(s)
12 mixtures, Submerging in deionized water for 24 hours at 50°C, followed by air drying for 24 hours prior to testing.	dynamic modulus in compression dynamic modulus in tension fatigue: the number of cycles to get 1% permanent mstrain.	no correlation for the ratio dynamic modulus in compression to dynamic modulus in tension; best correlations of 0.79, 0.81 with ER1*SSA and ER2*SSA fatigue ratio; best correlation of 0.84, 0.83 with ER1*SSA and ER2*SSA	221, 591, 592
5 stones, 5 binders (25 mixes), two criteria: 1. More stone coverage if $\gamma$ stone is large and $\gamma$ binder is low. 2. Stronger bond if more equal distribution of polar to dispersive parts	Rolling bottle test (EN 12697-11 clause 5)	Assumptions could not be confirmed: no correlations  Not clear why: SSA is not included in this prediction, binder may form a good adhering but brittle film which could break during the rolling bottle test; or a strong cohesive binder film which is not well adhering is formed which will not break during rolling action	596
1 binder + 3 aggregate types; each type coated with 2 types of polyethylene preconditioning: AASHTO T283	repeated unconfined, compressive loading, in controlled stress mode at 25°C and at 1 Hz under haversine loading	No comparison to bond strength ratios; water sensitivity was predicted from the change in free energy from the dry binder-aggregate adhesion to the water-aggregate adhesion. This approach could predict the effects of poly-	599

		ethylene; it was not possible to predict the ranking of uncoated aggregates	
1 unmodified PG 64-22 + 1 PMB PG 76-22  Sasobit and an amine-based liquid anti-strip additive were used at percentages of 2% and 1% respectively;  2 aggregates: limestone + novaculite	Pull-Off Tensile Strength (POTS)	A comparison to bond strength ratios was not made; free energy of adhesion obtained from SFE measurements were compared to that of pull-off tests; results did not correlate well except that both the methods (pull-off and SFE) indicated that combination of Sasobit and liquid anti-strip increases the moisture susceptibility.	108
3 bitumens (AAB, AAD, and ABD)  2 aggregates: limestone (good field performance in terms of resistance to moisture damage) + andesite (poor observed field performance)  binder-aggregate samples were submerged in distilled water for time periods of 0 hr, 12 hr, 24 hr, and 48 hrs.	Uniaxial pull-off using DSR  moisture conditioned samples were all prepared with a film thickness of 30 µm and tested at 23°C with a loading rate of 0.01 mm/s (aggregates surfaces slightly polished)	For each test, the total work of fracture was derived. Latter was higher for limestone as compared to andesite (for each binder and at each conditioning level). Change in the total work of fracture compared to the dry sample was calculated (in limestone this tended to increase with conditioning time, in andesite this tended to decrease). The average of this change related well to the values given by the energy parameter (ER2), R2 = 0.89  A lot more conclusions were derived (not described here)	211
1 binder (AC 60-70); + 2 aggregates: limestone and granite, (with and without hydrated lime added).	indirect strength ratio with varying concentrations of hydrated lime (0.5-2.5%) according to AASHTO T283	Bond strength ratios were not compared, but data show that ER ratios increase when adding hydrated lime and this is in agreement with a better indirect tensile ratio	603
2 unmodified binders (40/60 +160/220); 40/60 binder was modified with liquid anti-stripping agents (0.5 w%);  4 amine-based (AAS1, AAS2, AAS3 and AAS4) + 1 non-amine anti-stripping agent (NAAS);  3 limestone (L1, L2, L3) + 3 granite aggregates (G1, G2, G3)	static immersion test (ASTM D1664)  rolling bottle test (EN 12697-11)  boiling water test (ASTM D3625-96)  A total water immersion test  An ultrasonic method	Ultrasonic method + static immersion tests were not discriminative; other 3 tests all ranked limestone combinations as good and granite combinations as worse: G1 > G2 > G3.  Calculated energy ratios identified G1, as the most moisture sensitive mixture. In addition to G1, parameter ER2 identified most L3 and G3 mixtures as moisture sensitive. ER1 * SSA and ER2 * SSA ranked L1 and G1, G3 as moisture sensitive. For 3 aggregates (L2, L3, G2) the bond energy calculation gave a negative free energy of adhesion in the presence of water (no thermodynamic drive for stripping).	604

		No full correspondence to respective experimental tests.	
4 aggregates: 2 limestone + 2 granite 3 bitumens: 15, 50 + 100 pen grades; aggregates similar to paper 604	rolling bottle (EN 12697-11) saturated ageing tensile stiffness (SATS) (combines ageing with water damage)	SFE calculation predicted well binder influence, by all energy ratios; Influence of aggregate type: only ER1 gave a good trend between measured and predicted performance in laboratory. For other energy ratio's predicted levels are less good (no correlation coefficients indicated)	606
4 aggregates, various empirical degrees of stripping and 3 binders, 2 unmodified and 1 polymer modified.	Rolling bottle (EN 12697-11 clause 5) Boiling water (EN 12697-11 clause 7) Bitumen bond strength (ASTM D 4541)	The results of SFE calculation indicated that all combinations should be well resistant to moisture damage, which did not correspond the experimental test results.	609

### 2.3.1.1.2 Correlations between calculated bond strengths and field experience

In papers 591 (Bhasin, 2006), 592 (Little et al., 2006), 593 (Masad, 2006) and 594 (Bhasin et al., 2006) bond strength calculations and the various energy ratios were compared for eight mixes with known field performance. The comparison of field performance with the bond energy parameters, ER1 and ER2, and the energy ratios multiplied with the SSA shows that all ratios can distinguish good from poor performing field mixes. For each ratio, threshold values of the bond energy parameter could be derived. The authors concluded that bond energy parameters can be used to segregate mixtures based on their moisture sensitivity, but that these data cannot be used for qualitative comparisons between various parameters. Since, unlike laboratory tests, it is difficult to control and quantify the moisture sensitivity of field mixtures on a uniform scale due to the differences in environmental and field conditions that influence these mixtures. In paper 593 (Masad, 2006), the author investigate the use of surface energy components combined with DMA data on the mastics to predict fatigue and healing in further detail. This approach is not discussed in this report. In paper (594 (Bhasin et al., 2006), the same data were used but in this case they were ranked according to the ratio of the total free energy ratios and the free energy ratios calculated separately for the acid base components, as shown below:

$$R^{\text{Total}} = \left| \frac{\Delta G_{AS}}{\Delta G_{WAS}} \right| \quad R^{AB} = \left| \frac{\Delta G_{AS}^{AB}}{\Delta G_{WAS}^{AB}} \right| \quad (11)$$

In this paper, for both energy ratios threshold values to identify moisture susceptible binder aggregate combinations are proposed. The authors conclude that the portion of the bond energy that results from the interaction of the acid component of asphalt and the base component of aggregate contributes the most to the total adhesive bond strength of the mix. So in fact there are in total six bond energy ratios that can distinguish well from poor performing aggregate binder combinations.

### 2.3.2 Sessile Drop measurements in dry and wet conditions

In some studies the bitumen/aggregate affinity is derived from contact angle measurements, between bitumen drops in direct contact with a (flat) aggregate surface. In such tests surface

energy components are not determined, however later tests allow a direct measurement of bitumen/aggregate interaction, which can be measured both in air as well as in water. Therefore, a literature summary on these types of tests is included.

In paper 586 (Korn, 2004), a procedure to measure contact angles of bitumen drops on substrates in air and in water is developed. In this proposal the temperatures for wetting and respectively de-wetting by water are determined by the bitumen softening points. In a first step, a procedure to bring equally sized drops of bitumen on a substrate is described. For this purpose, the bitumen was heated, in this case up to 150°C, while the substrate was kept at room temperature. Several drops of bitumen were placed on the substrate by using a needle. Afterwards the covered substrates were heated to a temperature, 25°C to 30°C above the softening point. The contact angle data of bitumen to the substrate in air were recorded after 10 minutes at 70°C. Subsequently, the substrate with the wetted bitumen drop was placed under water at a temperature which is 5°C below the R&B softening point, in this example at 40°C. The drop contact angle was measured again after 2 hours storage under water. The difference in contact angle before and after water storage is then calculated. Threshold values for the change after 2 hours respectively 24 hours water storage have been set and used as a measure of the resistance to stripping.

Several references have applied this type of tests as described in papers 586 (Korn, 2004), 597 (Nehrigs, 2009) and 601 (Wistuba et al., 2012) while paper 587 (Schellenberger, 2004) is using a similar approach, measuring contact angle under water while adapting slightly the procedure. In paper 586 (Korn, 2004) clear differences between stone types and between various bitumen types could be observed, especially in case of modified bitumen such as anti-strip additives, waxes or polymers. However, it should be noted that for polymer and wax modified bitumen the wetting temperatures needed to be considerable higher, because of the increased viscosity. The authors also noted that differences in surface texture influenced the contact angles, and finally, the authors noted that there is no relation between the total surface energy of a binder and the wetting of this binder on a particular stone.

In paper 587 (Schellenberger, 2004) as mentioned, the procedure was adapted and in this test all unmodified binders gave rather low contact angles, so a good wetting was not achieved. The test could clearly show the effect of additives which was also aggregate type dependent. Furthermore, the author noted that this test cannot be used to investigate PMBs, as it does not allow preparing small drops when the bitumen is polymer modified. In the paper, the effect of additives was confirmed in rolling bottle tests and in boiling water tests. In paper 597 (Nehrigs, 2009) the same procedure as in paper 586 (Korn, 2004) was used to evaluate the effect of adhesion improvers, however no effect was observed when measuring contact angles in the dry situation, only the water conditioning step allowed to distinguish the binders. In paper 601 (Wistuba et al., 2012) very similar tests as in paper 586 (Korn, 2004) were conducted, the authors report the need for minimum standards for image quality, in order to improve the repeatability and reproducibility of the test method.

In the papers 014 (Aguiar-Moya et al., 2013), 596 (Hirsch et al., 2009), 605 (Aranowski et al., 2014), 607 (Radenberg, 2014) and 608 (Aguiar-Moya et al., 2015) contact angles were only evaluated in the dry situation. Some studies described in papers 014 (Aguiar-Moya et al., 2013), 596 (Hirsch et al., 2009), 608 (Aguiar-Moya et al., 2015) indicate that effects of additives like adhesion promoters can be observed even when testing dry contact angles, while other papers 605 (Aranowski et al., 2014) and 607 (Radenberg, 2014) indicate that these test cannot differentiate binders with and without adhesion promoters.

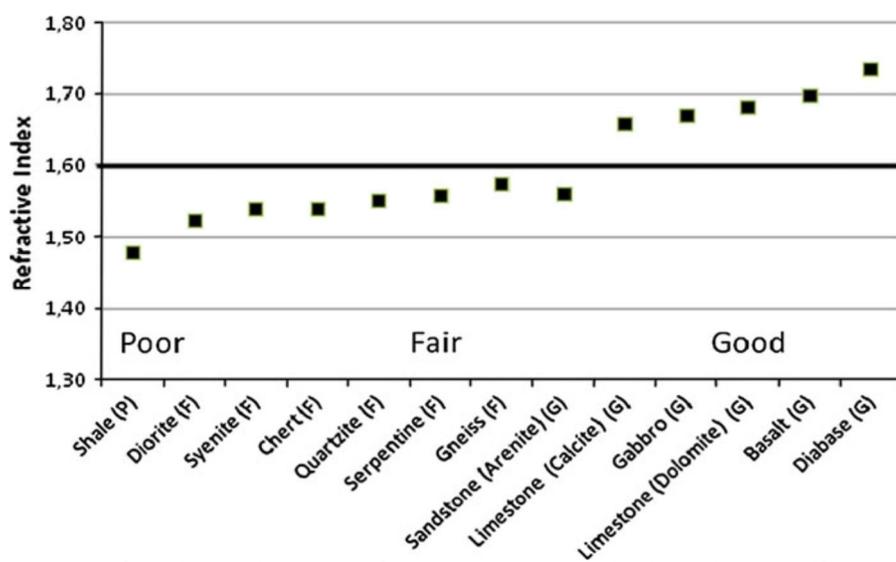
In summary, it seems that contact angle measurements in the dry and wet state may be a successful way to estimate the water sensitivity. However, at this moment the validation is mainly limited to comparing binders with and without adhesion improvers, or other modifications. Although this test looks promising there are still a lot of open questions: what

is the effect of the test temperature, should binders be compared at an equal viscosity state or at an equal temperature, what is the effect of using a polished or a flat aggregate surface and how large will the effect be on the spreading of bitumen drops?

