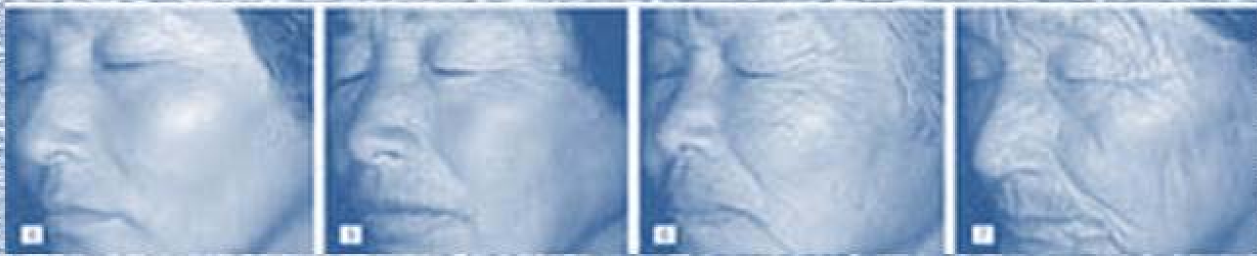
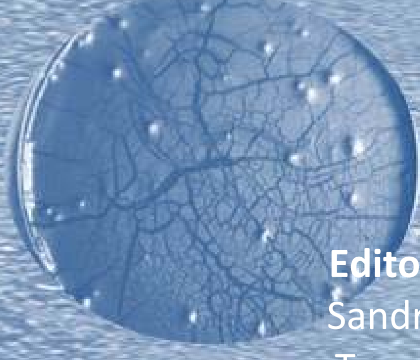
# Aging of Asphalt Symposium
# Delft, the Netherlands September 17th 2014

Erkens, S.; Scarpas, Athanasios

# Aging of Asphalt Symposium

## September 17th 2014, Delft, the Netherlands





**Editors:**
Sandra Erkens
Tom Scarpas

ISBN 978-94-6186-524-3

TU Delft Delft University of Technology

Challenge the future

**Authors:**
Sandra Erkens
Tom Scarpas
Ronald Blab
Ron Glaser
Charles Glover
Markus Oeser
Laurent Porot
Hilde Soenen

Delft, 2014
ISBN 978-94- 6186-524-3

# 1 Executive summary

Technical specifications for the asphalt concrete properties are developed to be able to specify mixtures that will perform well in pavement applications. Being able to identify and determine properties related to pavement performance in practice is crucial for both road authorities and contractors, since it allows for design and risk management by determining design life times and reliability. However, the properties of Asphalt Concrete (AC) change over its lifetime and since most pavement layers last for a decade or more these changes are crucial in determining the performance in practice.

For many of the standard materials the effect of aging is implicitly dealt with in the safety factors that also account for other effects such as the variation rest periods/healing and variations in traffic and weather in the design methods and specifications. Rapid changes in the materials used (increasing percentages reclaimed asphalt, bio-bitumen, rejuvenators, waste materials) and in the production of both bitumen (new refining methods resulting in different composition of bitumen) and asphalt concrete itself (warm mix asphalt, porous asphalt concrete, rubber asphalt mixtures) lead to increased uncertainty in the effects of aging. As a result, the uncertainties in pavement performance increase, which means the prediction of maintenance and the necessary budgets is getting more inaccurate.

In order to maintain the ability to reliably design and maintain pavements and determine the most cost-effective solutions for a given situation, a better understanding of the aging processes and objective methods to take into account aging effects on material properties is needed. This need is widely recognized, in the USA the Mechanical Empirical Design Guide takes aging into account through aging tests on the bitumen used and in Europe CEN TC227 works on establishing a method to assess the aging sensitivity of asphalt mixtures. This symposium aimed at combining the existing information and insights from ongoing research into recommendations that will allow the development of methods to determine aging sensitivity and the impact on pavement performance, facilitate the exchange of obtained data and stimulate further developments

The resulting recommendations are:

- Do make long term aging sensitivity of binders part of the bitumen standards and take the results from the aging sensitivity of binders into consideration when assessing AC properties. Be aware that RTFOT testing only gives an indication of the sensitivity of a penetration grade binder to aging during hot mix production and construction, it doesn’t work for hard grades, PMB’s or warm mixes.

- Because of the many variables involved, developing one test method to characterise aging sensitivity seems improbable. However, PAV aging is both practical and, if tests at various conditions are carried out, able to give kinematic properties. A PAV protocol for testing at two temperatures and time intervals could provide practical characterisation information for the short term and enable model development and validation on the long term. RCAT and other aging procedures could also be used in this sense, but considering the availability of equipment and the wide spread experience, PAV is the best candidate to allow the rapid development of international experience with the approach.
  Based on the current standards and the work presented during the symposium, PAV tests at 90 and 100 degrees Celsius and 20 and 40 hours, respectively, are suggested. The low values for temperature and duration are based on the current standards and fit both the USA and

CEN procedure, while research shows that after 40 hours at 100 degrees the chemical (FTIR) and rheological (DSR) properties of laboratory aged and field samples were similar (Section 6.5 and 8.5). At 100°C the temperature is low enough so that the effect of secondary reactions is negligible. As such, these conditions are appropriate for kinetic expressions for in service pavement performance. For high temperature processes and possibly also for repeated recycling (very long term) more sophisticated methods are needed.

- Set-up and maintain field monitoring of temperature and UV radiation in various climate zones, as well as regular sampling over time and height to keep checking the predicted changes (from both tests and models), versus the actual changes in properties order to ensure reliability of the data as well as the applicability for pavement performance prediction. In setting up field tests, it is important to get both the composition of the virgin bitumen and the composition after mixing, transport and placement in the pavement. These compositions provide the starting points from both the material and pavement structure point of view and can be used to assess the development of aging products over time. There is a lot of discussion about the impact of binder recovery methods on the observed composition, so until it is proven that this does not have an influence, for comparisons the same recovery method should be used.

- Set up a coordination and support action on AC-Aging to continue to exchange information and experiences, both in research and in construction projects.

- develop an IR testing protocol, to facilitate the exchange of results and information.

- Compare the bitumen composition that is found through various recovery methods to establish if there is an effect and if so, develop a procedure to address this.

- To further understanding of aging, a Round Robin test on the differences in test conditions between US and EU, allowing better access to each other’s data and knowledge would be useful.

- When developing aging tests for AC, it would be useful to look at the US experience. As long as there is no fundamentally correct method for assessing the aging, it would be preferable to standardize it as much as possible in order to allow cooperation and exchange of data.

# 2 Contents

## Table of Contents

# 3 Introduction

## 3.1 Introduction to the symposium

The properties of Asphalt Concrete (AC) change over its lifetime. This is due to a combination of repeated traffic loads and the chemical and physical interaction between the material and its environment, such as moisture, oxygen and ultraviolet rays. The former, traffic related, change in properties is commonly referred to as fatigue. The latter, environment related change, is called aging.

Since most pavement layers last for at least 10 years, aging is an important issue in characterizing AC mixtures. If only properties of recently produced material are determined, this can lead to unrealistic expectations, both under or over-estimating the expected performance, in practice.

In the symposium a number of experts from various countries exchanged data, experience, knowledge and theories on aging of both bitumen (or asphalt) and AC. This document summarizes the background information, set-up and results from this symposium and aims to contribute to the development of an objective assessment of aging sensitivity of AC.

## 3.2 Structure of the document

In this document some background concerning the current requirements for aging assessment are given Chapter 4. Chapter 5 gives the list of participants and the symposium program. The summaries of the presentations and discussions are given in Chapter 6. In Chapter 7 the results from the overall discussion and the advice arrived at towards the end of the symposium are presented and finally, the copies of sheets the speakers used are included in Chapter 8.

# 4 Background on aging in specifications

## 4.1 The relevance of aging

The importance of aging in bituminous materials is based on the fact that most pavement damage occurs only after a considerable service life, from 10 to 20 years for surface layers to considerably longer times for binder and base layers, depending on the structural design approach used. The material properties change during this time due to aging, especially for the surface layers which are exposed to moisture, large temperature changes, oxygen and UV light. As a result, it are the aged material's properties that determine its sensitivity to damage. This means that o assess the suitability of a material for a given application, not just its original properties, but also some indication of how these properties change over time or an indication of a minimum performance that will be retained over time is needed. However, aging is a complex process, affected not only by the material characteristics, but also by the production and construction process and local environmental conditions and governed by chemical and physical relations that aren't known yet. Despite that, there are some test that are used to get an indication of the resistance to aging. In this chapter some of the common aging tests are described. It is by no means a complete list, the aim is to show examples of the current practice of dealing with aging in specifications as a background for the symposium content.

## 4.2 Aging tests: bitumen

### 4.2.1 Short term aging: RTFOT

Aging tests can be separated into tests on bitumen and tests on the asphalt mixture. For bitumen a common test to represent the short term aging of bitumen that takes place during mixing, transport and placement is the Rolling Thin Film Oven Test (RTFOT, AASHTO T240 [1],ASTM D 2872 [2] and EN 12607-1 [3]). Besides in the actual standards, descriptions of this test can be found in [4] and [5].

In this test bitumen is placed in glass bottles in a circular rack in a strictly specified oven.. The rack contains eight bottles in total with 35 grams of bitumen per bottle. The oven is heated to 163°C before placing the bottles in the rack and they are left in the oven for 75 ([3] ) or 85 (**Error! Reference source not found.** and [2]) minutes of testing. The rack rotates the bottles at a rate of 15 revolutions per minute while the oven is at a temperature of 163°C. During the test air is being blown into the oven at 4000ml/minute, with the air-inlet such that it blows into each bottle at the lowest point in the revolution . After testing the mass loss, or more specifically the mass change (since some bitumen may increase in density due to oxidation), is determined. The fact that some bitumens increase in mass while others decrease, indicates that during the test both a loss of volatiles and increasing moleculair size due to oxidation occur. This was corroborated by a study [6] using inert gas, it that case it was found that only a mass decrease was measured.

#### 4.2.1.1 USA

The material from two of the eight bottles is used to determine the change in mass, the material from the other bottles is used for DSR testing (T315 [7]) to obtain the G*/sinδ after short term aging, in the dynamic shear test which is used in AASHTO M320 [8], as part of the requirements for binders in performance graded binders. Alternatively, the material can also be aged further using the pressure aging vessel.

#### 4.2.1.2 Europe

In Europe also, the mass loss is determined based on the average of two bottles. The additional material is used to determine the change in penetration, ring and ball temperature and viscosity at

60$^{o}$C. The standards for penetration bitumen (EN 12591), polymer modified (EN 14023) and hard paving grade (EN 13924) bitumen specify requirements for the mass loss, change of penetration and/or the change in ring and ball temperature for most grades of bitumen. For soft binders (designed and specified by the dynamic viscosity at 60$^{o}$C), the European standards specify the use of the Thin Film Oven (TFO, EN 12607-2 [9])instead.

#### 4.2.1.3 Relation with field aging

In the BitVal project **Error! Reference source not found.** the aging procedures used in the European standard were investigated as a first step towards performance based binder specifications in Europe. The approach build on a large number of international publications, mostly from the USA and Europe.
In the project also the aging procedures were investigated. In case of the RTFOT different types of bitumen were used to make bitumen samples and asphalt mixtures, manufactured in different types of plants. The penetration at 25 °C, R&B softening point and ductility at 17 °C were determined for the bitumen before and after RTFOT and on the material taken from the coated materials. In the BitVal report **Error! Reference source not found.** it is concluded that:

- The bitumen source and the grade of the bitumen have a major role on the thermal susceptibility to hardening with coating.
- The manufacturing process and the composition of the asphalt mixture did not have a significant effect, on average, on the hardening of the bitumen in the experiment.
- The predictive capacity of the RTFOT method is satisfactory. In particular, it makes it possible to assess the change of R&B softening point with an acceptable precision.
- The RTFOT was a little more severe overall than mixing asphalt for the experiment conducted. Therefore, the RTFOT is a good method to indicate the risk of premature hardening of asphalt mixtures. Conversely, it will under predict the sensitivity to rutting.

More recently Besamusca et al. [10] concluded that RTFOT represents the aging due to mixing and such for penetration grade binders, but due to the fixed test temperature of 163 °C, it is not representative for hard grade, polymer modified and warm mix binders. For hard grade binders and polymers, this is probably because these materials do not mix as well as penetration binders. For warm mix binders, the test temperature is probably unrealistically high.

### 4.2.2 Long term aging: PAV

The pressure aging vessel (PAV, AASHTO R28 [11], EN 14769 [12]) is meant to simulate long term aging, the aging that occurs during the pavement service life. The current PAV test was developed during SuperPave **Error! Reference source not found.** as a modification of the aging vessel that had been in use in bitumen research for many years. In the current test, steel pans are filled with previously RTFOT aged bitumen that is then placed in a pressure vessels which is placed in an oven. The test uses both increased temperature and increased pressure to accelerate the aging. The aim is to achieve an amount of aging that is comparable to several years of service life in a pavement. In developing the test, bitumen reclaimed from field cores was used as a reference, using the bitumen from the whole core. More recent results indicate that the top part of field cores is aged much more than lower parts. This indicates that assessing the aging effect based on bitumen reclaimed from whole cores rather than only the top 1 or 2 centimetres underestimates the aging effect ([13], [14]). As such, PAV conditions are now thought to represent only limited aging times for the material at the top of a pavement. This appears to be true for most laboratory aging methods, Besamusca et al. [15] showed this for 70/100 bitumen in various (combinations of) lab tests compared to the aging in the field, the relative importance of aging due to production is, for bitumen 70/100 and porous asphalt concrete, considerably less important than predicted by the Shell bitumen handbook (Figure 2).

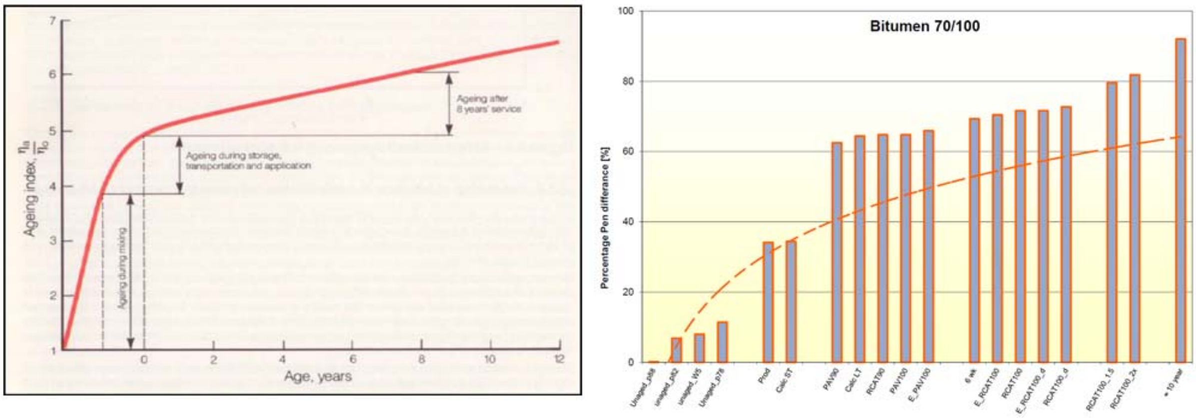



**Figure 1: Aging effect graph from Shell (left) versus effect aging and various lab tests from Besamusca et al** Error! Reference source not found. **(right)**

### 4.2.2.1 USA

In the USA, the PAV procedure entails ageing 50 g of bitumen in a 140 mm diameter container (giving a binder film that is approximately 3,2 mm thick) within the heated vessel, pressurised with air to 2,07 MPa for 20 hours at temperatures between 90 °C and 110 °C. The test takes 20 hour. Testing of the PAV (and RTFOT) aged bitumen in the DSR, bending beam rheometer and direct tension test is required for performance grading of bitumen.

### 4.2.2.2 Europe

In Europe the suggested sample size is the same as in the USA (50 grams in 140 mm containers, from the RTFOT (EN 12606-2), but different sizes containers are allowed as well. In case of a different size, the amount of binder must be adjusted to ensure a layer thickness of approximately 3,2 mm. The pressures and temperatures used overlap with those used in the standard used in the USA, but there are small differences, in Europe the pressure is 2,1 MPa (versus 2,07 in de USA) and the temperature range is 80$^{o}$C to 115$^{o}$C (versus 90 °C to 110 °C).
The current European bitumen standards do not require PAV aging or testing of PAV aged binder to assess the sensitivity to long term aging.

## 4.2.3 Rotating Cylinder Aging Test (RCAT)

The Rotating Cylinder Aging Test (EN 15323 [16]) uses a rotating flask with a bitumen layer at a specified temperature and oxygen flow for a fixed period of time. A grooved stainless steel rod of 34mm diameter is placed in the testing cylinder during the test. Typically, the effect of aging is assessed based on binder tests at the end of the procedure, but it is possible to take samples during testing in order to use a kinetic approach. The sample has a mass of approximately 650 grams, with a maximum of 900 grams.

Despite the versatility of the RCAT, RTFOT and PAV set-ups are more widely available and as such have become more or less the standard procedure for bitumen aging in Europe.

### 4.2.3.1 Short term aging

In case of short term aging, a temperature of 163$^{o}$C and a rotation speed of 5 rounds per minute are used. The air flow is 4 litres per minute. After the binder is placed in the set-up, it is allowed to heat up for half an hour without rotating or adding air. After that, the rotations and air flow are started and they continue for 235 plus or minus 5 minutes (circa 4 hours).

#### 4.2.3.2 Long term aging

In long term aging, the test is performed at 90°C. If the specimen was short-term aged using the RCAT, both the oven and the specimen (cylinder containing specimen is kept outside the oven) are allowed to cool down to the lower test temperature. Once the oven reaches the lower test temperature, this is maintained and the specimen is placed inside. It is left without rotations and airflow for half an hour.

If the specimen has had another kind of short-term aging, it is left in the pre-heated oven for one hour without rotating and airflow.

After this starting period, the sample is rotated at 1 round per minute and subjected to an oxygen flow of 4,5 litre per minute for 140 hours, plus or minus 15 minutes. During testing, usually at 17 and 65 hours, samples can be taken.

#### 4.2.3.3 Aging of mastic

The RCAT can also be used to age mastic (defined as bitumen plus filler), added in the same ratio as used in the mixture. The amounts are determined in such a way that there is a total of 550 ml of mastic in the flask. For this test, the test cylinder, roller and the filler are pre-heated to 150°C. The filler is placed into the cylinder and after homogenization the bitumen is added to it, the roller is placed in the cylinder and the whole system is put back in the oven. After the over temperature has stabilized, typically this takes 5 to 10 minutes, the rotation is started (1 round per minute), this is continued for 30 minutes. At the end of that period, samples are taken for mastic identification.
After this, either the procedure for short term aging (after heating the cylinder plus content to 170°C) or that for long term aging (after allowing the cylinder plus content to cool to 90°C) is performed.

## *4.3 Asphalt concrete*

### 4.3.1 USA

In the SHRP A383 [17] report a short and long term aging procedures were tested on specimens and mixes with two different types of bitumen, two types of stone and two void percentages (4 and 8%, respectively). They tested extended mixing and short-term oven aging for loose mixtures and long-term oven aging, pressure oxidation aging and a low-pressure oxidation test in a triaxial cell for compacted specimens. They assessed the effect of aging by testing the modulus and determining the indirect tensile strength and peak strain. Since modulus testing is non-destructive, they tested the modulus on the same compacted specimen at various steps of aging, for the loose mixture and the destructive tests this is of course impossible so here also the variation between specimens plays a role. From the data, it seems that in most cases the stiffness and strength increase with aging while the strain at break decreases, which would be consistent with the expected increased brittleness due to aging. The study also refers to field validation tests, but the results are not included in the report.

In the study it is recommended to include a maximum exposure time in the short-term oven test for loose mixtures and to adopt an equiviscosity temperature for compaction of the aged mixture to prevent compaction effects from influencing the specimen properties. For specimen aging they recommend limiting the temperature in oven aging to 85°C (185°F). For the pressure oxidation tests, both with air and oxygen, they not a decrease instead of an increase in stiffness. This is attributed damage to the sample, which they call disruption due to the relieve of the gas pressure. As a result, they recommend low pressure or confined systems for aging cores. Their suggestions for aging of AC are:

- for short-term aging: oven-aging of loose mixtures at 135°C (275°F) for 4 hours
- for long term aging:
    - dense mixtures: oven-aging of specimens at 85°C (185°F) for five days
    - open graded mixes or mixes with soft binders: low-pressure oxidation (triaxial cell) technique at 85°C (185°F) for five days

In the MEPDG [18] ,which was published ten years later, the above procedures were not adopted. Instead, the effect of aging on the bitumen properties is determined using bitumen aging tests and this is related to the effect on the stiffness of the mixture through regression relations that take the mix composition into account (Figure 2).

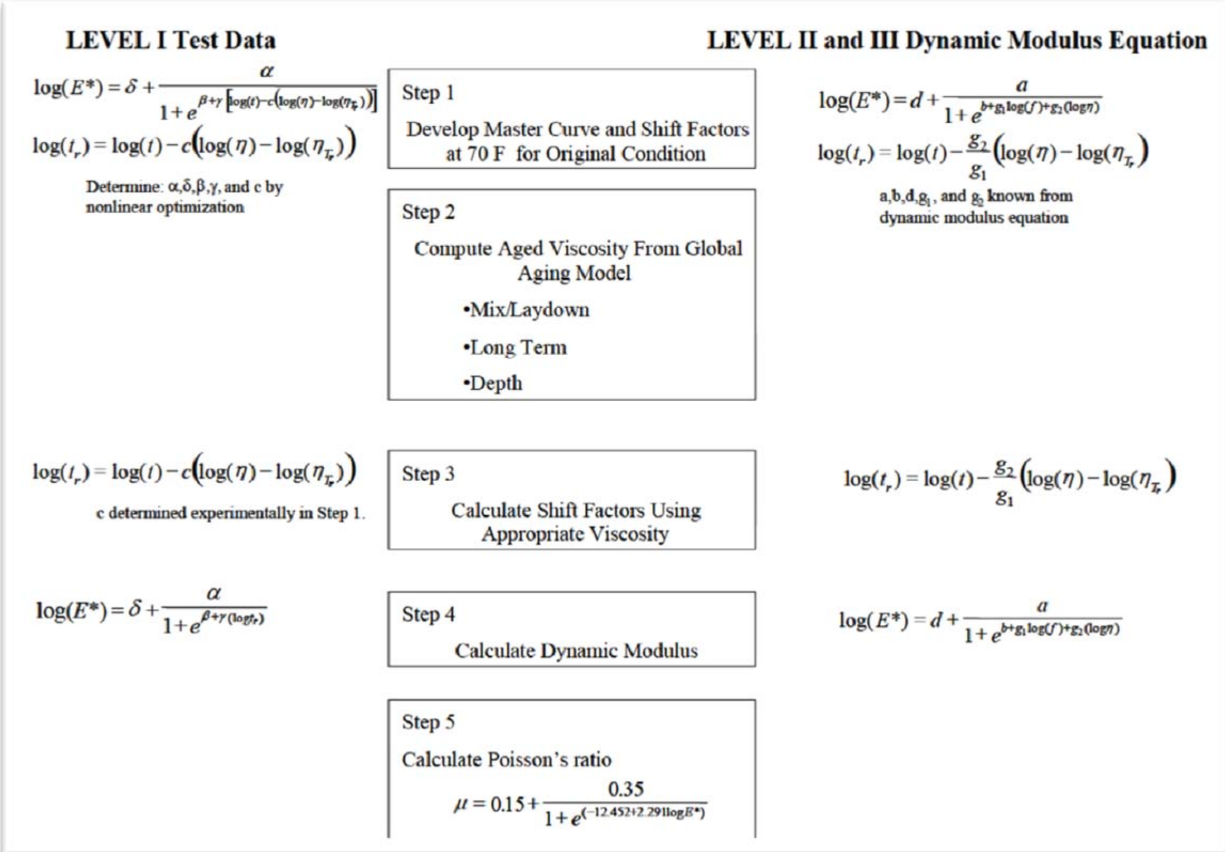



**Figure 2: Aging of AC properties in the MEPDG works through regression based on bitumen aging (copy of fig 2.2.3 NCHRP 1-37A, Guide for Mechanical Empirical Design of New and Rehabilitated Pavement Structures, Final Report, Part 2- Design Inputs, Chapter 2 – Material Characterization, March 2004)**

### 4.3.2 Europe

Although the current standards for Asphalt Concrete do not require either aging of the asphalt concrete itself, the CEN standards do provide tests for aging of AC. For example, CEN TC 227 is currently working on a draft standard which allows the assessment of the effect of oxidative aging of asphalt mixtures (prEN 12697-52:2014, [19]). This standard aims to provide methods for laboratory aging of both lose (pre-compaction) asphalt concrete and AC cores, either produced in in the laboratory or obtained from the field. The aged material can be used to make specimens and assess the effect of aging on the mixture properties or binder can be extracted from the aged AC to assess the effect of aging in the presence of filler and aggregates on binder properties.

When simulating short-term aging on the loose mixture, it is applied in a layer of 25±5mm, the temperature and conditioning time are not specified, but left to the individual member states to decide. However, it is advised not to take a conditioning temperature higher than the ring and ball temperature of the RTFOT aged binder, to prevent excessive draining of bitumen. It is noted that this temperature is on the safe side (i.e. low) and as an alternative determination of the softening point ring and ball on a homogeneous mastic of RTFOT-aged binder and filler (ratio of binder to filler according to the actual mix design) is mentioned. Also, there is a note referring to the SHRP-A-383 report and the conditions in it (135$^{o}$C for 4 hours). Obviously, there is a considerable difference between these suggested temperatures, which will lead to a lot of variation in testing and in results. With the large difference in suggested temperatures it may even lead to different mechanisms being tested.

The long term aging method for a loose AC mixture also only specifies the thickness in which to apply the mix and it includes the same note on choosing a test temperature that prevents excessive drainage, while at the same time other notes mention previous work by BRRC, RILEM and the university of Brunswig, using a PAV. They all use a similar approach but different temperatures and conditioning times. The BRRC ageing method sets a conditioning temperature of 60 C for 336 hours, the RILEM ageing method uses 85 C for 216 hours [20] and the Brunswig Ageing (BSA) method stores the specimens at 80 C for 96 hours and uses a pan with a perforated plate for improved airflow. The text for the concept standard also includes a note which states that PAV at 90$^{o}$C and 2,1 MPa for 20 hours gives comparable results to this RILEM protocol.

For aging of AC cores there are two approaches foreseen, one uses only temperature conditioning in an oven and is similar to the approach used by SHRP/AASHTO (which specifies a conditioning temperature of 85 C for 120 hours), the other involves forced flow with a gaseous oxidant. Although these aging procedures are based on research in one or more EU countries, the experience with them is still limited and the tests are not yet part of the CEN standards for asphalt concrete.

Besides this standard under development, there is also a test standard for hot mix asphalt saturation aging (SATS **Error! Reference source not found.**). This standard aims to assess the durability of adhesion in base and binder courses by aging specimens in the presence of water. The test is currently limited to mixtures with a binder content between 3,5 and 5,5% of 10/20 hard paving grade binder and air voids between 6% and 10%. In this tests five AC cores are first partially saturated (≤80%) by putting them in a vacuum desiccator covered with distilled water for half an hour at a pressure of 40-70 kPa. After this, the specimens are placed on different levels in the SATS set-up. The set-up is partially filled with water, causing one specimen to be under water and the other four at various heights above the water level. The specimens are left in the set-up at a pressure of 2,1 MPa and a temperature of 85$^{o}$C for 65 hours. The dynamic stiffness (using the indirect tension test, EN12697-26 Annex C) is determined before and after conditioning and the average of the stiffness ratios of the four specimens that were placed above water level are used to obtain the mixture stiffness ratio. Currently, this test is used in the United Kingdom. Experience with this test in other countries is very limited.