### 2.3.3 Hamaker approach

The Hamaker equation is used for non-polar materials and materials which have polar but no directional bonds, as for example hydrogen bonds. Latter approach was used in three papers to evaluate the adhesion between bitumen and aggregate both in the dry state as well as in water.

In a first paper 610 (Lyne et al., 2010) Hamaker constants of a typical bitumen with several aggregates, were calculated based on dielectric and refractive index data, which were obtained from literature. These Hamaker constants were calculated, for the intervening medium air and also for the medium water. When changing the intervening medium from air to water, the part of the Hamaker constant related to polar interactions and based on dielectric data (A1) increased, while the part related to dispersive interactions and based on the refractive index (A2) decreased a lot. It is expected that molecular forces related to dipoles increase with polar liquids like water, while dispersive interactions decrease. For air as an intervening medium, A1 contributed with 1 % of the total Hamaker value. For water as an intervening medium, A1 contributed with 9 % to 25 % of the total interaction. The calculation showed that if water comes in between the aggregate and the bitumen, the interaction forces between bitumen and aggregate decrease by 80-90 %. This reduction is the main reason for stripping. The authors also showed that the dispersive part, derived from refractive index data is dominant in the bitumen stone interaction, in air, and also in water. As the dispersive terms are dominating, the data also imply that adhesion increases (dry as well as in water) as the refractive index of the aggregate and the bitumen are larger. In this paper the ranking of the field performance of several aggregates, derived from literature data, corresponded to the ranking based on the calculation of the Hamaker constant.



**Figure 2-3: High refractive index value for aggregates and minerals classified according to their degree of resistance to stripping; P poor, F fair and G good [Paper 611: Lyne et al., 2013]**

In a second paper 611 (Lyne et al., 2013) the authors focused on the variation in the dispersive component of minerals via their refractive indices, which were found in literature. In this study, it was assumed that the bitumen-air-aggregate and the bitumen-water-aggregate adhesive interaction can be represented by the dispersive component of the Hamaker's constant. The data indicated that aggregates and minerals that have a refractive

index, higher than a cut-off value of around 1.6 are expected to be less susceptible to stripping. In this paper, the authors also related stripping and refractive index values to the elemental composition of the minerals. Some relations were found: alkali metals tend to lower the refractive index, alkali earth metals and transition metals have a tendency to maintain the refractive index above 1.6. The authors concluded that the elemental composition of minerals has a clear influence on the refractive index and therefore also on the dispersive interaction ability with bitumen. It was also indicated that other mechanisms which are not dependent on an interaction may still occur, such as alkali metals, which form water soluble salts will contribute to stripping when present in higher concentrations.

In a third paper 612 (Lyne et al., 2013) the authors evaluated several bitumen aggregate combinations. In this study the refractive indexes were measured using ellipsometry, which allowed calculating the dispersive component of the Hamaker constant. Three aggregates and seven binders were included in the study. Regarding the binders, the refractive indices varied only little, between  $n = 1.550$  and  $n = 1.598$ , while the spread in refractive index among the three aggregate samples was much larger. This observation corresponds to the observation that the stone surface determines the adhesion behaviour more compared to the bituminous binders. From the refractive index data on bitumen, the cohesive energy of the binders was estimated as the dispersive component of the Hamaker equation in the medium air or water (using bitumen as material 1 and 2). In the paper adhesive and cohesive energies were compared, based on the refractive index of the aggregate. If the aggregate has a refractive index that is higher than the binder, then the link bitumen/aggregate is stronger compared to bitumen/bitumen, and cohesive failure of the bitumen will be more likely. If the aggregate has a refractive index of the same magnitude as the bituminous binder, then adhesive failure will be as likely as cohesive failure. The critical refractive index value, discriminating good from fair aggregates was reported previously to be 1.6. This value is very close to the refractive index measured on bitumen, and is therefore a threshold for cohesive versus adhesive failure. This observation indicates that stripping is related to a bitumen/aggregate adhesion that is weaker than bitumen cohesion.

#### **2.4 Conclusions for binder/aggregate interaction – correlation with water sensitivity of asphalt mixture (level 1)**

When summarizing the test procedures to determine SFE components of bitumen, typically the SFE is composed of a large dispersive part, and sometimes also small acid and/or base components. There is some variation between different binders but it is small and it is not clear how this relates to other properties. Softer binders tend to have lower polar components and slight differences between naphthenic and paraffinic bitumen have been observed. The effect of bitumen modifications is very small. When comparing different test methods, some references have reported rather large differences between different test methods. Regarding test precision, it seems to be very difficult to measure the small parts, acid and base accurately. The effect of sample preparation is not well investigated, but it has been reported that a microtome cut surface of bitumen is different compared to an air-cooled bitumen surface.

With respect to aggregates it was observed that there is a much larger variation between the SFE components of aggregates compared to the variation seen for bitumen. Aggregates typically have large base components, although when looking at minerals there are specific minerals which have only small acid and base components. There are basically two test methods commonly used for aggregates, the universal sorption test and the sessile drop method. In both cases the sample preparation of the aggregates is critical, and needs to be better evaluated and a standardized method would be very helpful. For example, there is still a question if possible absorbed water layers or other impurities on the aggregate surface are removed or need to be removed, which has not yet been answered sufficiently. For the

sessile drop test the flatness or the absence of sufficient flatness has been reported to influence the test result, and as aggregate texture is removed, improved adhesion due to mechanical interlock is not considered in this test. In the Universal Sorption Device, the specific surface area is measured and can be included in the evaluation. Regarding test precision, it seems to be, as for bitumen, difficult to measure small parts accurately.

Regarding the calculation of bond strengths it seems that small differences in acid and base components of bitumen can have a large effect on the adhesive bond strengths in dry and also in wet conditions, especially for aggregates with a large mostly base component. Consequently, small errors in the acid base determination of the bitumen can have a large effect. In addition, as could be expected, minerals (and sometimes also aggregates) with low acid and base components show more attraction to bitumen than to the polar solvent water, and these aggregates based on the bond strength calculations do not show a thermodynamic tendency for stripping.

Regarding the validation, the calculated bond strengths provide a prediction of the behaviour at equilibrium conditions, but one can question when such conditions are appropriate and valid. This question can be asked for field behaviour, but also for our laboratory tests. What conditioning times (curing) are needed to achieve equilibrium conditions? How is this related to the binder viscosity? In order to check the theory should we not need to conduct our asphalt tests at an equivalent viscosity temperature/state as well? Another very important aspect that needs to be considered are the surfaces itself; are the surfaces, of the bitumen and the aggregates, used in the predictive tests similar as the ones that deliver the bitumen-aggregate adhesion in an asphalt mixture? In an asphalt plant, aggregates are heated to and dried at very high temperatures while bitumen and aggregate also come into contact at high temperatures. As bitumen consists of probably millions of molecules, it could very well be that an air-cooled surface is rather different from the surface that adheres to the aggregate when this happens in a state where the molecular mobility is high. Indications for this have been reported in literature, for example the difference seen when looking at a cut bitumen surface compared to an air-cooled one, and also when discussing the lack of the effect of adhesion improvers on the SFE components. Finally, as reported in literature there is still a possibility of mechanisms, not dependent on an interaction, such as alkali metals, forming water soluble salts. As a number of studies, based on SFE calculations and predictions, have obtained good relations to laboratory tests and to field behaviour, the concept looks promising, but the aspects mentioned here will need to be considered and evaluated.

Another approach in which the change in bitumen drops is evaluated after they have obtained good adhesion when submerged in water, also seems promising. However, also in this case questions about the effect of viscosity and the influence of aggregate flatness need to be addressed. Finally, the Hamaker approach, which is mainly relating bitumen/aggregate adhesion to dispersive interactions, seems to be able to establish a ranking between different aggregate types. Nevertheless, at the moment a laboratory validation including various bituminous binder is not yet available. Moreover, also in this case, possible sample and/or more suitable surface preparation effects have not been studied in detail.

In general, some fundamental questions with regard to adhesion mechanisms which take place in asphalt mixtures still remain. A quite important one is if stripping is really an adhesive failure, or if cohesive failure, which could also lead to pothole formation, is contributing and to what extent? How important are other mechanisms that have been postulated, like the formation of a weak interface, or a brittle interface? From field experience, it seems that stripping happens after long periods of cold weather, with freeze thaw cycles, so it may be worth to use this in the conditioning when looking at water sensitivity. Another question that can be posed here is how important is the binder brittleness when it comes to stripping under field conditions? And what is the influence of the aggregate surface on this brittleness?

### 3 Binder/aggregate interaction – loose mix with water conditioning (level 1-2)

In this chapter the analysis of the literature review with respect to binder/aggregate interaction is discussed in more detail. As already described in the introduction, this section will deal with the outcome of tests conducted on loose coated aggregate (level 1-2) in order to probe for the adhesion or bonding of bitumen with aggregates. Whenever possible correlations between relevant bitumen and/or aggregate properties (level 1) and/or with the water sensitivity behaviour of asphalt mixtures as investigated in the laboratory (level 2) or validated in the field (level 3) will be addressed.

Although a large number of papers (about 140) from the database were identified with respect to the interaction of bituminous binders with aggregates (which includes also articles evaluating the water sensitivity of asphalt mixtures), only in a limited number of publications a possible relation between the nature of the bitumen and its adhesive properties and/or its impact on the water sensitivity of a corresponding asphalt mixture is discussed (about 18). Especially, a large majority of the papers in which the water sensitivity of asphalt mixtures is probed for, are related to a more general context of mainly the mix design and performance testing of HMA and WMA, the use of RAP/RAS and (in situ) recycling processes, the study the impact of additives such as fibres, pigments, anti-stripping agents, rejuvenators, etc. and the use of secondary materials such as crumb rubber, steel slags or fly ashes. Therefore, latter papers are not discussed in full detail in this report, although any relevant information from these papers has been considered in this report.

Taking into consideration deliverable D.1, in particular chapter 9 “Binder/aggregate interaction”, the following test conducted on loose coated aggregate will be addressed in the next sections:

- Pull-off tests such as Bitumen Bond Strength (BBS, AASHTO TP-91) and Pneumatic Adhesion Tensile Testing Instrument or PATTI test (based on ASTM D4541).
- Test methods as described in EN 12697-11 for the determination of the affinity between aggregate and bitumen including: rolling bottle test (clause 5), static immersion test (clause 6) and the boiling water stripping method (clause 7).