## 4.4 Literature

[1] AASHTO T 240-13, *Standard Method of Test for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test),*(ASTM Designation: D 2872-04, standard by American Association of State and Highway Transportation Officials, 2013

[2] ASTM D2872 - 12e1, “Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test)”, Developed by Subcommittee: D04.46, Book of Standards Volume: 04.03, 2012

[3] EN 12607-1, *Bitumen and bituminous binders — Determination of the resistance to hardening under the influence of heat and air — Part 1: RTFOT metho*d, CEN standard, November 2014

[4] Asphalt Institute, the, “*Performance graded asphalt binder specification and testing, Superpave series No.1 (SP-1)*”

[5] Nichols, C. et al, “*BitVal - Analysis of Available Data for Validation of Bitumen Tests*”, FEHRL report on phase 1 of the BitVAL project, download from http://bitval.fehrl.org/

[6] Parmeggiani, G., “Nitrogen Rolling Thin Film Oven Test”, 2nd Eurasphalt & Eurbitume Congres, Barcelona, 2000

[7] AASHTO T 315-12, *Standard Method of Test for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)*, standard by American Association of State and Highway Transportation Officials, 2012

[8] AASHTO M 320-10, Standard Specification for Performance-Graded Asphalt Binder, standard by American Association of State and Highway Transportation Officials, 2010

[9] EN 12607-2*, Bitumen and bituminous binders — Determination of the resistance to hardening under the influence of heat and air — Part 2: TFOT method*, CEN standard, November 2014

[10] Besamusca, J., Sörensen , A. and Southwell, Ch., “*Adressing Ageing Characteristics of Bituminous Binders in Europe*” , 5th Eurasphalt & Eurobitume Congress, 13-15th June 2012, Istanbul, Turkey

[11] AASHTO R 28-12, *Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)*, standard by American Association of State and Highway Transportation Officials, 2012

[12]EN 14769, *Bitumen and bituminous binders – Accelerated long-term ageing conditioning by a Pressure Ageing Vessel (PAV)*, CEN standard, April 2012

[13] Choquet, F., and Verhasselt, A., “Ageing of bitumen: from the road to the laboratory and vice *versa”*, Proceedings of the Conference on the SHRP and Traffic Safety on two continents, The Hague, Netherlands, Sep 22-24, 1993

[14] Michael J. Farrar, P. Michael Harnsberger, Kenneth P. Thomas and William Wiser*, “Evaluation of oxidation in asphalt pavement test sections after four years in service”,* International Conference on Perpetual Pavement, Ohio University, Columbus, Ohio, September 13–15, 2006

[15] Besamusca, J., Volkers, A., Water, J. vd.and Gaarkeuken, B.” simulating ageing of en 12591 70-100 bitumen at lab cond comp tot PA -5th Eurasphalt & Eurobitume Congress 13-15th June 2012 Istanbul

[16] EN 15323, *Bitumen and bituminous binders – Accelerated long-term ageing conditioning by the Rotating Cylinder Method (RCAT)*, CEN standard, april 2007

[17] Bell, C. A., AbWahab, Y. , Cristi, M. E. and Sosnovske, D., "*Selection of Laboratory Aging Procedures for Asphalt-Aggregate Mixtures*", Oregon State University, Strategic Highway Research Program report SHRP-A-383, National Research Council, Washington, DC 1994

[18] *Guide for Mechanical-Empirical Design of new and rehabilitated pavement structures, Final Report, Part 2 Design Inputs, Chapter 2 Material Characterization*, National Cooperative Highway Research Program, Transportation Research Board, National Research Council, March 2004

[19] prEN 12697-52:2014, "*Bituminous mixtures – Test Methods- Part 52: Conditioning to address oxidative aging*", concept standard CEN TC227 WG1, may 2014

[20] Manfred N. Partl, Hussain U. Bahia, Francesco Canestrari, Chantal de la Roche, Herve' Di Benedetto, Herald Piber, Dariusz Sybilski Rilem State of the Art Advances in Interlaboratory Testing and Evaluation of Bituminous Materials, Chapter 7: Hot Recycling of Bituminous Mixtures, RILEM, Springer Dordrecht Heidelberg New York London, ISBN 978-94-007-5103-3, 2013

[21] EN12697-45, *"Bituminous mixtures – Test Methods for hot mix asphalt – Part 45: Saturation Ageing Tensile Stiffness (SATS) conditioning test"*, CEN standard, April 2012

# 5 Organisation of the symposium

## *5.1 Participants in the symposium*

| Name | Affiliation | role |
|---|---|---|
| Stavros Avgerinopoulos | De Montfort University | participant |
| Ronald Blab | TU Vienna | Speaker |
| Irina Cotiuga | Latexfalt | participant |
| Sandra Erkens | TU Delft/Rijkswaterstaat | Organizer/Chair |
| Ron Glaser | Western Research Institute | Speaker |
| Charles Glover | Texas A&M university | Speaker |
| Jaap van de Heide | Rijkswaterstaat | participant |
| Maarten Jacobs | BAM | Invited, unable to participate |
| Kim Jenkins | Stellenbosch University | participant |
| Diederik van Lent | TNO | Participant |
| Xueyan Liu | TU Delft | Participant |
| Bert-Jan Lommers | Latexfalt | Participant |
| Andre Molenaar | TU Delft | Participant |
| Steven Mookhoek | TNO | Participant |
| Sayeda Nahar | TU Delft | Participant |
| Marcus Oeser | TU Aachen | Speaker |
| Laurent Porot | Arizona Chemical | Speaker |
| Harry Roos | VBW | Invited, unable to participate |
| Tom Scarpas | TU Delft | Organizer/Chair |
| Alex Schmets | TU Delft | Participant |
| Hilde Soenen | Nynas | Speaker |
| Katerina Varveri | TU Delft | Participant |
| Martin vd Ven | TU Delft | Participant |

## 5.2 Symposium Program

| | | |
|---|---|---|
| **Tuesday 16/09/2014** | | |
| **Arrival of international participants** | | |
| **Wednesday 17/09/2014** | | |
| **09:30 – 10:00** | **Opening** | |
| 09:30 – 09:45 | Tom Scarpas | Welcome |
| 09:45 - 10:00 | Sandra Erkens | Setting the stage: Are current aging protocols capable of addressing field aging ? |
| **10:00 – 12:15** | **Session 1:** | |
| 10:00 - 10:45 | Charles Glover | Field Aging of Bituminous Materials and the Challenge of Laboratory Simulation |
| 10:45 – 11:30 | Ron Glaser | Advances in asphalt binder oxidation understanding with practical implications: Chemical and rheological behavior. |
| 11:30 – 12:15 | Hilde Soenen | What happens during aging and where is aging happening? |
| **12:15 – 13:00** | **Lunch** | |
| **13:00 – 15:15** | **Session 2:** | |
| 13:00 – 13:45 | Ronald Blab | How to understand field aging of bitumen - recent experimental and modeling efforts |
| 13:45 – 14:30 | Laurent Porot | Viscous to Elastic Transition: a way to qualify aging |
| 14:30 - 15:15 | Markus Oeser | Preventing Asphalt Binder Oxidation Using MMT-Nano-Particles |
| **15:15 – 15:45** | **Coffee Break** | |
| **15:45 – 16:30** | **Session 3:** | |
| 15:45 – 16:30 | Sandra Erkens | Discussion & drafting of conclusions and recommendations |
| 16:30 - | Tom Scarpas | Closure |
| **19:00 -** | **Dinner** | |

# 6 Symposium summary

The aim of this symposium is to combine as much of the existing knowledge and experience about asphalt concrete aging as possible, to provide an overview as well as a sound basis for current day decisions about sufficiently reliable aging tests as well as future research to further our understanding of the mechanisms involved. For that reason, the speakers that were invited cover the whole range, from binder to asphalt concrete aging, from chemical to mechanical properties, form laboratory to field experience and from models to collected data.

In this Chapter the contributions from the various speakers as well as the discussions that took place after their presentations are summarized. The slides they used can be found in Chapter 8, while the overall summary and conclusions are given in Chapter 7.

## *6.1 Charles Glover: Field aging of bituminous materials and the Challenge of Laboratory Simulation*

### 6.1.1 Summary of presentation

Charles Glover considers aging a result from oxidation, over considerable depth. Oxidation causes binder embrittlement, changes rheology and fatigue resistance. He shows measurements and predictions of pavement temperatures at various levels, their model predicts temperatures very well. They use those temperature predictions as input for their kinetic oxidation model, which expresses oxygen absorption or viscosity as a function of aging time. The aging rate depends on temperature, he has data showing this effect and the relation between prediction and measurement.

Glover-Rowe parameter, G’/(n”/G’) @15 $^{o}$C and 0.005 rad/s is related to the ductility at 15$^{o}$C and 1 cm/minute, is based on the Maxwell model. As such it doesn’t work for very ductile materials, but it does for more aged materials.
Charles is convinced that porosity doesn’t play an important role, because there is plenty of oxygen present and it is replenished due to daily temperature changes. The relatively high aging rates in porous AC in the Netherlands would in that case be the result of relatively thin mastic layers, not the porosity in itself.

They use a pressure oxidation vessel, 3 month procedure. It can be used on the original binder to assess binder aging sensitivity, the effect on the binder rheology can be measured and the effect and rate of aging for that binder in the field can be predicted. The effect on AC properties is NOT in this method.

He shows a graph about POV and PAV aging versus field aging, quite a bit of difference but there are relations. The crucial step is relating the activation energy in the high pressure PAV to 1atm, which it is for field conditions. The advantage is that the PAV tests takes only a week. The parameter they use for aging is carbonyl content.

He indicates that the main challenge in taking aging into account involves finding a fast, practical aging test to determine a mixtures aging sensitivity. The actual aging will be location dependent, you could combine the local information with the measured sensitivity to determine suitability.

### 6.1.2 Discussion

*Ron Glaser:* PAV combined with RTFOT supposedly represents the real aging, but does it? In the data it looks relatively fresh. Is it severe enough?
Re: YES, especially for high temperatures such as in Texas RTFOT plus PAV underestimates the field aging, this is less of an issue for the Netherlands.
*Irina Cotiuga:* LATEXFALT research showed huge differences between laboratory and field aging
*Ron Glaser:* There are indications that the degree of oxidation for "short term aging" is not kinetically limited, but reactant limited and mostly happens because of the air in the loose mix voids. This air is rapidly consumed and this explains why warm mix resistance to rutting is generally not different from that of hot mix. Most of the oxidation occurs after leaving the drum, and its extent is limited by available air in the loose mix prior to compaction.

*Andre Molenaar*: Your approach is mostly focussed on oxygen, not on the effect of fines and such, did you look at that?
Re: a little works was done into filler effects on diffusivity, and this seems to match the theory. But there is not much data on this and no data at all about whether and is so how, coarser aggregates effect aging.

*Sandra Erkens*: You say porosity doesn't play a role if it is higher, yet we found that the aging of PA in the Netherlands is much more than your model would predict, how would you explain that?
Re: This t could be related to the thinner binder films, which would decrease the diffusion distance.
*Martin van de Ven*: That is partially in line with the results from asphalt on dikes, which after 30, 40 years still have penetration values of about 30, starting from pen 70/100. Those mixture have a high binder content (above 6%), but also a low porosity (around 4%). The low speed of aging is generally contributed to both these factors.

Irina Cotiuga: Did you try tests with thicker films in the PAV, to see if aging rate decreases.
Re: no, we used 3mm films in all tests, but we did vary specimen size.

## 6.2 *Ron Glaser: advances in asphalt binder oxidation understanding with practical implications: chemical and rheological behaviour*

### 6.2.1 Summary

Ron Glaser shows aged bitumen over specimen height for naturally aged ALF (the FHWA Turner Fairbanks accelerated loading facility) cores, they show a considerable variety over the height, with most of the aging at the top. The effect on the rheology is also considerable. Ron stresses the importance of gradients, temperature gradients are largest at the surface which means faster reaction rates. The temperature gradients over the pavement thickness leads to an aging and therefore a stiffness gradient. These ideas were developed based on observations of numerous field cores.

There is a need for field validation of laboratory studies and models, because in forensic studies, especially without the original materials, a lot remains unsure.

They studied chemical oxidation kinetics on 34 binders, using 50 micro meter film thickness at various temperatures. They combine a slow & fast reaction in their model, the generic form of the model is given in his slides. Their Arrhenius equation resulted in quite similar activation energies, which might indicate that the temperature characterisation is not necessary. Also, they found that this relation also works for PMB. He stresses that per binder you need only two oxidation points, four if you use pressure aging, to characterise a binder with respect to his model.

A plot of the change ins S=O + C=O versus Dlog10(Gc) shows linear relations per source (FTIR).
Ron explains that you can get your material's reaction rate from the intercept of the linear slope of the long term curve. But how do you quickly get those curves? One way is Pressurized Differential Scanning Calorimetry (PDSC).
Unfortunately, the aging mechanism appears to be more complex at higher temperatures and pressures. They now have a model that fits preliminary results through the range of temperatures and pressures. It looks like at higher T's sequential reactions take place. Their model includes different radicals, a small, active one (hydroxide i.e.), the other two are larger and not mobile at ambient temperatures.

### 6.2.2 Discussion

*Hilde Soenen*: how do you characterise naphthenic aromatics versus the others?
Re: Actually, we use SARA in our early data, now we use the more complete SAR-AD. Naphthenic aromatics decrease with oxidation and correlate to kinetically determined reactive material and master curve cross over parameter changes

*Sandra Erkens*: You mentioned the fact that PAV and RTFOT is not severe enough as a question to Charles after his presentation, do you have a solution?
Re: The PDSC method allows aging comparative up to 150 year old pavements (binder no longer solvable), it also has the advantage that it doesn't give you points, but a continuous curve. Longer PAV testing would also work and this wouldn't require new equipment. Whichever test you use, to moving toward predicting pavement performance, in my opinion, can only be done with oxidation kinetics characterization of the pavement bitumen. When you combine them with permeation and diffusion considerations to compute the oxygen gradients and thermal gradients and march those through time to get properties gradient which can be evaluated by FEM, you can get there.

*Kim Jenkins*: Did you do any work on chip seals, the aging there is quite severe?
Re: the seal is so thin that the diffusion path is very small and the UV becomes also important.
Irina Cotiuga*:* but the binder in seals is often not straight run.
*Kim Jenkins*: Quite often it is.
*Martin van de Ven*: the thickness is large compared to films in AC, but there is no filler, so less blockage of diffusion.

## *6.3 Hilde Soenen, what happens during aging and where is aging happening?*

### 6.3.1 Summary

The presentation consist of three parts, the first focusses on laboratory aging with RTFOT+PAV, the second on field aging using recovered binders and the third on field aging of binder films.

Hilde discusses the rheological and chemical changes they found after these tests and she raises the question how important the aging temperature is. Nynas looked into various types of binders, to see if there was a difference in aging properties.
Hilde indicates that the aging index (defined as the ratio of original versus aged stiffness) is temperature and frequency dependent, with a more pronounced effect on the lower stiffnesss

values (the lower frequency/higher temperature range), as well as source dependent (i.e with respect to the. initial hardness).

They included visbroken binders in their research and they found these binders exhibit more sensitivity to fast aging. Also, due to RFOT and PAV aging the visbroken binders get a totally different fatigue slope (in DSR) while for straight run binders the fatigue lines shifts, but retain their slope.

They also looked into the effect of temperature on aging and aging products, comparing a straight distilled binder with an oxidized binder, binder aged using PAV and binder that is dark aged at room temperature:

- Room temperature aging only showed an increase in alcohols, no rheological change or change in molecular weight was found.
- PAV @ 60 and 100'C: showed an increase in carbonyl groups, poly aromatics and alcohols or sulfoxide as well as an increase in molecular weight and more structure in rheology.
- Oxidized bitumen: more poly aromatics, an increase in molecular weight and more structure in rheology

Furthermore, they looked into field aging in very old pavements *(Long Lasting Asphalt Pavements and Bitumen Ageing*, Xiaohu Lu , Per Redelius , Hilde Soenen , Mikael Thau, E&E conference 2012 and *Durability of Polymer Modified Binders in Asphalt Pavements*, Xiaohu Lu, Hilde Soenen, Serge Heyrman, Per Redelius, ISAP conference 2014) and there appears to be a clear relation between the air voids in the mixture and the reduction in penetration. This gives a clear indication that the mix composition affects aging and that binder aging alone is not sufficient to assess AC aging sensitivity. Comparing the effect on penetration and DSR stiffness (@10$^{o}$C) with those of RTFOT and/or RTFOT&PAV aged samples indicated that RTFOT+PAV is representative for AC mixes with low void percentages, but it underestimates aging of more open mixtures.