#### 3.1 Pull-off tests (BBS - PATTI)

In the paper 014 (Aguiar et al, 2013) the performance of asphalt mixtures applied in Costa Rica in terms of moisture damage is addressed. Because of the geographic location of Costa Rica, the country is subjected to one of the highest levels of precipitation in the world. As such, it is to be expected that moisture damage is the most common type of pavement failure in the country. Consequently, the present study consists of an effort to characterize the strength in the bond between the asphalt binder that is used locally (PG64-22) and several types of aggregates from different parts of the country (1 limestone and 4 distinct river gravels from several locations). Additionally, the neat asphalt binder was also modified with a commercial SBR, a modifier commonly used in Costa Rica since it is supposed to promote adhesion. To evaluate the strength of the bond between the asphalt binder and the various aggregate combinations, the Bitumen Bond Strength (BBS) test was used. The results were checked by means of a goniometer that measures the contact angle between the asphalt binder and the aggregate surface, which corresponds to a measure of wettability. Finally, a subset of the analyzed asphalt binder and aggregate combinations were used to prepare an HMA mixture and evaluate it under the Hamburg Wheel Tracking Device (HWTD). The BBS results showed differences in behavior due to the effect of moisture on bond strength when changing the aggregate source. Additionally, depending on the aggregate type, different types of failure were observed: cohesive versus adhesive. A decrease was identified in the

bond strength when the SBR was used. However, when using the modifier, the effect of moisture on bond strength was reduced.

**The BBS results were consistent with the contact angle measurements and with the HWTD results, showing that the test can eventually be implemented as a screening tool. However, no correlations were shown (only impact of test variables was demonstrated).**

In the paper 236 (Copeland et al, 2007) it was stated that the bond strength is a critical parameter in evaluating the ability of bitumen to resist moisture-induced damage. The influence of polymer modification and long-term aging in combination with moisture conditioning on bond strength of asphalt binders was measured using the modified pull off test method that has previously been developed to measure adhesive strength and evaluate moisture sensitivity of asphalt binders using the Pneumatic Adhesion Tensile Testing Instrument (PATTI). The pull-off tensile strength of dry specimens is a measure of cohesive failure strength whereas adhesive failure strength may be determined after moisture conditioning. The pull-off test is able to distinguish among binders with the same performance grade but different chemical properties. However, the exact effect of modification on bond strength cannot be determined without consideration of the binder's physical properties. Moisture conditioning was the most influential factor on bond strength. Long-term laboratory ageing increased cohesive strength of asphalt binders. However, aging combined with moisture conditioning decreased adhesive strength of binders. Comparisons of binder resistance to permanent deformation with pull-off tensile strength highlight the need for a test method that measures adhesive properties, namely bond strength, of bituminous binder and mastic. Finally, recommendations are provided to improve ability of pull-off test method for determining bond strength (in terms of test parameters and precision).

**The results of the pull-off tests were compared to the moisture sensitivity of asphalt mixtures, however only a qualitative indication of consistent results was mentioned (extreme cases). No quantitative correlation was demonstrated.**

Canestrari et al., 2014 stated in paper 317 that the durability of asphalt mixtures is strongly related to the adhesion properties developed at the interface between binder and aggregates. The loss of adhesion implies a rapid deterioration (e.g. stripping, raveling) of pavement layers under traffic loads, especially when the pavement is affected by the presence of moisture. Adhesion is a complex phenomenon related to the mineralogical and morphological nature of aggregates, as well as to the chemical binder composition and the environmental conditions. Nowadays, its evaluation becomes even more complicated as an increasing percentage of reclaimed asphalt (RA) is used in the production of new asphalt mixtures. Therefore, adhesion properties are also related to the mechanisms developed at the interface between virgin binder and aged binder that coats the RA aggregate surface. An innovative procedure to evaluate the compatibility of the system virgin binder/RA aggregate is proposed in this study. This procedure allows to simulate in laboratory the substrate of a reclaimed asphalt aggregate and can integrate the Binder Bond Strength test currently used to investigate bonding properties and water sensitivity of the system binder-virgin aggregates. Tests were conducted using different aggregate sources, several modified binders and two conditioning types (dry, wet).

**It was found that this procedure is able to catch the differences between different test configurations and variables. In particular, the artificial reclaimed aggregate substrate ensured higher adhesion performance compared to the virgin aggregate, especially in wet condition, regardless the modification level of the virgin bitumen adopted. Unfortunately, in this study no relationship was explored with the performance of the corresponding asphalt mixes in terms of water sensitivity.**

### 3.2 Rolling bottle test

In the paper 519 (Radenberg et al., 2014) recently reported on a very extensive study carried out in Germany dealing with the adhesion of mainly paving grade binders (classes 20/30, 30/45, 50/70, 70/100 and 160/220) with a variety of aggregates. In total the adhesion of 90 bituminous binders of which only 6 were polymer modified (either by an elastomer or plastomer) with 8 different aggregates varying in mineralogy (all commonly used in Germany) was evaluated while using the Rolling Bottle test (EN 12697-11 clause 7 while using fraction 8/11). In order to rationalize the test results, bituminous binders were extensively characterized by a series of both empirical (such as needle penetration, R&B, Fraass breaking point, etc.) as well as rheological test methods such as DSR or other performance related tests (BBR, force ductility, etc.). Additionally, both physical as well as chemical properties of bitumen were assessed in particular the contact angle or generic composition (by SARA analysis) was determined. Also, the characteristics of the used aggregates (such as surface energy) were determined. In a final stage of the research project, possible correlations between the above reported data with the water sensitivity of an asphalt mixture was probed for (applying EN 12697-12 part A at 15°C). For this purpose, a standard SMA8 mixture comprising of the same constituents as characterized in the first phase of the investigation was proposed. A selection of both bituminous binders (# 13) as well as aggregate (# 2) was made in order to reduce the number of tests to be carried out.

**Although, a large number of parameters was identified to play a major role in the adhesion of paving grade binders with different aggregates (among them the nature of the aggregate and rheological properties of binders), it was not possible to establish any systematic correlation between the physical or chemical properties of the bitumen, the results of the rolling bottle test program and the measured water sensitivity (ITSR values) of the SMA8 mixtures as illustrated in the figure 3-1 below.**

Gestein	Bitumen	Verhältnis $\frac{N_{\text{makro Nass}}}{N_{\text{makro Trocken}}}$ [%]	ITSR [%]	Abrieb "normiert" [%]	Umhüllungsgrad nach 24 h [%]
Rhyolith	2.1 20/30	181	101	0,76	zu geringe Datenmenge aufgrund von Verklumpungen
	2.2 20/30	72	100	0,77	
	6.R1 30/45	145	115	1,21	
	1.1 50/70	70	100	1,17	
	1.2 50/70	66	104	1,19	
	2.1 50/70	94	125	1,51	
	2.2 50/70	158	91	1,40	
	2.1 70/100	107	128	1,25	
	5.1 70/100	112	104	0,84	
Basalt	2.1 20/30	131	99	0,89	60
	2.2 20/30	138	81	0,86	50
	6.R1 30/45	159	94	1,33	70
	1.1 50/70	171	102	1,31	65
	1.2 50/70	128	95	1,33	70
	2.1 50/70	193	106	1,51	65
	2.2 50/70	234	81	1,14	55
	2.1 70/100	243	94	0,64	40
	5.1 70/100	89	57	1,47	75

**Figure 3-1: Comparison between test results as obtained from the rolling bottle test and the water sensitivity of SMA8 mixtures [Paper 519: Radenberg et al., 2014]**

In the paper 508 (Renken et al., 2010) the results of an extensive test program on the adhesion of bitumen on aggregates, comprising combinations of 6 bituminous binders (four 50/70 from different producers and two PMBs) and 5 aggregates (whose adhesion properties can be classified from uncritically to critically) are reported. All bituminous binders were characterized both by empirical test methods (R&B, needle penetration, Fraass breaking point, etc.) as well as performance related methods (DSR, BRR, elastic recovery, etc.).

On these combinations the affinity of bitumen and aggregate was tested according the three options of EN 12697-11 (rolling bottle, boiling water test and static water test). Moreover, by carrying out contact angle measurements, the surface energy of all binders was probed for. Four asphalt mixtures (AC 11, AC 16, SMA 11 and PA 8) were prepared using a selection of four bituminous binders and 2 aggregates. The water sensitivity for latter mixtures was measured both by applying the conventional indirect tensile strength test (EN 12697-12 part A) as well as by a direct tensile test (not included in European standards). Furthermore, a rating regarding the adequacy for routine testing is given.

**In this study the impact of the type/nature of bitumen or aggregates on the water sensitivity of the corresponding asphalt mixtures was investigated (beside the influence of test specimens and/or temperature). With respect to the influence of the bitumen, the following conclusions can be summarized (see also Figures 3-2 and 3-3):**

- All together a systematic influence of the bitumen on the water susceptibility could be determined for all asphalt mixtures and aggregate types (Marshall test specimens);
- The influence of the provenance of the bitumen 50/70 is not uniform for AC11 variants, which means depended on the used aggregate. Statistically, there is no single influence of the bitumen on the results variability noticeable;
- For the AC16 variants PMB exercises an advantageous influence on the water susceptibility regarding the results of the Marshall samples for both used aggregates. For the other specimen types spreading results were obtained. An appreciable influence on the ITSR cannot be ascribed statistically to the bitumen.
- For the SMA variants PMB binders affects in comparison with bitumen 50/70 advantageously the adhesion quality.

Finally, despite the huge number of test results and available data, no correlations were reported, only the influence of particular constituents and/or test parameters was demonstrated.

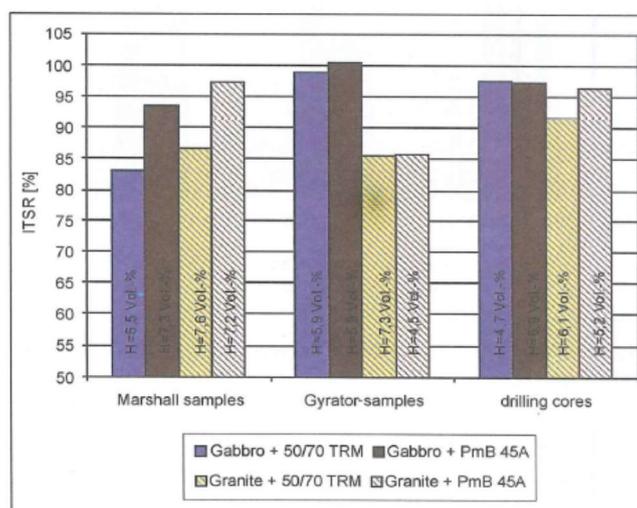
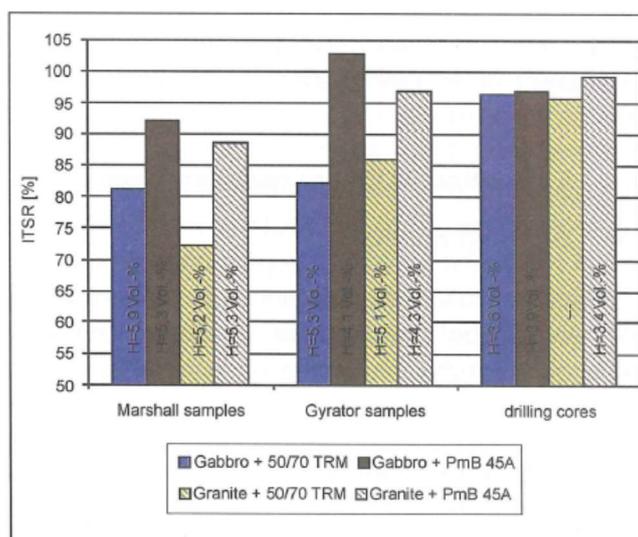


Figure 3-2: Influence of the bitumen type/sort on ITSR for AC16 mixture [Paper 508: Renken et al., 2010]



**Figure 3-3: Influence of the bitumen type/sort on ITSR for SMA11 S mixture [Paper 508: Renken et al., 2010]**

In the paper 533 (Renken et al., 2012) the results of an extensive test program on the use of 3 different waxes for the production of asphalt at lower temperature are discussed. Although, the study comprises in the first place the possible impact of latter additives on the performance (e.g. low temperature and fatigue behavior) of several asphalt mixtures such as AC11 and SMA 11 while using both paving grade as well as polymer modified binders, it is also stated that the adhesion of the bitumen with the aggregate (as probed by the Rolling bottle test) is not negatively influenced. **However, no systematic correlations between bitumen characteristics and test results of the rolling bottle and/or water sensitivity of asphalt mixtures were demonstrated.**

### 3.3 Papers analysis sum up

The following conclusions can be drawn from the paper review:

- In general, a small number of papers (6) are available reporting on the outcome of studies investigating the binder/aggregate interaction on level 1-2. Moreover, in only three studies an attempt was made to correlate those results of binder/aggregate interaction testing with the water sensitivity of asphalt mixtures comprising similar constituents. No field experiences were reported.
- All papers consider the adhesion between a binder and aggregate as important in order to guarantee durable asphalt mixtures. Nevertheless, adhesion is perceived as a complex phenomenon related to the binder composition, the mineralogical nature of the aggregates and the environmental conditions (e.g. exposure to moisture).
- Results of pull-off tests are consistent with either binder properties (e.g. contact angle measurements) or asphalt performance in terms of water sensitivity. However, no correlations were demonstrated, limiting their use to a possible ranking of binders and/or the identification of extreme cases (high risk).
- While using the test methods as described in EN12697-11, it was not possible to establish any systematic correlation with the results of water sensitivity tests (ITSR). It was also recognized that a large number of parameters played a major role in the adhesion of bitumen with aggregates or the water sensitivity of asphalt mixtures. Among them, the nature of the aggregate is considered as the most dominant. Other variables include both the rheological behaviour of the binder (impact of test temperature and

therefore indirectly the viscosity of the binder) as well as the volumetric design of asphalt mixture and/or fabrication of test specimens (e.g. void content).