Finally, they did tests with binder films exposed to climatic conditions, which resulted in much more change than RTFOT+PAV. Even in the lab, exposed to sunlight, but no other weather effect, the changes were considerable. The effect appeared to be about 120 micro meter deep.

They find that RTFOT+PAV are suited for dense materials (2-4% voids), assessing aging sensitivity in open pavements may need a longer laboratory aging time.
They suggest testing specimens that are aged as specimens to get information on which properties deteriorate first due to aging.

### 6.3.2 Discussion

Andre Molenaar: we tried to age PA samples, but they fell apart in the process. Yet, suppose I select an aging procedure that copies all the effects on the rheology, wouldn't that be enough? We did this for a PA mix and it corresponded with the FTIR and DSR of a 10 year old specimen from the road.
Re: Was it repeatable, or just fitting the aging to that specific core?

## *6.4 Ronald Blab: How to understand field aging of bitumen – recent experimental and modelling efforts*

### 6.4.1 Summary

Ronald Blab presents the TU Vienna approach to understanding aging. It is based on the SARA-fractions, separating these fractions even further. They used Confocal Laser Scanning Microscopy, Atomic Force Microscopy, and Environmental Scanning Electron Microscopy to "look into" the bitumen. They consider the binder to consist of micelles in a matrix, which they link to the bees-matrix structure shown in AFM analyses of bitumen. TU Vienna used the fractioned components to create artificial bitumens, with known composition. They showed that there are no bees in the AFM if there are no asphaltenes in the binder, and with increasing asphaltene content, the number of bees increases.

For aging they distinguish three types of aging agents:

- UV and dust (surface active)
- $NO_2$, $O_2$, $OH^-$ radical (reactive gasses, active in the top part of pavement)
- water soluble reactants (HNO, $H_2SO_x$, $H_2O$), active over the full pavement depth

They consider the matrix to be the part of the binder that is oxidized and they combine it with a recovering mechanism that is based on the reorganisation of the polar products, moving towards the asphaltenes, creating a highly polar micelle centre.

They work on a multi-scale model, based on mathematical formulations that allow them to upscale elastic and visco-elastic properties. They aged the components of their binder and added them, adding the same amount of asphaltenes, aged or not, resulted in the same response (stiffness), more asphaltenes gave stiffening/aging: therefore they conclude that aging is an increase in asphaltene content.

From field test they found that binder and base layers have the same rheological properties, very close to the properties directly after construction. Longterm aging appears to be restricted to the surface course.

In their experience, RTFOT matches well, chemically and rheologically, to short term aged material, RTFOT and PAV match rheologically, but not chemically to pavement conditions and it leads to SBS degradation.

They developed an alternative aging test, using corrosive gasses in a triaxial set-up. In the ITT you do see a stiffening effect, as well as in the DSR binder test. The test is performed at 60 $^{o}$C and takes 4 days. Samples tested compare rheologically to RTFOT and PAV.

## 6.5 Laurent Porot, Viscous to elastic transition: a way to qualify aging

### 6.5.1 Summary

Laurent Porot states that with aging both the chemical composition and the properties change. In his presentation he discusses work they did to relate hardening of bitumen to changes in chemical structure that can be recorded through FTIR. For this, they looked at the cross over modulus (phase angle of 45 degrees), which can be seen as the transition of predominantly viscous to elastic response or vice versa.

In their study, Arizona Chemical looked at various bitumen grades, sources and aging levels as well as bitumen recovered from pavements. They tested them for penetration and ring and ball temperature, composition with FTIR and mechanical response using DSR.
They carried out their aging via PAV tests, repeating PAV aging cycles and sampling the bitumen between cycles for analyses. They found that PAV aging of the bitumen at 100$^{o}$C for 40 hours gave a similar pen to RAP ( pen 15-20 [x0,1mm]). In their FTIR analyses they determined the area of the S=O and C=O over the C-H areas. In the DSR test they did a temperature sweep at a fixed frequency of 10 rad/s and looked at the cross-over properties (G* and T).

Plotting penetration versus softening point, like in the plot for the various binder grades, Laurent shows that all their results fall on more or less the same line, the binders from different sources, the different grades, the binders aged in consecutive PAV cycles and bitumen from RAP. The fact that the RAP binders fall around the line of the five PAV cycles indicates that these five cycles span field aging. However, it is not robust enough.Although there is a relation between the number of cycles and the age of the RAP it appears that the original composition of the bitumen also plays a role.

In the study, they looked into the Penetration Index as an aging indicator, but although PI increases with increased aging (more PAV cycles), when it is plotted against the ICO (area under the C=O peak in FTIR) the trend is not consistent.

They compared the C-H peak (area) for different binder grades from the same source and for binders of the same grade, but different sources. They found it was more or less constant. Similarly, they found that the cross-over temperature and G* are more or less constant for a given binder grade, even if the sources differ. For different grades of the same source, the cross-over temperature shifts while the stiffness remains around $10^7$ Pa.
The ICO peak area increased consistently over the PAV cycles, ISO did not. Actually, ISO increased over the first few cycles and then it decreased and stayed more or less constant. When looking at ICO and ISO peak area values, the field samples mostly fell between 1 and 3 PAV cycles. The cross-over temperature increases with increasing PAV cycles, and G* decreases. The change in cross-over temperature is an indication of hardness and the change in cross-over modulus of temperature susceptibility. Thus, when the material ages it both hardens and becomes less temperature susceptible, resulting in a more elastic behavior at a wider temperature range

From their testing program they suggest plotting the cross-over modulus versus ICO, indicating that bitumen with ICO less than 0,05 and G* of $1x10^7$ Pa or more are non-aged, ICO between 0,02-0,12 and G8 between $3x10^6$ and $1x10^7$ Pa is aged and bitumen with ICO> 0,05 and G* less than $3x10^6$ is overaged. This could be used to assess RAP suitability of re-using in AC mixtures.

### 6.5.2 Discussion

*Ron Glaser*: This approach is useful for assessing RAP quality or monitoring pavements for remedial action. I prefer using cross-over, it is much simpler.
*Sandra Erkens*: but sometimes we see that the rheology matches, but chemistry doesn’t, and that worries me.
*Charles Glover*: what matters is not so much the rheological state at failure, but how long it takes a material to get there.
*Ron Glaser*: adding fresh binders is mostly physical blending, rheology is the important parameter for that.

## *6.6 Marcus Oeser: Prevention of Asphalt Binder Oxidation using MMT-Particles*

### 6.6.1 Summary

At TU Aachen they used montmorillonite (clay) nano particles to modify bitumen. In penetration binders this causes an increase in penetration and a decrease in $T_{r\&b}$ (“aging” like changes), with increasing mixing time (i.e. 2-150! minutes). With PMB this does not happen. For mixing times up to 30 minutes the effect is small.
The idea is that the MMT particles, which are plate like in shape, can act as “screens” or radiation/diffusions retarders in the mastic.

For 10% MMT the reduction of aging in RTFOT+PAV is more than the increase due to the MMT.
The effect on adhesion, AC properties and binder chemistry still needs to be addressed.

### 6.6.2 discussion

*Charles Glover*: did you measure oxidation directly?
Re: no only, indirectly through rheology.

*Ronald Blab*: how does the ozon aging effect the chemistry?
Re: according to the chemists involved, it is closer to the field values than those from PAV aging.

*Kim Jenkins*: were the models you developed for a specific tests and how would they respond to a different type of test?
Re: the creep recovery tests were used for fitting the model.

*Martin van de Ven*: is the thickness and i.e. void content specified in the ozon aging test?
Re: not, it is just a prototype.

# 7 Conclusions, discussion and advice

## 7.1 Summary and conclusions

In the general discussion at the end of the symposium, the following topics were addressed:

### 7.1.1 RTFOT for short-term (production and construction) aging?

The participants agree that RTFOT tests provides a good indicator of bitumen aging sensitivity for binders used in HMA. For different types of production, other tests or test conditions may be needed.

However, the test does not give a prediction of field aging, because that strongly depends on mix composition and production effects (i.e. temperature). When using two different bitumens in exactly the same mix and using exactly the same production conditions, the bitumen that showed the most aging in the RTFOT will age most during actual production and construction, it is a sensitivity indicator and its relevance in relation to other factors like the type of filler are not well established.

### 7.1.2 PAV for binders?

PAV aging also doesn't provide an indication of binder field aging. In this case that is more serious, since the test is supposed to do just that. Many field results shown in this symposium (and in literature) show more aging than we get from PAV. Although true prediction of field aging is unlikely, for the same reasons as with RTFOT, capturing the right phenomenon is crucial.

Some participants indicate that in order to get a quick test ,we increased the temperature and pressure too much. As a result, we are not covering the actual phenomenon that occurs in the field, or at least not sufficiently. This suggestion has been made before, for example SHRP advices to use a temperature between 90-110 $^{o}$C to compensate for PG grade, it is worthwhile considering such a recommendation for the temperature in the CEN test.

A useful alternative approach to trying to get a single test that represents all variables in practice seems to be using the test to capture the aging sensitivity of the bitumen. This would require doing the test at two temperatures and two time intervals per temperature (i.e. four tests to characterize a bitumen) in order to be able to determine kinetic information. This information could then be used in models that take into account mix composition and local climate conditions in predicting pavement aging.
Based on the current standards and the work presented during the symposium, PAV tests at 90 and 100 degrees Celsius and 20 and 40 hours, respectively, are suggested. The low values for temperature and duration are based on the current standards and fit both the USA and CEN procedure, while research shows that after 40 hours at 100 degrees the chemical (FTIR) and rheological (DSR) properties of laboratory aged and field samples were similar (Section 6.5 and 8.5). At 100$^{o}$C the temperature is low enough so that the effect of secondary reactions is negligible. As such, these conditions are appropriate for kinetic expressions for in service pavement performance. For high temperature processes and possibly also for repeated recycling (very long term) more sophisticated methods are needed.

### 7.1.3 Aging for AC?

There is general agreement that aging for AC is important, especially for (low temperature) cracking, ravelling and fatigue resistance. Comparing fresh AC mixtures will not give a reliable indication of the field performance for those properties. Also, even if both short and long term aging sensitivity of the binder is known, the aging sensitivity of the AC depends also on many other variables such as:

the mix composition (more voids and/or thinner binder films result in more aging under the same conditions and also the composition of the aggregate, or at least the filler, appears to have an effect) and climatic conditions ( higher temperatures add to aging, so does UV light, at least on the surface and also water and/or moisture seems to have an effect).

However, if there is not yet a single test that can predict field aging of binders, it will be very difficult to come up with a test that will manage this for AC. So how do we relate the AC properties of fresh material to those of the aged material? Even if we could relate changes in chemistry/oxidation and rheology to their effect on the mixture properties, we would also have to know how the climatic conditions would affect the chemical changes. For AC a two step approach seems necessary, determine the mixture sensitivity to aging, for example through 4 PAV tests on the mixture or, as mentioned in Section 7.1.2, on bitumen to determine the kinetic information. This could then be the end result, an indication of the aging sensitivity, or it could be used in a model that describes chemical changes due to aging as a function of the climatic conditions and mix micro structure (porosity, film thickness) to predict the aging of a given mix in a specific climate (Figure 3).

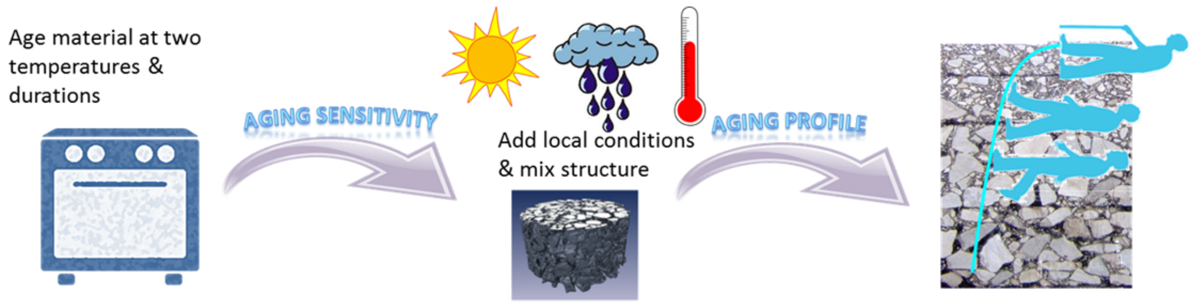



**Figure 3: Two step approach to determining the aging of Asphalt Concrete**

This would still require also assessing the effect of several levels of aging on the mechanical properties, but it would provide a robust system that also allows the assessment of aging of new materials In the laboratory uniformly aged specimens (or specimens made from aged material) can be tested and those properties can be used to ascribe properties to the material at various aging levels. Linking those properties to the ageing profile will eventually allow the analysis of pavements in time.

A simpler alternative, at least for the short term, could be the approach used in the MEPDG in the US, where standardised aging protocols are used to age specimens and there are requirements for the fresh as well as the aged material. In a given climate region, pavements that are near failure could be sampled to assess what the requirements for that type of mix in that climate zone should be.

### 7.1.4 General issues

There is no standard for Infra-Red measurements, which would be useful in case of standardisation of aging. It would at least ensure that the chemical composition information that is obtained can be compared between labs and countries.

The increase OH-groups/alcohol in bitumen over time is not covered by any of the current tests, this is something to keep in mind.

## *7.2 Recommendations*

- Do make long term aging sensitivity of binders part of the bitumen standards and take the results from the aging sensitivity of binders into consideration when assessing AC properties.

Be aware that RTFOT testing only gives an indication of the sensitivity of a penetration grade binder to aging during hot mix production and construction, it doesn't work for hard grades, PMB's or warm mixes.

- Because of the many variables involved, developing one test method to characterise aging sensitivity seems improbable. However, PAV aging is both practical and, if tests at various conditions are carried out, able to give kinematic properties. A PAV protocol for testing at two temperatures and time intervals could provide practical characterisation information for the short term and enable model development and validation on the long term. RCAT and other aging procedures could also be used in this sense, but considering the availability of equipment and the wide spread experience, PAV is the best candidate to allow the rapid development of international experience with the approach.
  Based on the current standards and the work presented during the symposium, PAV tests at 90 and 100 degrees Celsius and 20 and 40 hours, respectively, are suggested. The low values for temperature and duration are based on the current standards and fit both the USA and CEN procedure, while research shows that after 40 hours at 100 degrees the chemical (FTIR) and rheological (DSR) properties of laboratory aged and field samples were similar (Section 6.5 and 8.5). At 100°C the temperature is low enough so that the effect of secondary reactions is negligible. As such, these conditions are appropriate for kinetic expressions for in service pavement performance. For high temperature processes and possibly also for repeated recycling (very long term) more sophisticated methods are needed.

- Set-up and maintain field monitoring of temperature and UV radiation in various climate zones, as well as regular sampling over time and height to keep checking the predicted changes (from both tests and models), versus the actual changes in properties order to ensure reliability of the data as well as the applicability for pavement performance prediction. In setting up field tests, it is important to get both the composition of the virgin bitumen and the composition after mixing, transport and placement in the pavement. These compositions provide the starting points from both the material and pavement structure point of view and can be used to assess the development of aging products over time. There is a lot of discussion about the impact of binder recovery methods on the observed composition, so until it is proven that this does not have an influence, for comparisons the same recovery method should be used.

- Set up a coordination and support action on AC-Aging to continue to exchange information and experiences, both in research and in construction projects.

- develop an IR testing protocol, to facilitate the exchange of results and information.

- Compare the bitumen composition that is found through various recovery methods to establish if there is an effect and if so, develop a procedure to address this.

- To further understanding of aging, a Round Robin test on the differences in test conditions between US and EU, allowing better access to each other's data and knowledge would be useful.

- When developing aging tests for AC, it would be useful to look at the US experience. As long as there is no fundamentally correct method for assessing the aging, it would be preferable to standardize it as much as possible in order to allow cooperation and exchange of data.

Delft University of Technology

Challenge the future

# 8 Presentations

## *8.1 Charles Glover, Texas A&M , An Asphalt Oxidation Perspective on HighRAC Mixtures*

1

# Field Aging of Bituminous Materials and the Challenge of Laboratory Simulation

Charles J. Glover
Artie McFerrin Department of Chemical Engineering
Texas A&M University/Texas A&M Transportation Institute

Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

2

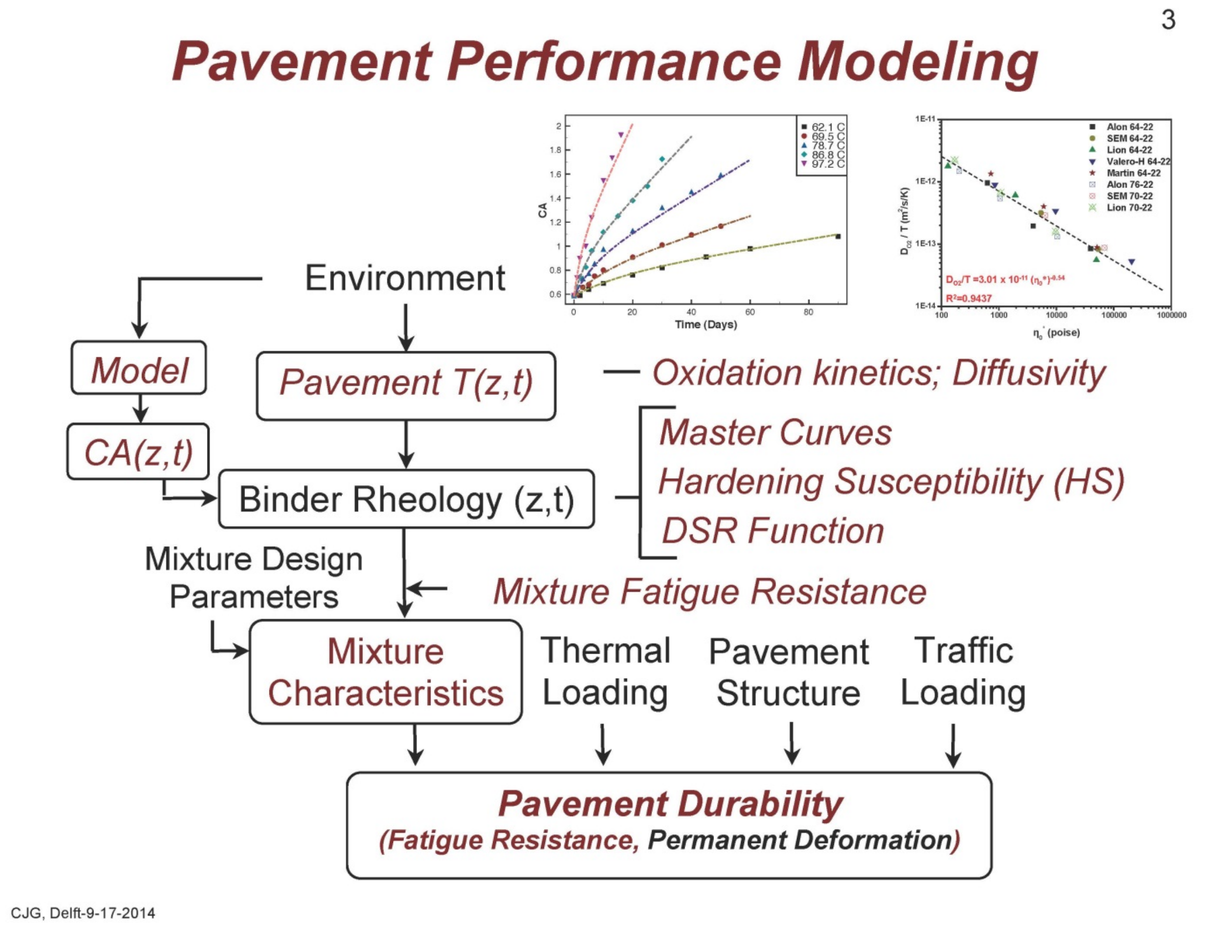
# Background

- Pavement binders oxidize and harden over time
  - A ***relentless process***
  - Occurs ***well below the immediate pavement surface***
  - Hardening ***results in binder embrittlement***: fracture at a lower strain
- Long-term goal has been to understand this process quantitatively and its ***impact on pavement durability, specific to each binder and pavement site*** – ***a 25-year effort***

Texas A&M Transportation Institute

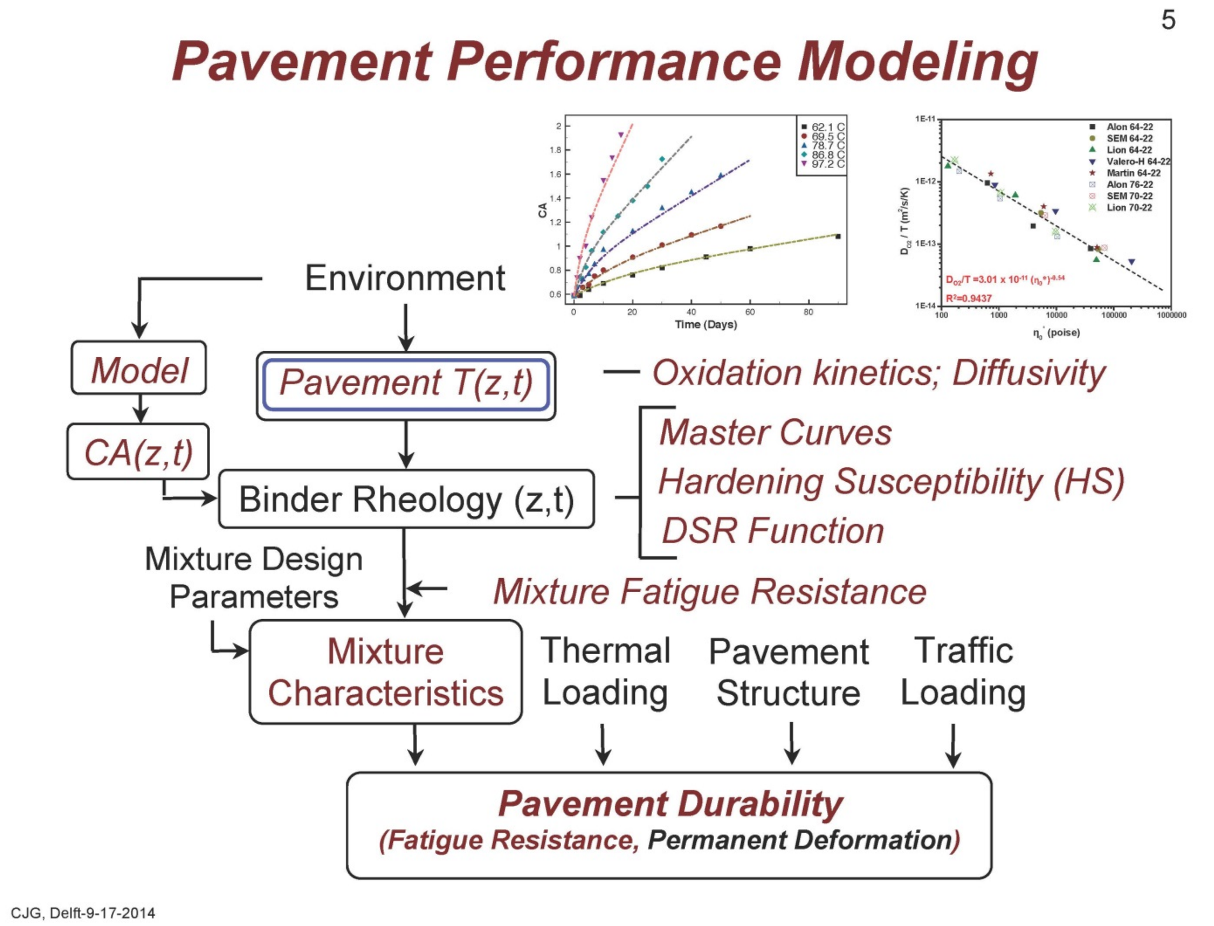
Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING


3
Pavement Performance Modeling
62.1 C
69.5 C
78.7 C
86.8 C
97.2 C
CA
Time (Days)
Alon 64-22
SEM 64-22
Lion 64-22
Valero-H 64-22
Martin 64-22
Alon 76-22
SEM 70-22
Lion 70-22
R²=0.9437
(poise)
Environment
Model
CA(z,t)
Pavement T(z,t)
Oxidation kinetics; Diffusivity
Binder Rheology (z,t)
Master Curves
Hardening Susceptibility (HS)
DSR Function
Mixture Design Parameters
Mixture Fatigue Resistance
Mixture Characteristics
Thermal Loading
Pavement Structure
Traffic Loading
Pavement Durability
(Fatigue Resistance, Permanent Deformation)
CJG, Delft-9-17-2014

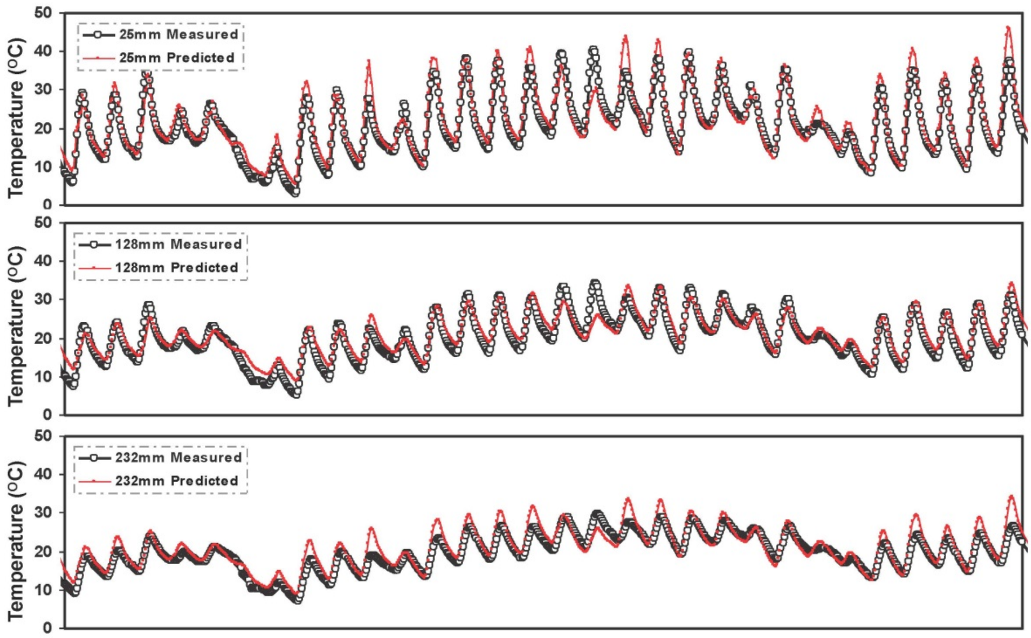
# Objectives

- To review some of this 25-year history, showing some details but **emphasizing the Big Picture:**
  - to predict pavement performance – ***design***
  - To show how any pavement can be a low-cost, effective, and efficient test section – ***forensics***
  - To provide an aging/durability test – ***fast aging test***


5
Pavement Performance Modeling
Environment
Model
Pavement T(z,t)
Oxidation kinetics; Diffusivity
CA(z,t)
Binder Rheology (z,t)
Master Curves
Hardening Susceptibility (HS)
DSR Function
Mixture Design Parameters
Mixture Fatigue Resistance
Mixture Characteristics
Thermal Loading
Pavement Structure
Traffic Loading
Pavement Durability
(Fatigue Resistance, Permanent Deformation)
CA
Time (Days)
62.1 C
69.5 C
78.7 C
86.8 C
97.2 C
Alon 64-22
SEM 64-22
Lion 64-22
Valero-H 64-22
Martin 64-22
Alon 76-22
SEM 70-22
Lion 70-22
R²=0.9437
CJG, Delft-9-17-2014