- Although no systematic correlation was demonstrated, an influence of the bitumen on the water sensitivity could be determined (while using the same asphalt mixture during testing). Generally, polymer modified binders do perform slightly better probably due to positive impact of a higher viscosity. No negative impact of ageing was measured.

Table 3-1 summarizes the correlations (or absence of) found between results of tests conducted on loose coated aggregate (level 1-2) in order to probe for the bonding of bitumen with aggregates and both material properties (level 1) as well as the water sensitivity of bituminous mixtures (levels 2 and 3).

**Table 3-1: Possible correlations found between test results probing for binder/aggregate interaction and water sensitivity of bituminous mixtures**

Paper	Correlated data	Type of correlation	# binders	# aggregates	Comment
Paper 014 (Aguiar-Moya <i>et al.</i> , 2013)	BBS (MPa) vs HWTD (mm)	Only consistency of test results	1	5	U
	BBS (MPa) vs contact angles (°)		1	5	PMB
Paper 236 (Copeland <i>et al.</i> , 2007)	PATTI (MPa) vs HWT (mm)	Only consistency of test results	3	N/A (Glass)	U
			8	N/A (glass)	PMB
Paper 317 (Canestrari <i>et al.</i> , 2014)	None	N/A	1	2	U
			3	2	PMB
Paper 519 (Radenberg <i>et al.</i> , 2014)	Rolling bottle (%) vs ITSR (%)	None	84	8	U
			6	8	PMB
Paper 508 (Renken <i>et al.</i> , 2010)	Rolling bottle (%), Static immersion (%) and Boiling water (%) vs ITSR (%) and Direct Tensile Test Strength (N/mm <sup>2</sup> )	None	4	5	U
			2	5	PMB
Paper 533 (Renken <i>et al.</i> , 2012)	Rolling bottle (%) vs ITSR (%)	None	4	2	U

LEGEND: U - Unmodified bitumen; PMB - Polymer Modified Bitumen; A - Aged bitumen N/A - not applicable. BBS – Bitumen Bond Strength; PATTI – Pneumatic Adhesion Tensile Testing Instrument; ITSR – Indirect Tensile Strength Ratio (EN 12697-12 part A); HWTD - Hamburg Wheel tracking Device .

## 4 Binder/aggregate interaction – tests conducted on compacted asphalt mixtures (level 2 and 3)

In this chapter the analysis of the literature review with respect to binder/aggregate interaction is discussed in more detail. As already described in the introduction, this section will deal with the outcome of tests conducted on compacted asphalt mixtures (level 2 and 3) in order to probe for the adhesion or bonding of bitumen with aggregates. Whenever possible correlations between relevant bitumen and/or aggregate properties with the water sensitivity behaviour of asphalt mixtures as investigated in the laboratory (level 1 and/or 1-2) or validated in the field (level 3) will be addressed.

Taking into consideration deliverable report D.1, in particular chapter 9 “Binder/aggregate interaction”, the following tests conducted on compacted asphalt mixture will be addressed in the next sections:

- Water sensitivity tests as described in EN 12697-12 including the Indirect Tensile Strength Ratio (ITSR), the Swedish FAS-455 water sensitivity method and the compression strength ratio (i/C) (also known as Duriez test).
- Recently developed tests currently not standardized such as the Coaxial Shear Test or CAST and the Moisture Induced Sensitivity Tester or MIST.

### 4.1 Water sensitivity of asphalt mixtures

In paper 031 (Nordgren et al., 2012) reported the results of a large scale project where the impact of the source of a paving grade bitumen 70/100 (7 different suppliers) was investigated on functional properties of a SMA16 mix such as: instance wear resistance, water sensitivity, low temperature performance and permanent deformation (rutting).

None of the seven tested mixtures showed low ITSR values (high water sensitivity) (Figure 4-1). The variation in tensile strength between mixtures may be linked to binder stiffness as well as the addition of cement additive and small differences in compaction and composition. The special freeze/thaw conditioning used for half of the specimens (FAS-455 method) showed, in this case, no decisive effect compared to the conventional testing procedure for water sensitivity.

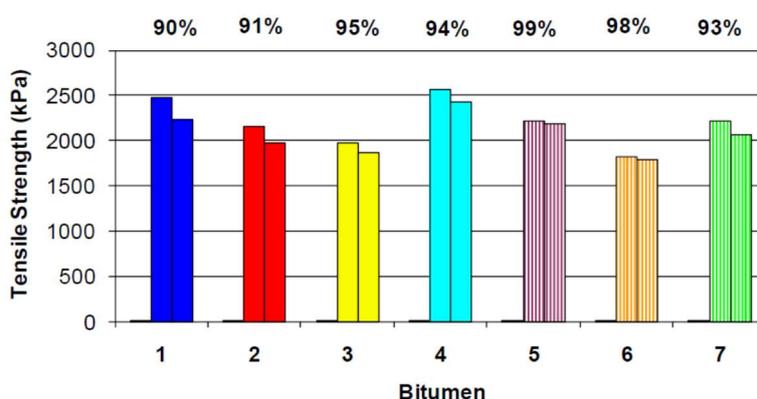


Figure 4-1: Water sensitivity results at 10 °C after winter conditioning [paper 031: Nordgren et al., 2012]

Ranking of the different types of bitumen according to ITSR was different from that of the rolling bottle test while using quartz aggregates and therefore no correlation between both tests could be established. Authors explained this by the fact that the

**ITSR method takes into account the total mixture, while in the rolling bottle test only adhesion between quartz aggregate and binder is assessed.**

**However, to the reviewer’s opinion, also the very high ITSR values of the SMA16 mixtures do not allow to differentiate in terms of the origin of the binder (all of the same penetration grade). Nevertheless, test results of the rolling bottle test all indicate a lack of adhesion of binders to quartz aggregates after 24hrs. Therefore, latter finding is in contrast with the high ITSR values.**

In the paper 041 (Deniz et al., 2012) reported the results of the effect of salt solution on both AC20 wearing course as well as SMA11 mixtures, including both a 50/70 paving grade as well as a PMB binder (SBS modified). Test specimens were conditioned over a long time (5 days) at 5°C before probing for the water sensitivity of the mixes while applying EN12697-12. The test results are summarized in Table 4-1.

**Table 4-1: Indirect tensile strength values for mixtures**

Specimen Type	Water Conditioning	Salt Solution Conditioning
Surface Course Type 1 0/20 (50/70 Bitumen)	68,6	73,6
Surface Course Type 1 0/20 (Modified Bitumen)	74,2	87,6
SMA Type 2 (Modified Bitumen)	81,0	86,6

In this study, also the stripping resistance of both binders was study while using the Nicholson static immersion test method (ASTM D 1664). While the stripping resistance of the 50/70 binder was between 30 – 40%, the SBS modified binder showed less susceptibility towards the action of water: stripping resistance of 75 – 85%.

**It could be concluded that there was no negative effect of the salt solutions on all mixes independently of the aggregate (limestone or basalt) or binder used especially taking into account the precision of the ITSR test method as currently stated in standard (R = 23%). The differences in stripping resistance between both binders were not reflected in the water sensitivity of the tested asphalt mixtures.**

In the paper 242 (Varveri *et al.*, 2014) a new moisture conditioning protocol for asphalt mix is presented which attempts to distinguish the contributions of long- and short-term moisture damage, i.e. moisture diffusion and cyclic pore pressure generation, namely MIST (Moisture Induced Sensitivity Tester, Figure 4-2). It is shown that the use of cyclic pore pressures has a significant effect and can be used as an accelerated moisture conditioning procedure.

In the study, six PA16 (porous asphalt mixture compositions) were tested. The mixtures differed in terms of the type of aggregates and bitumen used. The specimens were produced using either granite (known to be prone to moisture damage) or sandstone (with known good field moisture damage performance) aggregates. A conventional paving grade bitumen 70/100, a moderately polymer modified bitumen with 50/80 pen grade and a highly polymer modified one with 65/105 pen grade was used. A target bitumen content of 4.5 % by total mixture mass was selected for all the specimens. Hydrated lime filler was added at 4.8 % by mass of total aggregate. The different mixtures are denoted as: GP, GM, GH, SP, SM, SH, with the letters G and S denoting Granite and Sandstone aggregates respectively, while the letters P, M and H denote the used bitumen type (70/100, moderately and highly modified bitumen).

The evaluation of the proposed protocol for its ability to discriminate amongst mixtures in terms of moisture sensitivity was attained via the Tensile Strength Ratio (TSR). The mean TSR values (out of 3 replicas) after each conditioning period are shown in Figure 4-3. Also,

the coefficient of variation for every mix, at each conditioning level, was calculated and is presented on the top of the bars. It is observed that the TSR values decrease over conditioning time for all asphalt mixtures, which is in accordance with the expectations. The solid red line represents the threshold value below which an asphalt mixture is considered to be more susceptible to moisture damage, according to the Dutch standards.