6

# Temperature Calculations




Texas A&M Transportation Institute

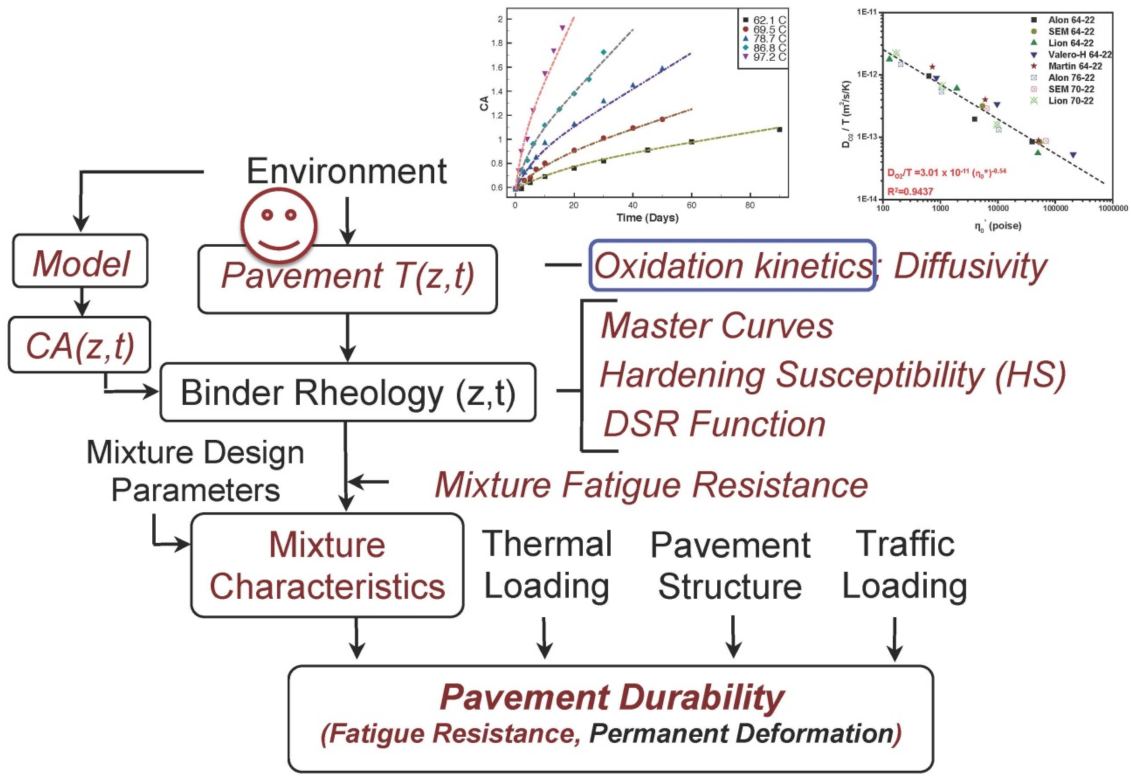
Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

CJG, PARC-7-15-14

7

# Pavement Performance Modeling

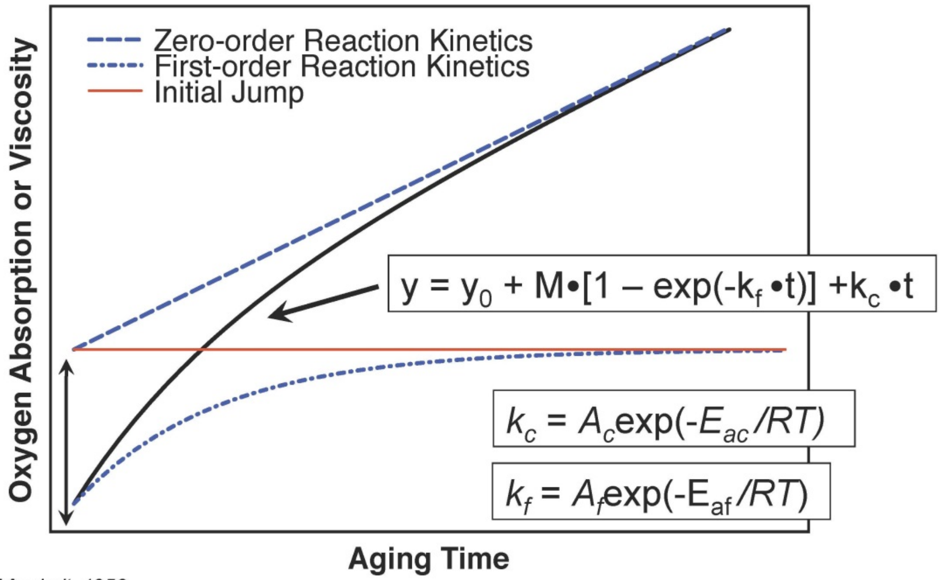



CJG, Delft-9-17-2014

ISBN 978-94-6186-524-3


8

# Background: Oxidation Kinetics




van Oort, *Durability of Asphalt, 1956*
Herrington, P.R. *Petroleum Science and Technology, Vol.16, 1998*

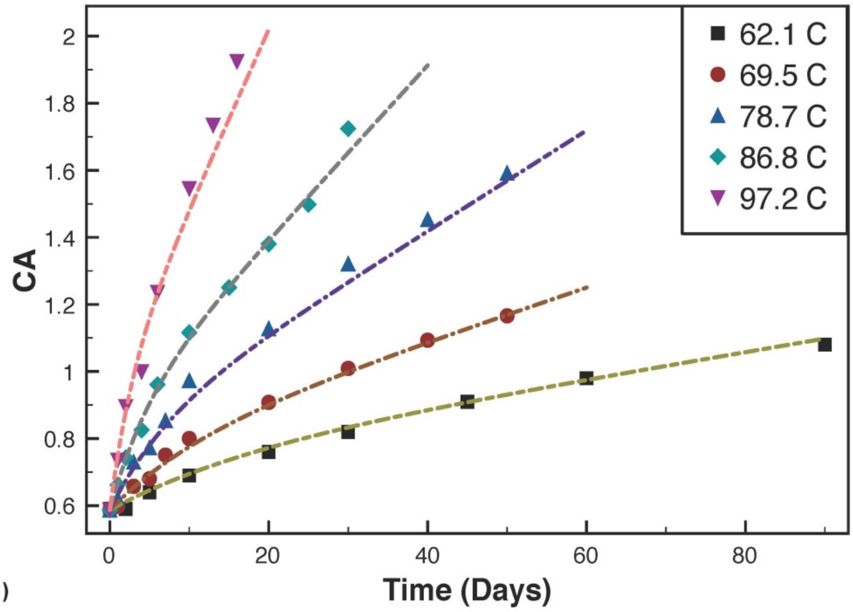
Texas A&M Transportation Institute

*Charles J. Glover*
*Symposium on Aging of Bituminous Materials*
*Delft, Netherlands*
*September 17, 2014*

Artie McFerrin Department of CHEMICAL ENGINEERING

9

# Oxidation Kinetics Data using Original Binder – 3 mos aging




Jin et al. (2011)

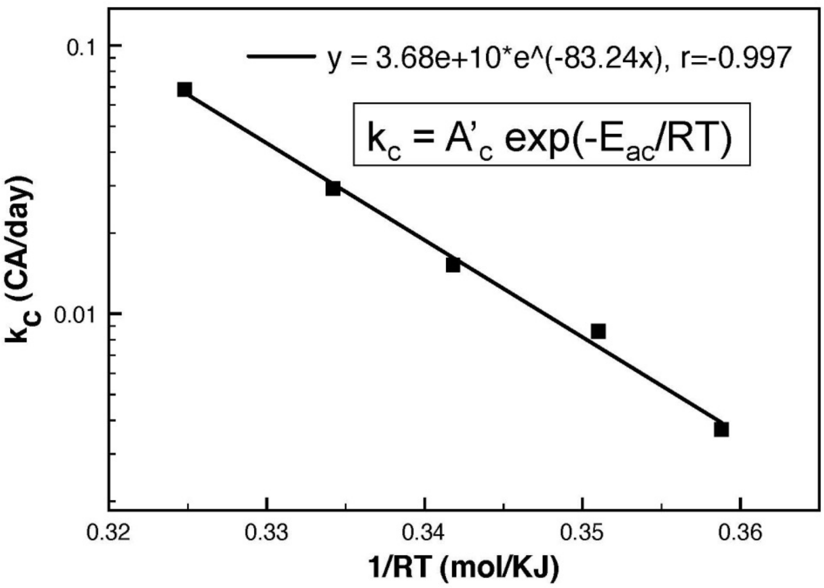
Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

10

# Constant-rate Reaction Kinetics



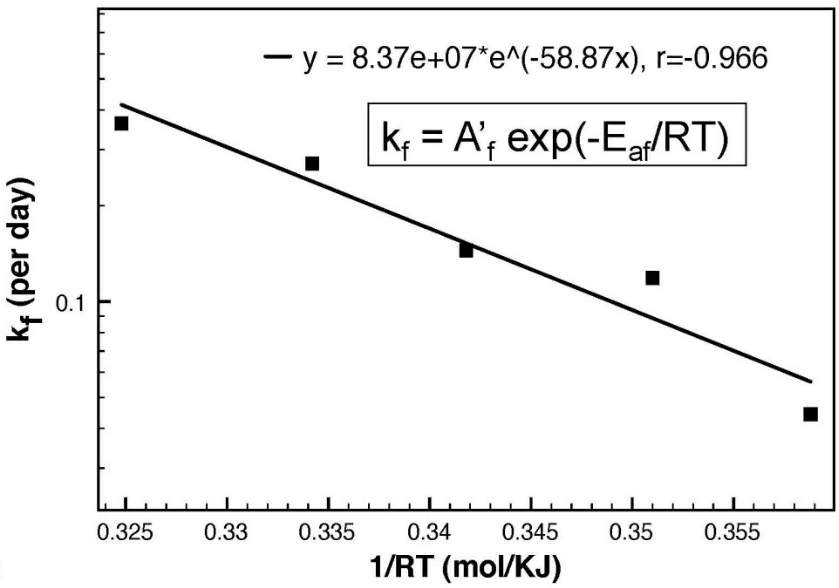

Jin et al. (2011)

$$CA = M \bullet [1 - \exp(-k_f \bullet t)] + CA_{tank} + k_c \bullet t$$

CJG, Delft-9-17-2014

11

# Fast-rate Reaction Kinetics



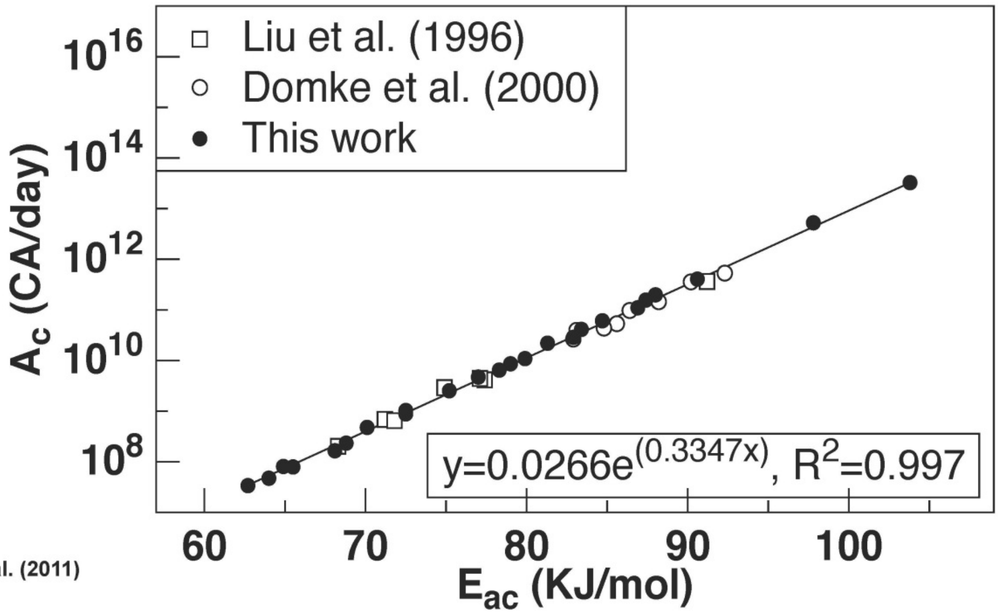

Jin et al. (2011)

$$CA = M \bullet [1 - \exp(-k_f \bullet t)] + CA_{tank} + k_c \bullet t$$

CJG, Delft-9-17-2014

12

# Kinetics Correlations




Jin et al. (2011)

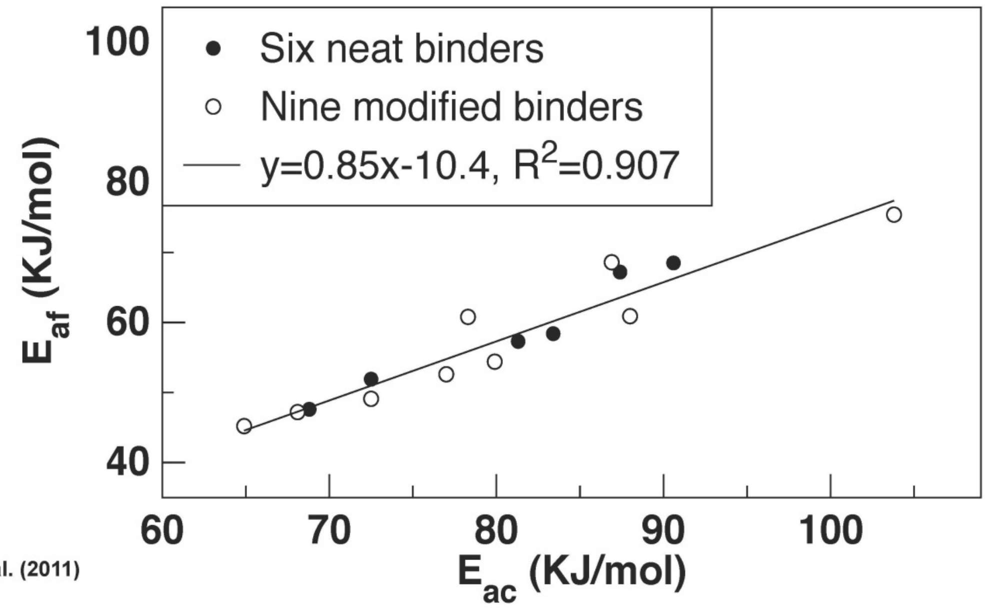
Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

13

# Kinetics Correlations




Jin et al. (2011)

Texas A&M Transportation Institute

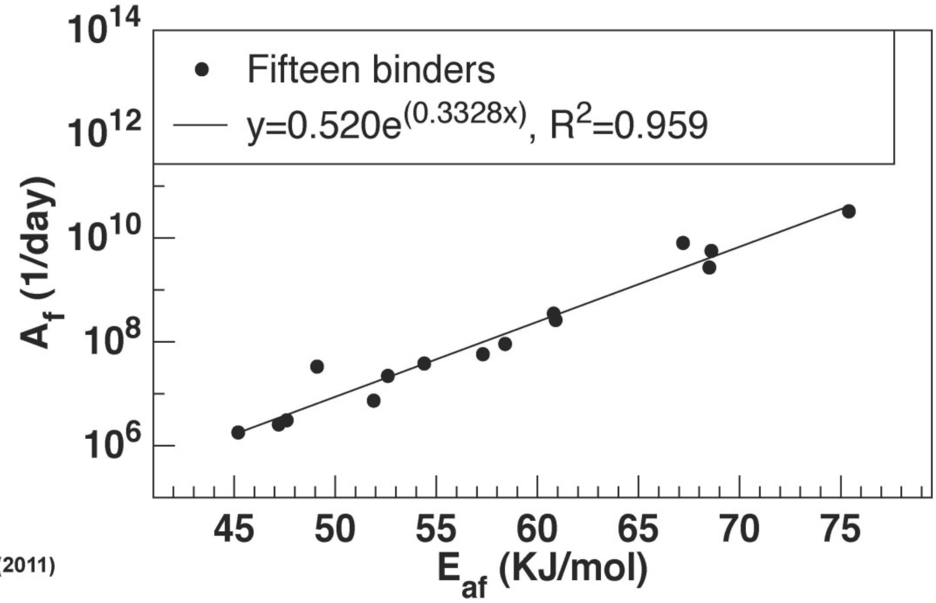
Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

ISBN 978-94-6186-524-3


14

# Kinetics Correlations




Jin et al. (2011)

Texas A&M Transportation Institute

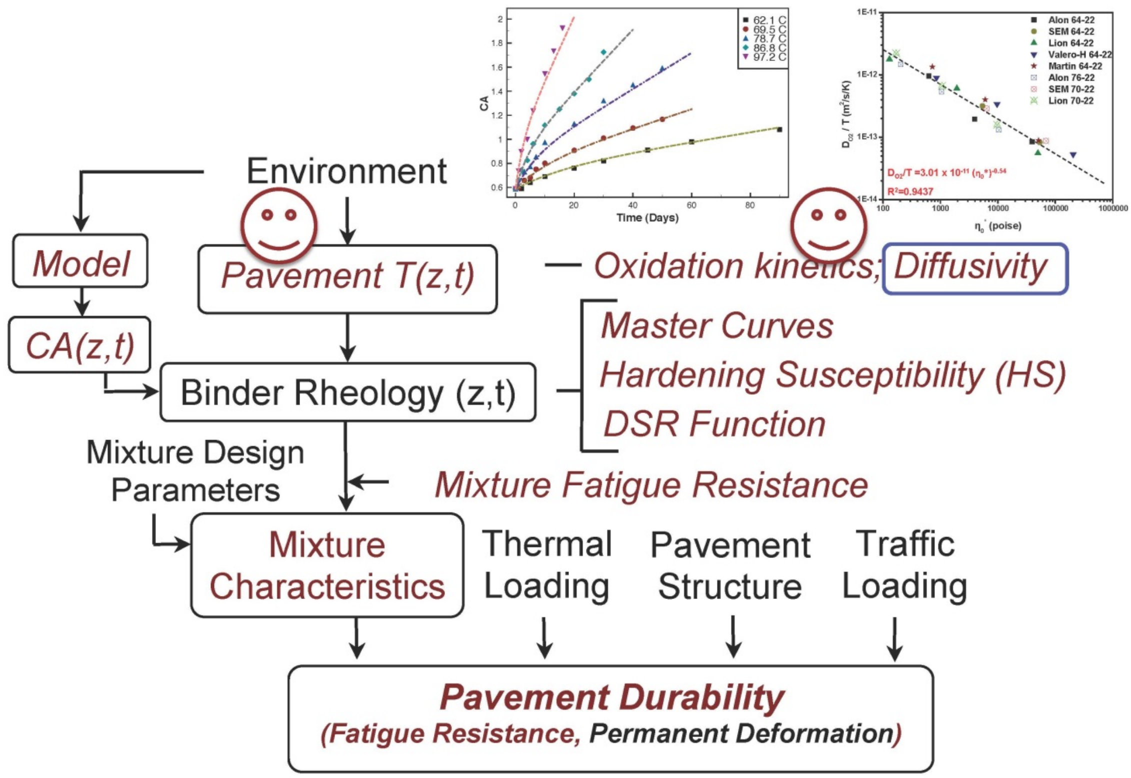
Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

ISBN 978-94-6186-524-3


15

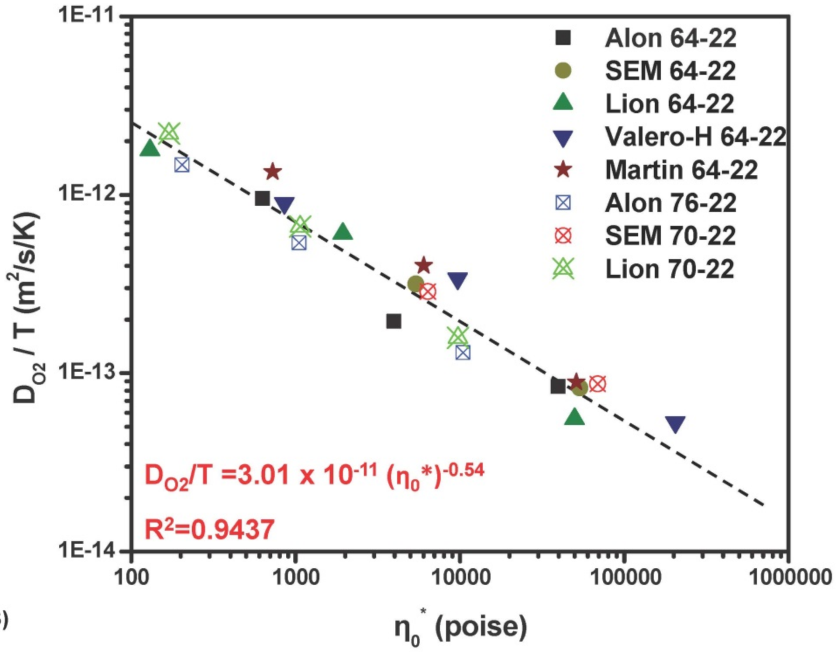
# Pavement Performance Modeling




CJG, Delft-9-17-2014

16

# Background: $O_2$ Diffusivity in Asphalt




Han et al. (2013)

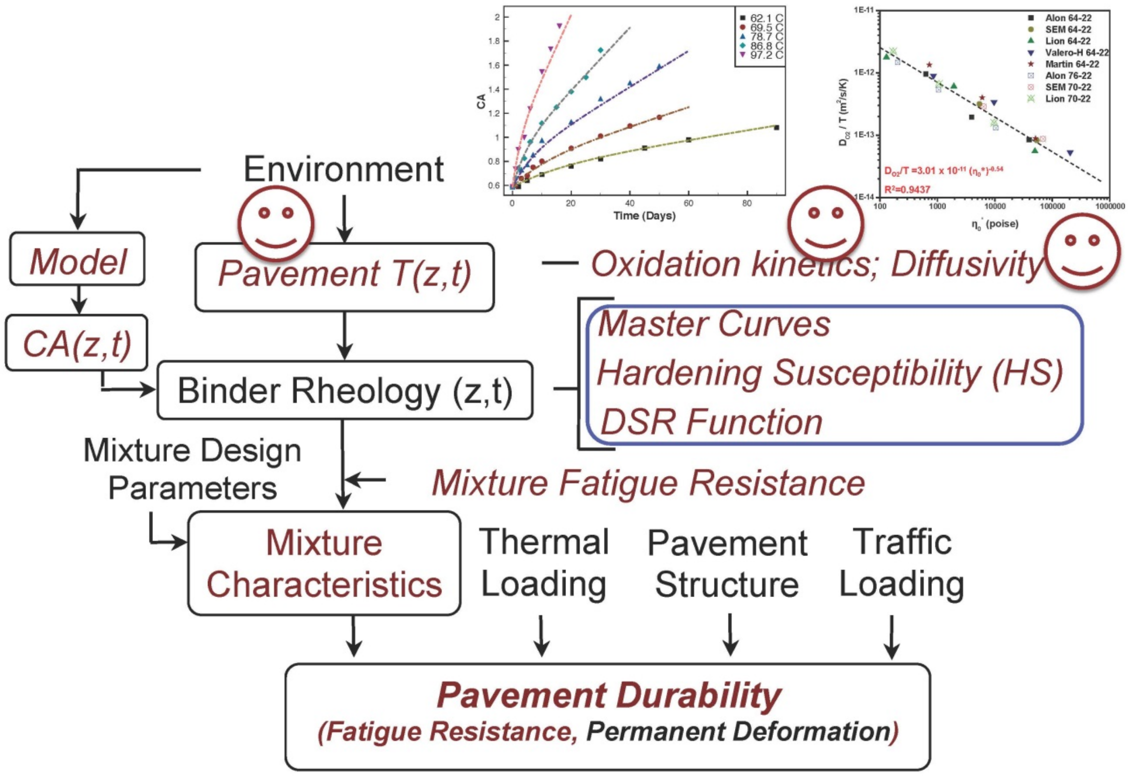
Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

17

# Pavement Performance Modeling

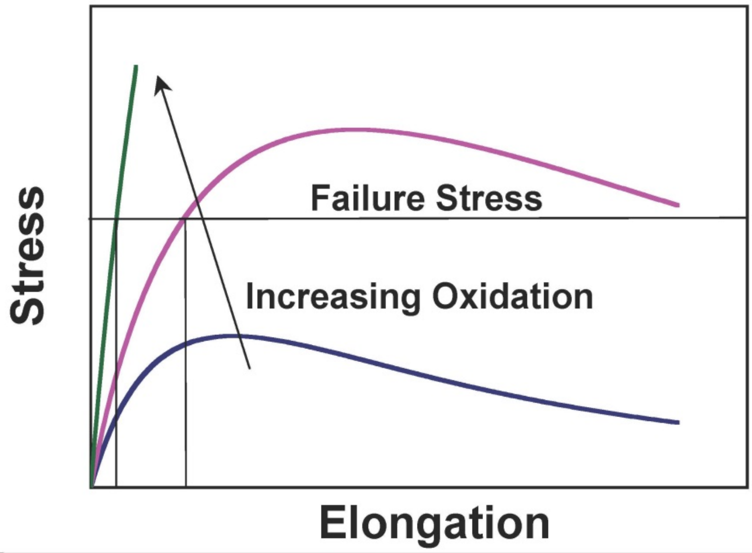



CJG, Delft-9-17-2014

18

# Background – A Key Concept: Binder Embrittlement

## IN SERVICE, BINDERS OXIDIZE, BECOME STIFFER AND LESS DUCTILE…A RELENTLESS PROCESS!



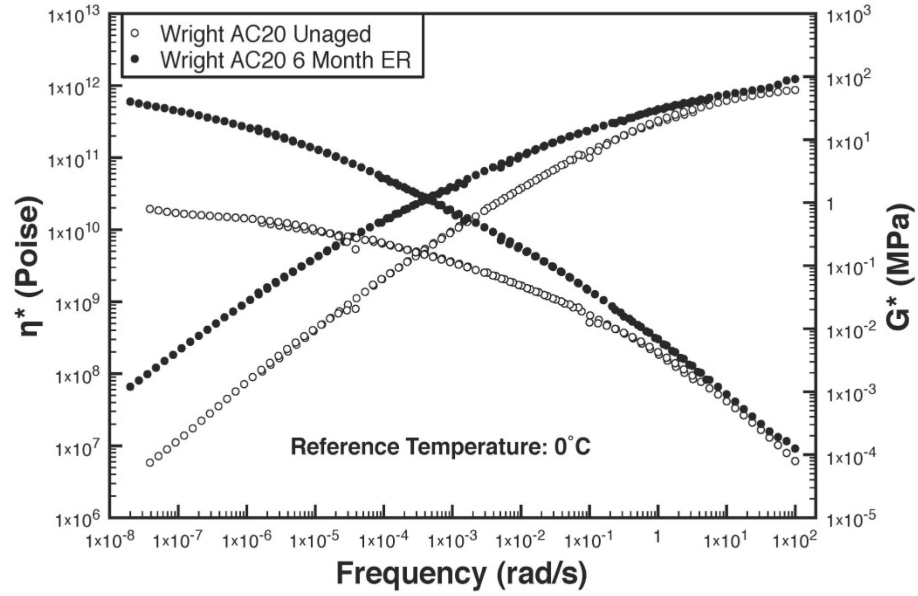

Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

19

# – Background –
# Binders Oxidize and Harden




Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

20

# – Background –
# Binder Rheology and Brittleness

## *Why DSRFn = G'/(η'/G')?**

***G'/(η'/G') = Glover-Rowe parameter***
***= G*ωcos²δ/sinδ***

****at 15 C, 0.005 rad/s***

**DSRFn:** *Ruan, Y., R.R.Davison, and C.J. Glover, "An Investigation of Asphalt Durability: Relationships between Ductility and Rheological Properties for Unmodified Asphalts," Petroleum Science and Technology, 21(1&2), 231-254 (2003).*

**G-R Parameter:** *(1) King, G., M. Anderson, D. Hanson, and P. Blankenship: "Using Black Space Diagrams to Predict Age-Induced Cracking," 7th Rilem Intl.Conf on Cracking in Pavements, vol 1, Scarpas, Kringos, Al-Qadi, Loizos (eds.), 2012. (2) R.M. Anderson, G.N. King, D.I. Hanson, P.B. Blankenship, AAPT 80, 615 (2011). (3) Rowe, G.M., Prepared discussion following the Anderson AAPT paper above, AAPT 80, 649-652 (2011).*

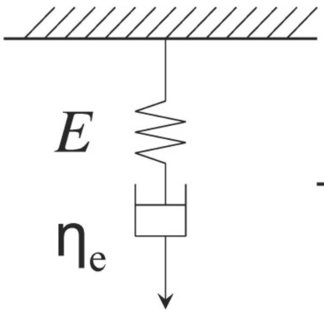
Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