Figure 4-2: Moisture induced sensitivity tester or MIST

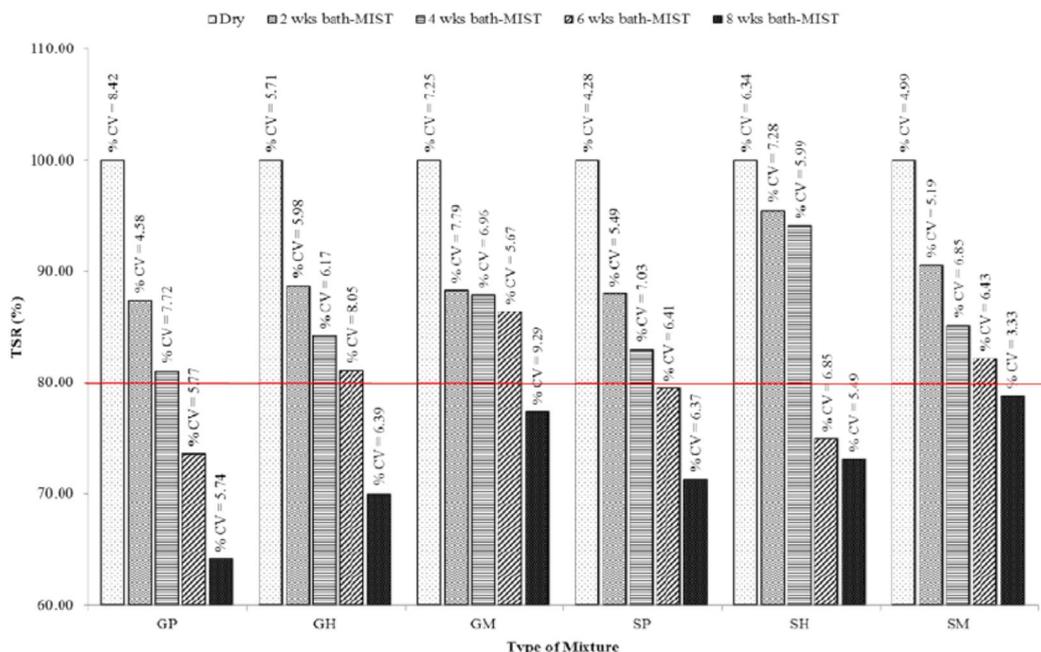


Figure 4-3: Mean TSR values after each conditioning period

With respect to the effect of the aggregate type results show that for all three binders, the sandstone aggregate mixtures have demonstrated better moisture damage performance than those containing granite aggregates (Table 4-2). In an earlier study by Kringos et al., in which the same materials were used, field observations also showed that sandstone aggregates have better moisture performance than granite.

In this study, by comparing the mixtures in terms of the type of binder used, it is shown that the use of polymer modified bitumen increases the resistance of the mixture to moisture damage (Table 4-2). Moreover, it is observed that moisture sensitivity increased when binders prepared with softer bitumen are used.

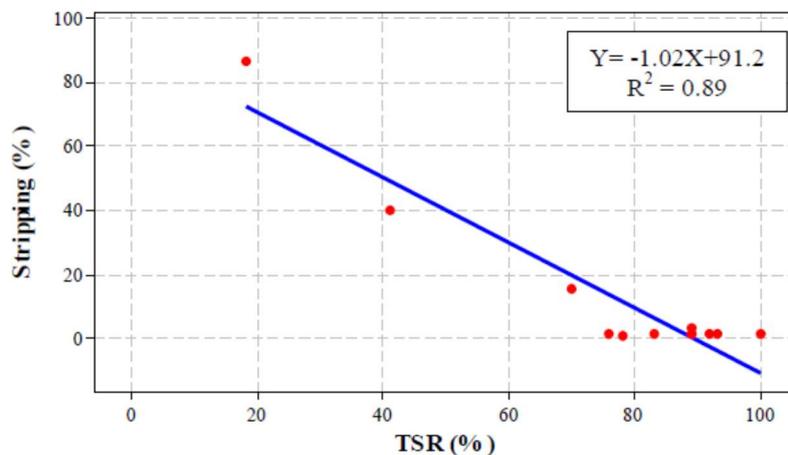
**Table 4-2: Mean ITS values for various PA mixtures**

Duration of combined conditioning protocol (weeks)	Mean Indirect Tensile Strength (kPa)					
	Type of mixture					
	SP	SH	SM	GP	GH	GM
0	569.14	800.87	906.55	634.07	856.89	850.52
2	550.04	780.50	877.26	589.51	790.68	816.15
4	518.21	769.04	825.06	546.22	749.94	812.33
6	496.56	612.43	795.77	496.56	721.93	798.32
8	445.63	597.15	762.67	432.90	623.89	714.29

In paper 287 (Amelian *et al.*, 2014) it was stated that the moisture damage in hot mix asphalt is one of the major concerns in durability of flexible pavements. In their research, a digital image analysis approach was utilized to convert boiling water test (ASTM D3625) from visual rating to objective evaluation. Digital images captured from mixtures were processed and analysed to identify the amount of stripping percentages. Some laboratory tests were conducted on specimens prepared from different types of aggregates to compare the stripping percentages obtained from image analysis of the boiling water test and modified Lottman test (AASHTO T283) results. In AASHTO T283 test, in addition to indirect tensile strength, the Dynamic Modulus  $E^*$  test and the Marshall Stability test were performed; therefore, three criteria including tensile strength ratio (TSR),  $E^*$  stiffness ratio (ESR) and retained Marshall stability (RMS) were used to compare the results of two methods. The dynamic modulus test was conducted in indirect tension mode. Assumption of Poisson’s ratio and a linear viscoelastic solution was used for the  $E^*$  calculation.

The scope of the study included a number of HMA mixtures varying in different types of aggregates which were used including quartzite, granite, andesite, limestone and slag, while using one paving grade binder 50/70. Moreover, in some cases an anti-stripping additive was used such as hydrated lime slurry or a nanotechnology based material (Zycosoil).

**Findings showed that the results of boiling water test have significant relationship with TSR and ESR. Good correlation was found between the three tests (Figures 4-4 and 4-5); however, the results of boiling test did not show significant relationship with RMS.**



**Figure 4-4: Correlation between tensile strength ratios limited to 100 % and stripping percentages in boiling test (ASTM D3625)**

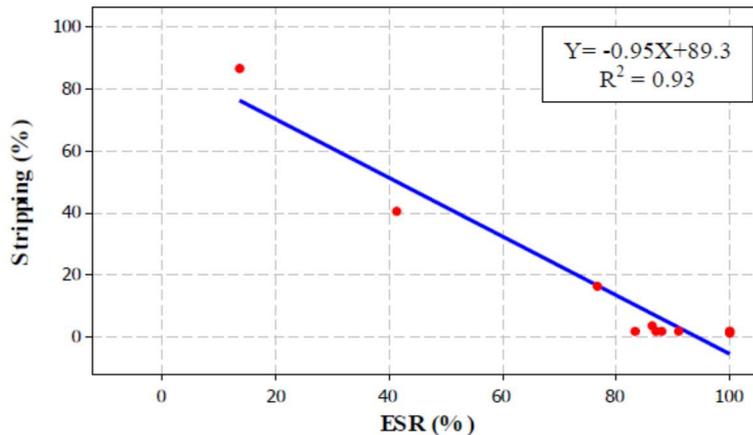


Figure 4-5: Correlation between E\* stiffness ratios limited to 100 % and stripping percentages in boiling test (ASTM D3625)

Despite the good correlations reported, it is noted by the reviewer that a large majority of the data points are all located in the lower right corner: low water sensitivity of HMA mixtures corresponding to almost no stripping observed in the boiling water test. Moreover, in the region of TSR or ESR value between 75 % – 100 %, almost no effect is seen in the boiling water test results (all < 20 % stripping).

In paper 485 (Gubler *et al.*, 2005) different test methods are compared to evaluate moisture susceptibility. This is of special importance because of the insufficient effectiveness of the test procedures according to EN standards currently used. In this research, experiments were conducted to investigate the effects of water and temperature on mechanical properties of mixtures with different air void content. The evaluation of such properties concentrates on the following three approaches: innovative Coaxial Shear Test (CAST, Figure 4-6), traditional Indirect Tensile Test or IDT (ASTM D4867) and empirical Cantabro Test (EN 12697-17). Specimens were prepared by means of Superpave Gyratory Compactor (SGC) and divided in two different subsets for controlled dry and wet conditioned testing. Test results indicated that the Indirect Tensile Test is not able to discriminate between wet and dry condition as the Coaxial Shear Test does. The CAST method reproduces closest the real field conditions and indicates clearly the risk of water damage for open graded mixtures (high air void content). Dense graded mixtures (low air void content) showed less influence probably due to the reduced amount of penetrating water. Cantabro tests provided also significant results in good correlation with air void content and material properties of asphalt mixes.

The indirect tensile test or IDT is able to discriminate between mixtures with modified and unmodified bitumen, while modified bitumen improved the Cantabro abrasion resistance on both dry and wet conditioned specimens. The CAST method is a sophisticated research tool allowing a more profound insight in the nature of water damage evolution.

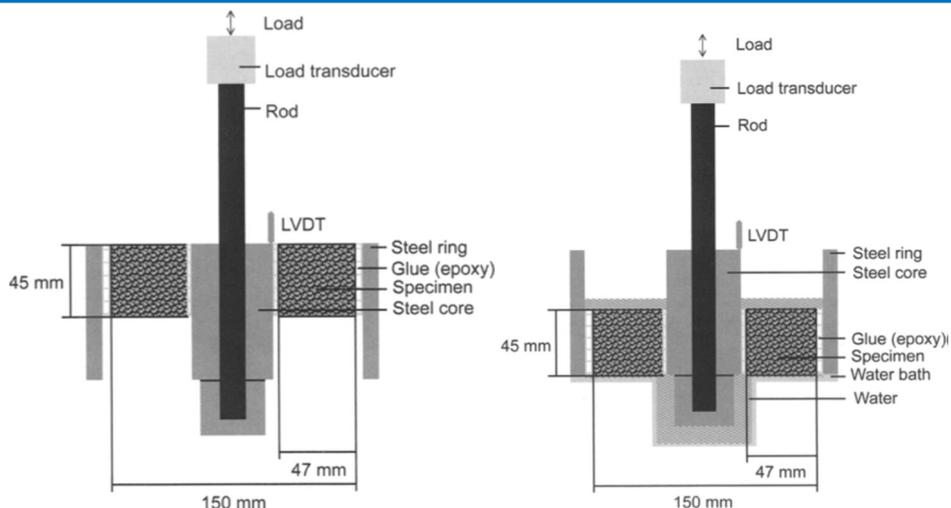


Figure 4-6: Setup of both dry (left) as well as wet (right) test using CAST

In the report 509 (Roos *et al.*, 2010), the results of an extensive test program including MA 11 and AC 22 asphalt mixtures which were prepared with two different PMBs, namely 25/55-55A and 10/40-65A (for each bitumen and mix type 4 binders originating from different suppliers were used). The asphalt mixtures were laboratory aged (MA: 60 and 165 minutes in a mixer; AC: 2 and 3 h in a heating cabinet). Binders were tested in 4 stages: freshly produced, recovered from the freshly-mixed asphalt mix; recovered after short short-term conditioning and recovered after long short-term conditioning. From the freshly produced as well as from the short-term ageing conditioned asphalt samples specimens were prepared and a series of (performance) tests were conducted on both binders as well as asphalt mixtures (stages 1 to 3). Special attention was given to the relationship of the elastic recovery. Moreover, static splitting tensile tests according to EN 12697-12 to determine adhesion behaviour were conducted.

However, no systematic correlations between the different ageing regimes and ITSR values could be established; results varied from one PMB binder to another (see Figure 4-7).

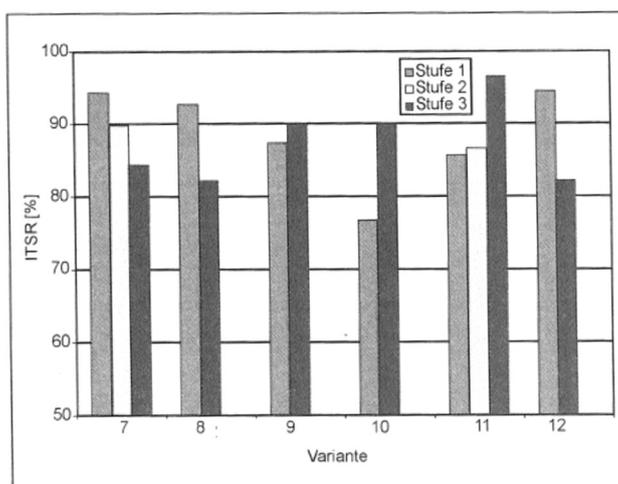


Figure 4-7: ITSR values of asphalt binder variants of stages 1, 2 and 3 (freshly prepared and short-term aged asphalt mixtures)

In the paper 566 (Puchard *et al.*, 2012) the results of efforts to introduce LT asphalt in Hungary are reported, in particular by conducting comparative performance laboratory tests on a series of AC11 wearing course variants containing viscosity modifying additives (fatty acid amides). Following laboratory testing, test sections were constructed while using a fatty acid amide with a dosing rate of 0.4% to both conventional 50/70 bitumen as well as a PMB (25/55-65 type). Mixing temperatures of LT variants was about 40°C lower as compared to the reference mix (without additive).

**The mechanical tests carried out on the produced asphalt mixes showed that water sensitivity of the mixes was in all cases adequate, being 92-96% (reference mix: 88%). Therefore, no interpretation in function of the nature of the binder could be made. Visual inspections demonstrated no defects up to now (2-3 years following construction) of any of the test sections.**

## 4.2 Papers analysis sum up

The following conclusions can be drawn from the paper review:

- In general, a small number of papers (7) are available reporting on the outcome of studies investigating the water sensitivity of asphalt mixtures also allowing an interpretation in terms of the nature of the binder and/or the interaction of the binder with the aggregate. In only one paper a link with experiences in the field was reported.
- Despite the small number of studies reviewed, the conclusions drawn divert to a large extent ranging from conflicting results between tests conducted on binder/aggregate and asphalt mixture levels, over consistency of test results to even reporting a correlation between stripping percentages and water sensitivity of the corresponding asphalt mixtures.
- A majority of the studies do not include a sufficient amount of data to draw statistically valid conclusions. However, most papers report a positive effect of the use of polymer modified bitumen on the water sensitivity of asphalt mixtures (probably due to beneficial effect of higher viscosity of the binder). The impact of the nature of the aggregate is recognized as well.
- In only one study, the effect of both short as well as long term ageing was evaluated. However, no systematic correlation between the different ageing regimes (including also a fresh binder) could be determined. Results varied from one PMB binder to another.
- In a majority of the papers asphalt mixtures variants are characterized by a low water sensitivity: ITR values ranging from 70 – 100% (complying with tender specifications in a given country). Given latter high values and taking into account the rather poor reproducibility of tests both on asphalt mixture as well as on the binder/aggregate level (see par. 6 for discussion on overall uncertainty), the establishment of correlations is highly unlikely.
- Two innovative procedures are presented to assess the water sensitivity of asphalt mixtures, namely the CAST and the MIST method. Both methods try to mimic more realistically the real field conditions with respect to water conditioning by a cyclic variation of the water pressure and temperature in comparison to the static conditioning as described in EN 12697-12. At present both method can be considered as research tools possibly providing more fundamental insight in the nature of water damage evolution.

Table 4-3 summarizes the correlations (or absence of) found between results of tests conducted on loose coated aggregate (level 1-2) in order to probe for the bonding of bitumen with aggregates and both material properties (level 1) as well as the water sensitivity of bituminous mixtures (levels 2 and 3).

**Table 4-3: Possible correlations found between test results probing for binder/aggregate interaction and water sensitivity of bituminous mixtures**

Paper	Correlated data	Type of correlation	# binders	# aggregates	Comment
Paper 031 (Nordgren <i>et al.</i> , 2012)	Rolling bottle test (%) vs ITSR (%) (FAS-455)	None – conflicting data	7	1	U
Paper 041 (Deniz <i>et al.</i> , 2012)	Static immersion test (%) (Nicholson ASTM D-1664) vs ITSR (%)	None	1	2	U
			1	2	PMB
Paper 242 (Varveri <i>et al.</i> , 2014)	Nature aggregate and/or bitumen vs ITS (following MIST cond.)	Consistency of results	1	2	U
			2	2	PMB
Paper 287 (Amelian <i>et al.</i> , 2014)	Boiling water test (%) (ASTM D3625) vs TSR (%) and ESR (%) (AASHTO T283) + Retained Marshall stability (%)	TSR: linear with $y = -1.02x + 9.12$ ( $R^2 = 0.89$ ) ESR: linear with $y = -0.95x + 89.3$ ( $R^2 = 0.93$ ) Retained Marshall: no correlation	1	5	U
Paper 485 (Gubler <i>et al.</i> , 2005)	Nature binder vs CAST	Possible to differentiate between unmodified and modified binder	1	1	U
	Nature binder vs IDT (ASTM D4867) Nature binder vs Cantabro test		1	1	PMB
Paper 509 (Roos <i>et al.</i> , 2010)	Origin of binder vs ITSR (%) at various ageing stages	none	8	2	PMB
Paper 566 (Puchard <i>et al.</i> , 2012)	Nature binder vs ITSR (%)	none	1	1	U
			1	1	PMB

LEGEND: U - Unmodified bitumen; PMB - Polymer Modified Bitumen; A - Aged bitumen; BBS – Bitumen Bond Strength; PATTI – Pneumatic Adhesion Tensile Testing Instrument; ITSR – Indirect Tensile Strength Ratio (EN 12697-12 part A); MIST - Moisture Induced Sensitivity Tester ; ESR – E\* Stiffness ratio; IDT – Indirect Tensile Test; CAST – Coaxial Shear Tester.

## 5 Binder ageing effect on binder/aggregate interaction (level 1-2)

The effect of ageing on the binder/aggregate interaction has been discussed in only a very limited number of publications (#3).

In the paper 232 (Bhasin et al., 2007) it is stated that an important material property that influences the performance of an asphalt mixture is the surface free energy of the asphalt binder and the aggregate. Surface free energy governs the adhesive bond strength between the asphalt binder and the aggregate as well as the cohesive bond strength of the asphalt binder. These bond energies in turn influence the resistance of the asphalt mixture to distresses such as fatigue cracking and moisture induced damage.

Asphalt binders undergo several different types of engineering and/or natural modifications that influence their chemical and mechanical properties. Three common examples of modifications are addition of polymers, addition of additives (e.g. anti-strip agents) and the oxidative ageing of the asphalt binder. In this study the effect of different types of modifications on the surface free energy components of the asphalt binder is explored. Furthermore, the change in surface free energy was used to calculate parameters such as the energy ratio which can be related to the performance of the asphalt mixtures although no real laboratories or field data are reported in this paper.

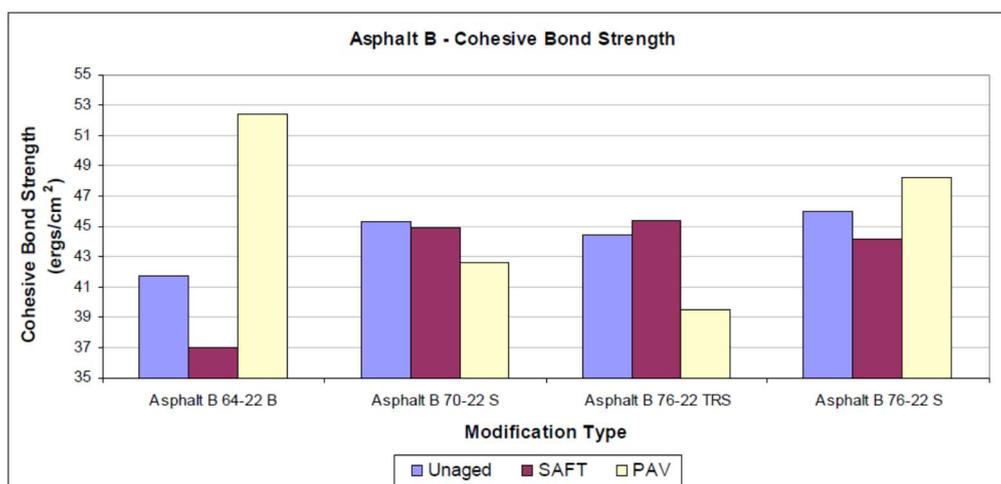
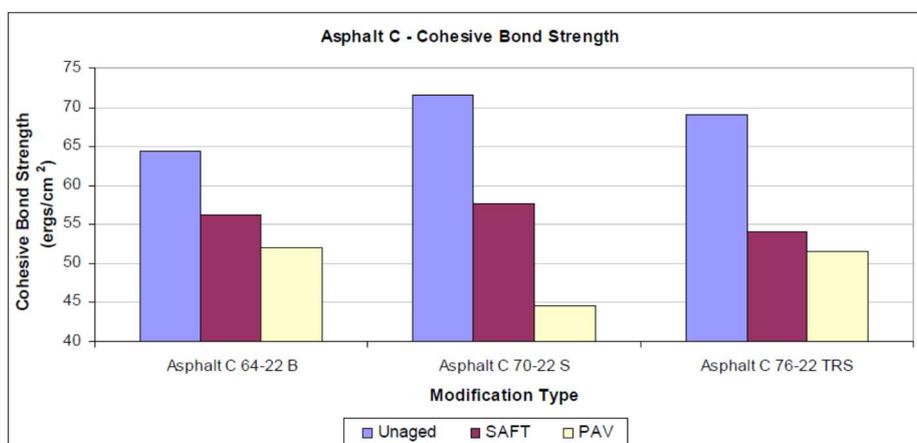
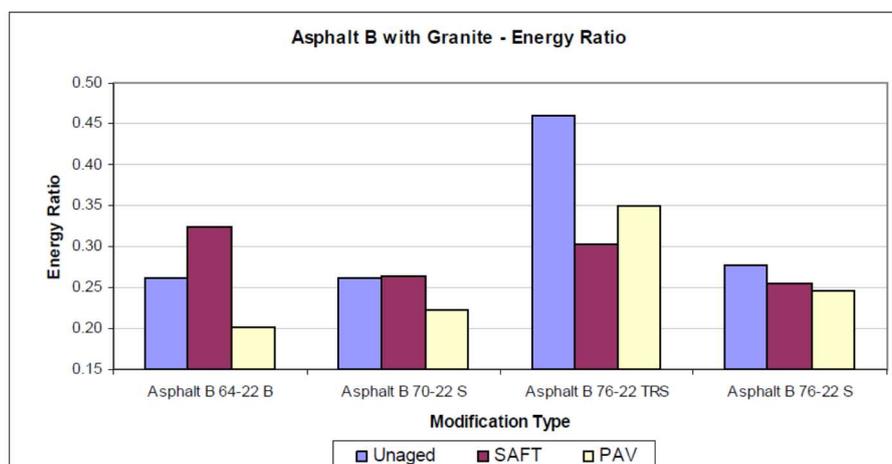


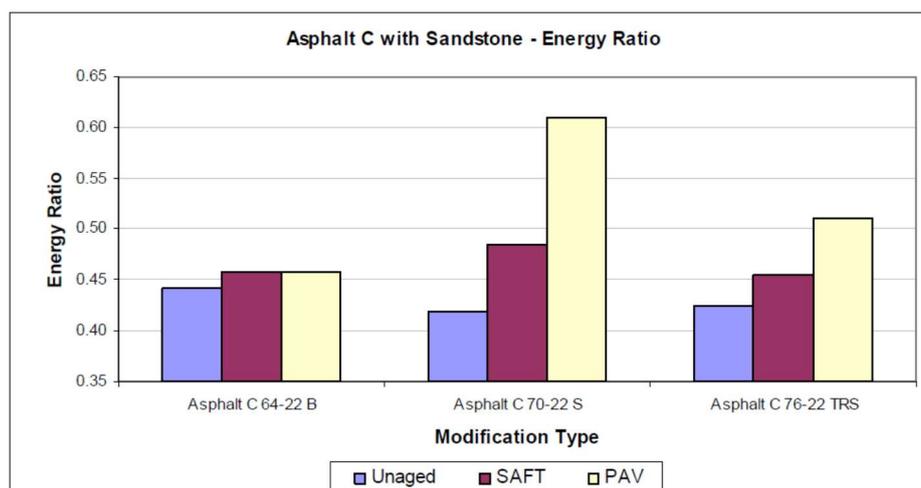
Figure 5-1: Effect of manufacturer modifiers and ageing on cohesive bond strength of asphalt binder from source B



**Figure 5-2: Effect of manufacturer modifiers and ageing on cohesive bond strength of asphalt binder from source C**



**Figure 5-3: Effect of manufacturer modifiers and ageing on ER of asphalt binder from source B with granite aggregate**



**Figure 5-4: Effect of manufacturer modifiers and ageing on ER of asphalt binder from source C with granite aggregate**

With respect to ageing, the impact of both short as well as long term conditioning was evaluated on the cohesive and the adhesive properties of bitumen. The short term ageing was carried out using the stirred-air flow test (SAFT) while the long term conditioning was conducted by the pressurized ageing vessel (PAV). Three different binders were taken up in the study: PG 64-22, PG 70-22 and a PG 76-22. Moreover, for each PG grade binders of three different suppliers (Asphalt A, B and C) were studied. Energy ratios were calculated in case of two types of aggregates, namely sandstone and granite.

**Results from this study demonstrate that in most cases long term aging reduced the work of cohesion indicating lower fracture resistance of the aged binder (Figure 5-1 and Figure 5-2). In the case of one unmodified binder and one modified binder the work of cohesion increased after long-term ageing. After long-term ageing, bituminous binders from one source demonstrated a decrease in the moisture sensitivity, while bituminous binders from the other source demonstrated an increase**

or no change with the moisture sensitivity with the two aggregates used in this study (Figures 5-3 and 5-4). The difference in the behavior of the two bituminous binders is attributed to the influence of ageing on the magnitudes of the polar functional groups.

In a paper 236 (Copeland *et al.*, 2007) the bond strength of a wide range of different types of bitumen (#11) is studied while using the PATTI test (Pneumatic Adhesion Tensile Testing Instrument).

It was demonstrated that the long-term ageing of bituminous binders increased their cohesive strength (Figure 5-5). However, ageing combined with moisture conditioning as a function of time decreased their adhesive performance as is illustrated in Figure 5-6. However, it is noted by the reviewer that a simple interpretation of the PATTI test results in terms of cohesive/adhesive failure is not that straightforward as authors do claim. Therefore, also making the link between adhesive failure and water sensitivity may be hampered as well.

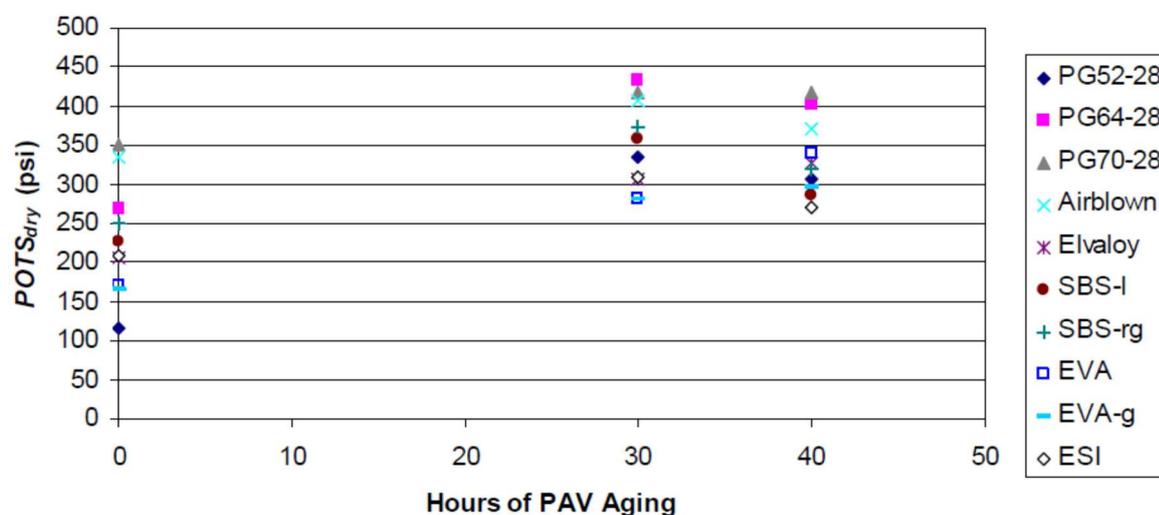


Figure 5-5: Influence of long-term laboratory ageing on POTS of asphalt binders in dry condition

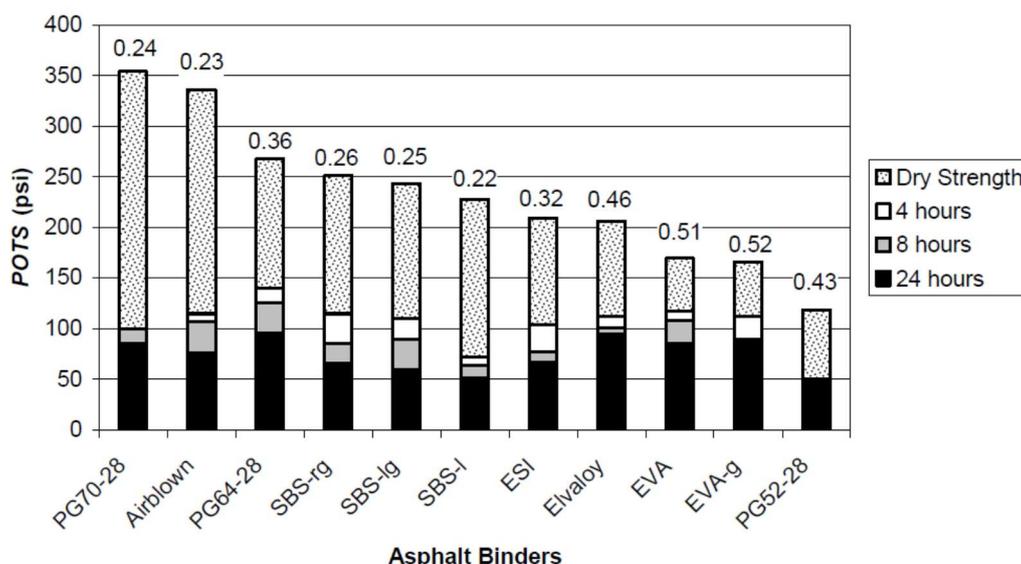


Figure 5-6: Influence of binder type on dry and wet POTS test results

A similar research approach using POTS testing before and after water conditioning (dry – wet) was followed by Canestrari *et al.* (Paper 317) in order to study the adhesion of fresh and ‘old’ or aged bitumen originating from RAP. In latter way, the compatibility between both binders was assessed. Latter study comprises three SBS modified binders with varying modification degree (ranging from 1.8%, 2.8% up to 3.8%) in order to simulate an increased viscosity of the binder with ageing. They are classified as S (soft), M (medium) and H (hard). Two aggregates of different chemistry were used as substrate, namely limestone and granite. In order to mimic in the laboratory a RAP aggregate, virgin aggregates were pre-coated with the hard (H) bitumen.

In figure 5-7 the effect of the pre-coating both for basalt as well limestone is illustrated.

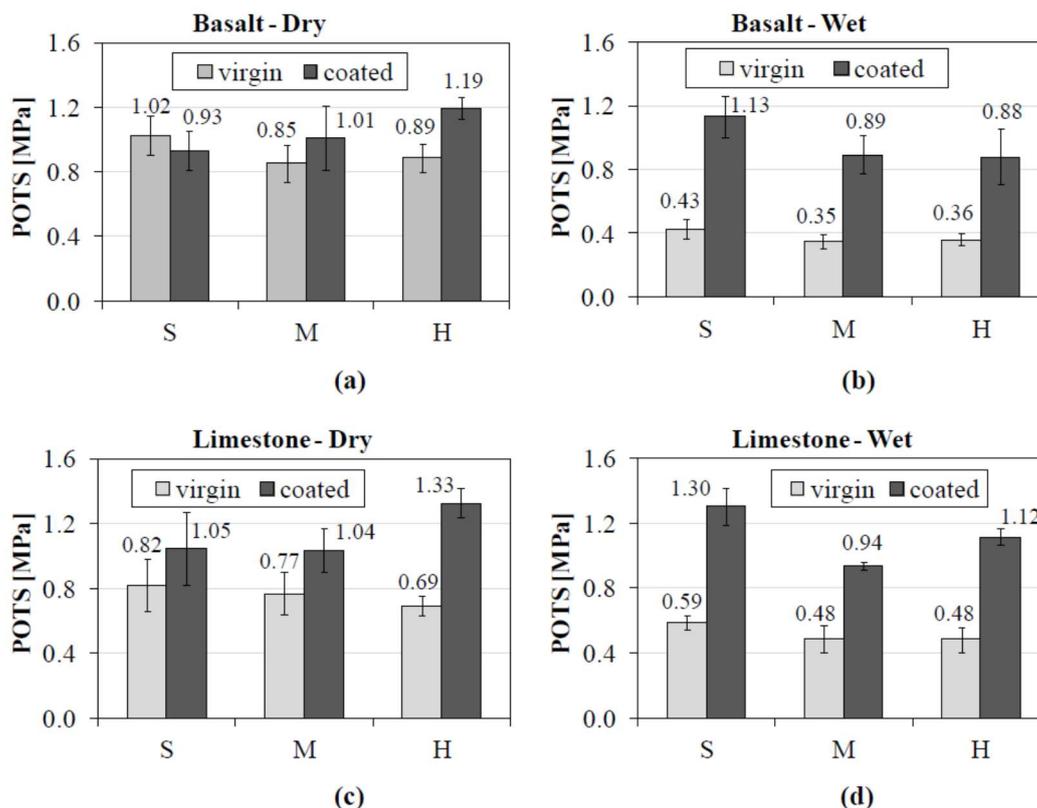


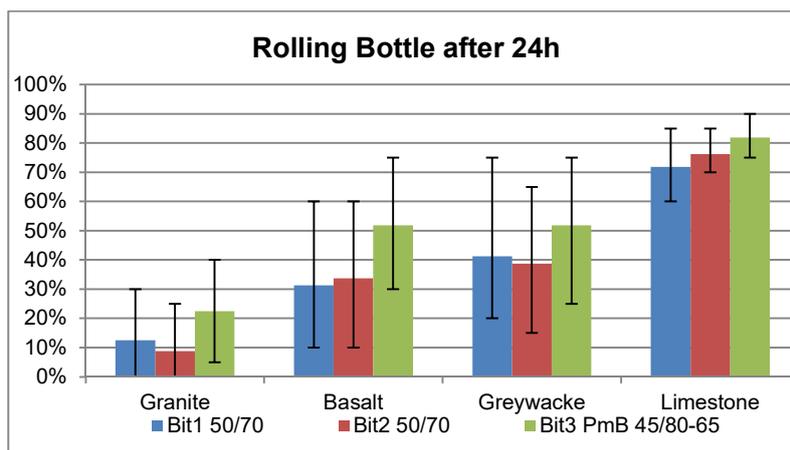
Figure 5-7: Pull-off tensile strength results: comparison between virgin and coated aggregate in dry and wet conditions for basalt and limestone

From this study it was concluded that the presence of a thin film of aged binder in the artificial RAP aggregates ensures the development of a higher adhesion with the virgin binder. This result is detectable both in terms of failure type (cohesive) and bond strength values, regardless of the bitumen use and the conditioning type (dry or wet). In particular, the loss in performance due to the effect of water experienced by the virgin aggregates is much more evident than the loss experienced by the coated aggregates.

The overall study allowed concluding that the use of RAP in the production of new bituminous mixtures does not penalize the bond interactions between virgin binder and aggregates. On the contrary, the artificial RAP substrate, used to simulate a real RAP aggregate, appears able to provide an improvement in the adhesion performance of the mixture and to reduce the water sensitivity of the system binder-aggregate considerably.

## 6 Overall uncertainty for binder/aggregate interaction (level 1-2)

On one hand, the precision of the test methods used for assessing the binder/aggregate interaction is sometimes unsatisfactory. A typical example which is carried out on loose mixtures involves the Rolling Bottle method according to EN 12697-11 clause 5. In the current version of latter standard the following precision data is stated: repeatability  $r = 20\%$  and reproducibility  $R = 30\%$ . The results of a recent round robin campaign conducted in 2014 within the framework of RILEM TC 237 SIB TG1 unfortunately confirmed the poor precision of the test method as illustrated in Figure 6-1, (paper 584 Porot et al., 2016).



**Figure 6-1: Results of the rolling bottle test (EN 12697-11 clause 5) for 12 aggregate/binder combinations; error bars correspond to the range of values obtained**

It is generally recognized in literature that the subjective influence of the visual assessment of the stripping percentage is playing a major role (paper 585 Wistuba et al., 2012 and paper 583 Lamperti et al., 2016). Consequently, the discriminating power of latter test method is rather poor and limits the application of the test method to a relative ranking between binder or aggregate or the identification of critical (risk assessment) binder/aggregate combinations. In the future, it is recommended to replace the visual assessment by an (semi)-automatic digital image analysis.

Moreover, in the paper 582 (Besamusca et al., 2012) the outcome of the work carried out by the Industry Group Adhesion (within the framework of the CEN TC227 and 336 Ad-hoc 'Adhesion – durability') was described. The extensive study included 5 paving grade bituminous binders (50/70) and one polymer modified binder, six different types of aggregates and nine tests methods (both level 1-2 as well as level 2 tests). Beside the fact that no easy-to-use, simple and reliable test method for addressing adhesion between bitumen and aggregate could be identified, it was also concluded a major confounding factors governing to a large extent the test results was the temperature dependence of binder properties such as viscosity. Consequently, it was therefore concluded that just addressing adhesive properties of a binder is quite unlikely.

On the other hand, test conducted on compacted asphalt mixtures (level 2 – 3) also show a rather large spread of test results. As an example the water sensitivity test according to EN 12697-12 part A (Indirect tensile test in combination with water conditioning) is characterized by  $R = 23\%$ . A round robin test conducted in 2015 in Belgium (unpublished results) did align quite well with latter precision data:  $R = 16\%$ .

It is generally recognized that the uncertainty for binder/aggregate interaction is largely arising from the fact that while assessing the water sensitivity of asphalt mixtures other parameters/factors than adhesion also play a role in the outcome of the test such as choice and grading of the mixtures including bitumen content, sample preparation (compaction mode and energy) and conditioning method (time, additional frost-thaw cycles,...). In particular, the impact of the air voids content has been recognized and well documented: see figure 6-2 (paper 485, Gubler et al, 2005) for a typical example of the logarithmic correlation between indirect tensile strength and air voids content. Therefore, interpretation in terms of adhesion is often hampered.

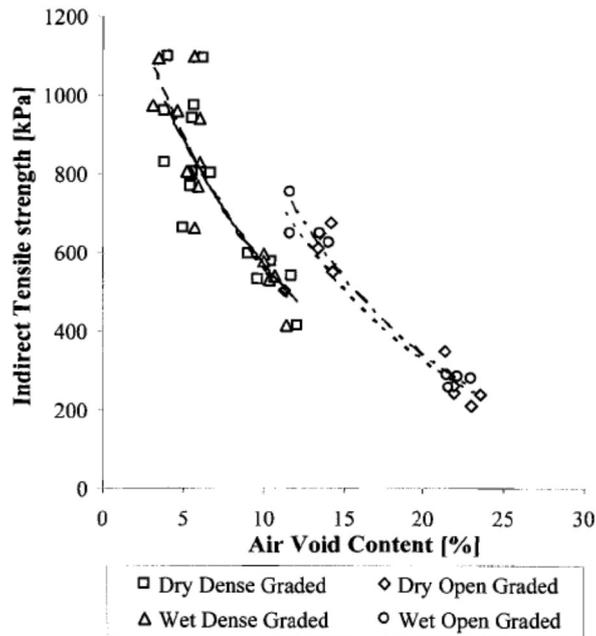


Figure 6-2: Comparison of indirect tensile strength between wet and dry series for dense (AC) and open graded (PA) asphalt mixtures

## 7 Conclusions for binder/aggregate interaction – correlation with water sensitivity of asphalt mixtures (level 1-2, 2 and 3)

The analysis of the possible relationships between the interaction or adhesion of bituminous binders with aggregates and the water sensitivity of asphalt mixtures, showed the following potential relations which are further summarized below according to the different levels as discussed previously. In Table 7-1 a synthesis is provided of the overall evaluation of applicable tests for the adhesive properties of bituminous binders correlated with the water sensitivity of asphalt mixtures.

### **Level 1-2 summary:**

#### Pull-off tests: BBS (AASHTO TP-91) and PATTI (ASTM D4541):

- Although a qualitative indication of consistent results with both contact angle measurements as well as water sensitivity of asphalt mixtures has been reported, no quantitative correlations have been demonstrated. Only the impact of test variables including the type of bituminous binder is shown.
- A major concern is that pull-off tests are only capable to probe for the adhesive properties of bituminous binders in a wet (water) environment. In dry test conditions the failure mode is generally of cohesive nature.
- Pull-off test are being criticised for a number of reasons including the use of an artificial (aggregate) substrate, the rather poor precision of the method and the difficulty to interpret the exact failure mode following the test.

#### Rolling bottle test (EN 12697-11 clause 5):

- A major concern is the low discriminating power of the method mainly due to the poor reproducibility of the test. Latter is largely caused by the subjective visual interpretation of the stripping degree following the test. It is recommended to take up a digital image analysis in the future to improve precision of the test.
- Although a large experience with the test method does exist in Europe and a huge number of data has been gathered and reported, generally a quantitative correlation with asphalt performance test such as water sensitivity is lacking. Only in extreme case an identification of poorly performing bitumen/aggregate combinations is possible (e.g. highly siliceous aggregates).
- Consequently, it is recommended to apply the method only as a screening test to exclude high-risk bitumen/aggregate combinations or to establish a relative ranking of bituminous binders during mix design of asphalt mixtures.

#### Nicholson static immersion test (ASTM D1664):

- A major concern is the low discriminating power of the method as coated aggregates are just immersed in water at 25°C for a given time (normally overnight).
- Moreover, the subjective visual interpretation of the stripping degree (95% criterion) is further limiting the usefulness of the method.

#### Boiling water test (ASTM D3625):

- The test shows potential to link the stripping of the binder to the water sensitivity of the corresponding asphalt mixture, especially at high risk bitumen/aggregate

combinations. However, such evidence is rather scarce and needs to be extended to confirm such statement.

- A concern is the low discriminating power of the method mainly due to the poor reproducibility of the test. Latter is largely caused by the subjective visual interpretation of the stripping degree following the test. It is recommended to take up a digital image analysis in the future to improve precision of the test.
- Another obstacle relates to the possible important effect of the binder viscosity on the test result. This phenomenon indicates that kinetic factors interfere with the principle of the test method.

### **Level 2 and 3 summaries:**

#### Indirect Tensile Strength Ratio (ITSR):

- There is a wide experience with the water sensitivity test according to EN 12697-12 part A (quite similar to modified Lottmann test used in US). Based on the test result most EU countries have set specifications (ITT of mixtures).
- The test has been criticised for several reasons, including: the rather high spread of test results, the large effect of other parameters influencing the test results such as air void content, the static conditioning being applied (see also CAST and MIST) and the difficulty to correlate test results with field performance.
- Nevertheless, the test has also been successfully utilized for evaluating the possible effect of a constituent (e.g. binder type) or additive (e.g. lime) while keeping at all times the other parameters/materials for a given asphalt mixture constant.

#### Coaxial Shear Test (CAST):

- The test has been recently developed at EMPA and offers the possibility to induce mechanical damage due to repeated loading, temperature cycles and water conditioning of gyratory compacted asphalt test specimens. It is therefore anticipated that water induced damage in the field will be better simulated, especially in comparison with the traditional static conditioning as applied in the water sensitivity procedure according to EN 12697-12.
- Although the test results of this sophisticated tool look promising, the method is currently still at a research level. More experience and data is to be gathered in order to be able to formulate any recommendations regarding this innovative test methodology for possible normalization in the future.

#### Moisture Induced Sensitivity Tester (MIST):

- The MIST test is new moisture conditioning protocol which attempts to distinguish the contributions of long- and short-term moisture damage by evaluating moisture diffusion and generating cyclic pressures.
- Although the test results of this sophisticated tool look promising (mainly focusing on porous asphalt characterized by a high void content), the method is currently still at an academic research level. More experience and data is to be gathered and validated in the field in order to be able to formulate any recommendations regarding the usefulness of this innovative test (conditioning procedure) in the future.

**Table 7-1: Overall evaluation of applicable tests for adhesive bitumen properties related with water sensitivity of bituminous mixtures**

Bitumen test	Pros	Cons	Availability in Europe <sup>(1)</sup>	Standardized in Europe	Limitations
<b>Bitumen Bond Strength (BBS)</b>	Large experience in US based on AASHTO TP-91 method. Effect of bitumen can be demonstrated – screening and ranking of binders possible. Has been used for evaluating interaction with aged binder (RAP).	Use of artificial substrates; Failure mode varies in function of conditioning; High spread of results.	Rarely	No	No assessment of adhesive properties of bitumen in dry conditions (cohesive failure)
<b>Pneumatic Adhesion Tensile Testing Instrument (PATTI)</b>	Large experience in US based on ASTM D4541 method. Qualitative ranking of bitumen has been demonstrated – screening and identification of extreme cases possible. Effect of binder ageing has been shown.	Use of artificial substrates; Failure mode varies in function of conditioning; High spread of results.	No	No	Adhesive properties of bitumen only possible in wet conditions
<b>Rolling bottle test</b>	Easy to perform test. Influence of nature of binder and/or additives has been shown.	No correlation with water sensitivity demonstrated; Impact nature of aggregate dominant.	Often	EN 12597-11 clause 5	Poor reproducibility due to visual assessment of stripping; only relative ranking/screening possible
<b>Nicholson Static Immersion Test</b>	Test method based on ASTM D1664, widely used in US; Easy and quick test to perform	Subjective assessment of stripping. No correlation between test results and water sensitivity (ITSR)	Rarely	No (2)	Questions raised about discriminating power of test method
<b>Boiling water test</b>	Test method based on ASTM D3625 as used in US; Significant correlation with water sensitivity test, especially for extreme cases (high risk)	Often poor precision due to subjective assessment; Binder viscosity may be interfering factor.	Rarely	No (2)	If visual evaluation of stripping is carried out, method limited to ranking or screening of bitumen/aggregate combinations
<b>Indirect Tensile Strength Ratio (ITSR)</b>	Wide experience in EU (ITT asphalt mixes); equivalent test used in US	Reproducibility rather poor; Static water conditioning discrepancy with field performance	Usually	EN 12697-12 part A	Not possible to study 'pumping' effect caused by traffic or evolution of water sensitivity with time
<b>Coaxial Shear Tester (CAST)</b>	Better simulation of real field conditions; Potential to provide fundamental insights in water damage mechanisms	Few experience at present as innovative method at research level	Rarely	No	More experience needed
<b>Moisture Induced Sensitivity Tester (MIST)</b>	Potential to mimic more realistically moisture damage mechanisms Possibility for study evolution of water damage	Few experience as method has recently been developed (research phase)	Rarely	No	More experience needed

(1) Considered ranking scale: Usually - often - occasionally – rarely – no; (2) Similar or equivalent test available in Europe as EN standard.

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