21

# MAXWELL MODEL



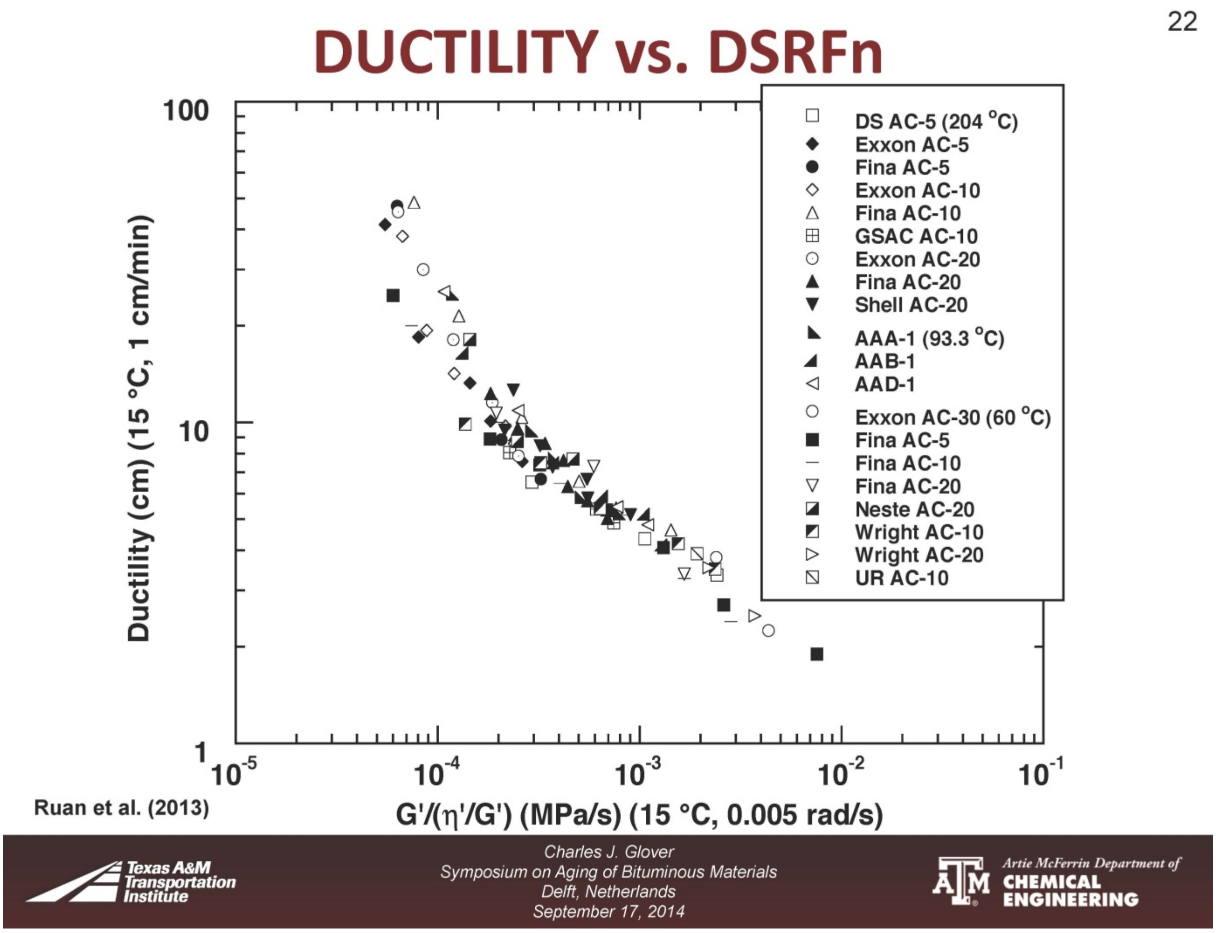

$$\frac{L_o}{U_o}\frac{E}{\eta_e}T + \frac{dT}{d\alpha} = \frac{E}{\alpha}$$

$$G' \qquad \frac{\eta'}{G'}, \qquad \frac{G'}{\frac{\eta'}{G'}}$$

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

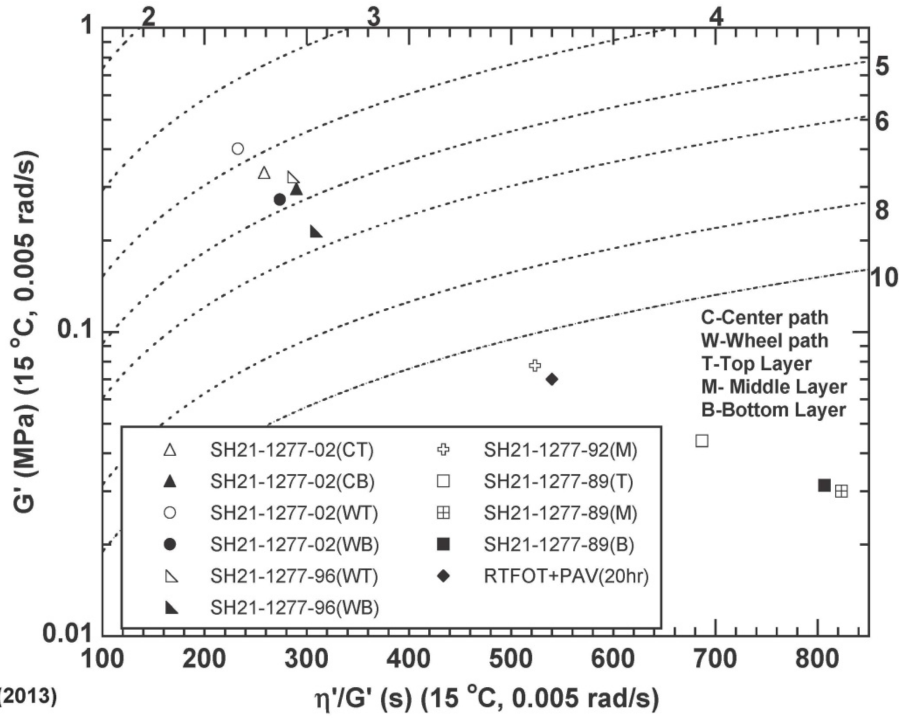
Texas A&M Transportation Institute

Artie McFerrin Department of CHEMICAL ENGINEERING


22
DUCTILITY vs. DSRFn
Ductility (cm) (15 °C, 1 cm/min)
100
10
1
10^-5
10^-4
10^-3
10^-2
10^-1
G'/(η'/G') (MPa/s) (15 °C, 0.005 rad/s)
DS AC-5 (204 °C)
Exxon AC-5
Fina AC-5
Exxon AC-10
Fina AC-10
GSAC AC-10
Exxon AC-20
Fina AC-20
Shell AC-20
AAA-1 (93.3 °C)
AAB-1
AAD-1
Exxon AC-30 (60 °C)
Fina AC-5
Fina AC-10
Fina AC-20
Neste AC-20
Wright AC-10
Wright AC-20
UR AC-10
Ruan et al. (2013)
Texas A&M Transportation Institute
Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014
Artie McFerrin Department of CHEMICAL ENGINEERING

23

# G' vs. η'/G' MAP FOR PAVEMENT MATERIALS




Ruan et al. (2013)

Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

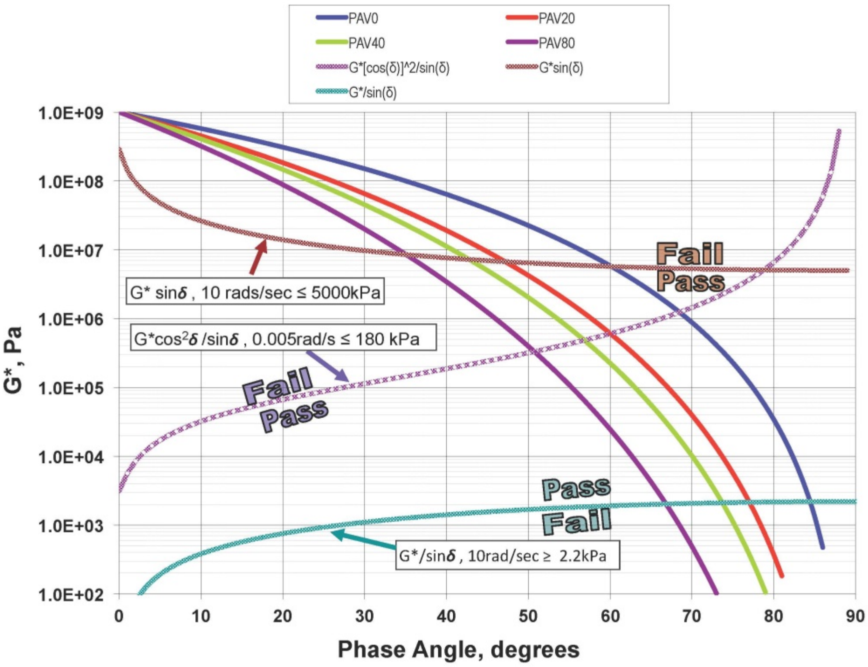
Artie McFerrin Department of CHEMICAL ENGINEERING

24

# BLACKSPACE MAP FOR PAVEMENT MATERIALS

*Rowe, G.M., Prepared discussion following AAPT paper, AAPT 80, 649-652 (2011).*

*"Glover – Rowe" parameter named by Gayle King: see slide 20.*



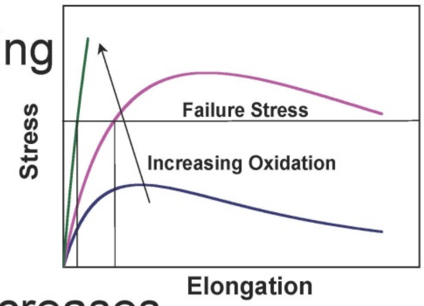

Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

# BINDER RHEOLOGY AND BRITTLENESS - DSRFn

- Binders harden with oxidative aging
  - G’, η’ increase; δ decreases
  - Stresses build faster and relax slower under deformation
  - Consequently, failure strain decreases

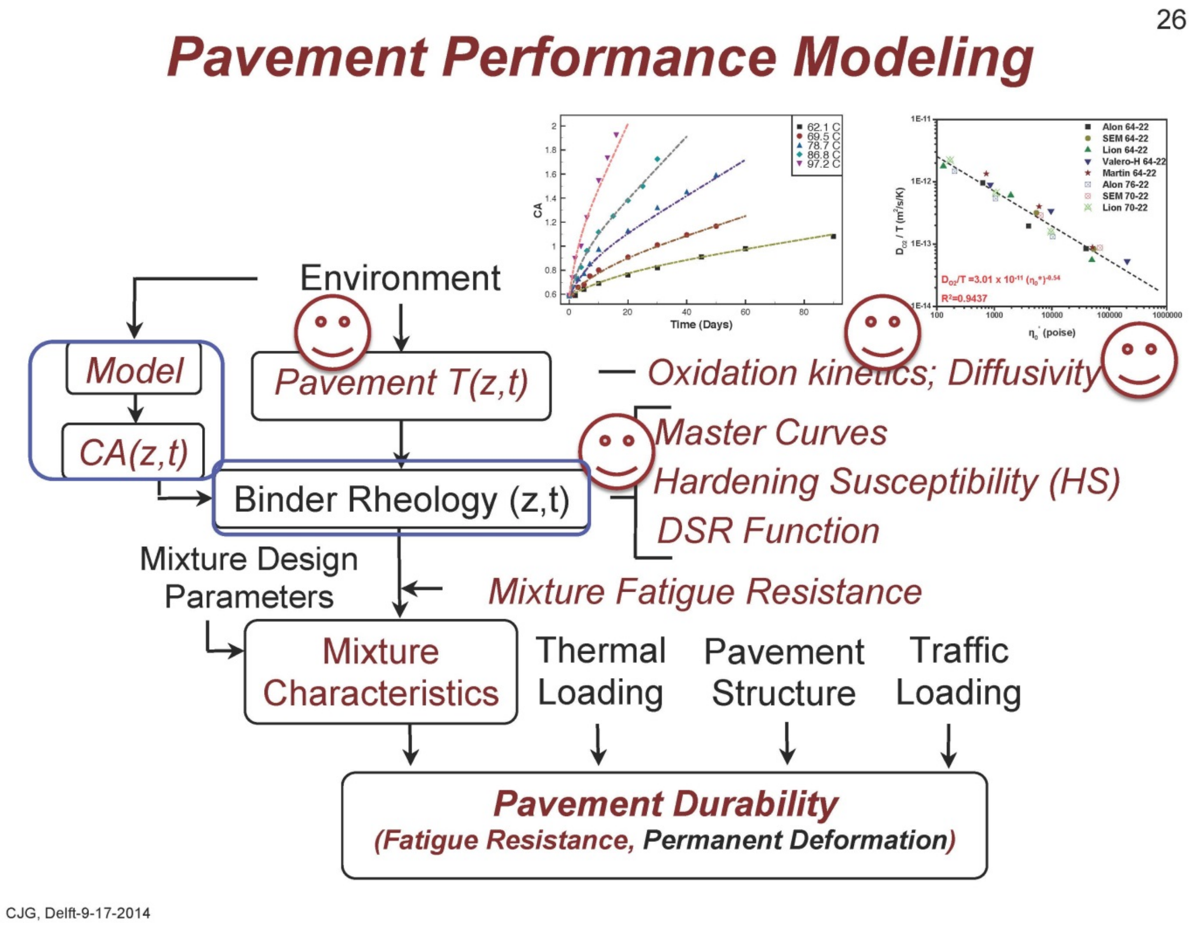



- Binders march across the DSR map with increased oxidative aging (“march to death”)
- DSR Function characterizes stress building (elastic spring) versus stress relief (viscous flow)

Texas A&M Transportation Institute

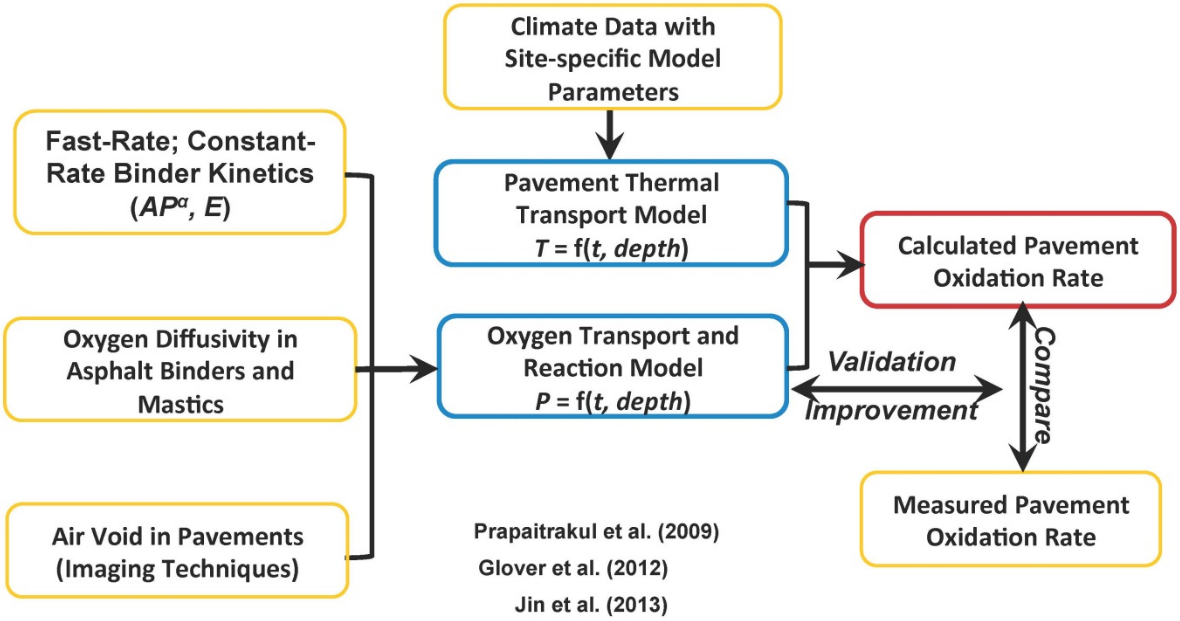
Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING


26
Pavement Performance Modeling
Environment
Model
CA(z,t)
Pavement T(z,t)
Oxidation kinetics; Diffusivity
Binder Rheology (z,t)
Master Curves
Hardening Susceptibility (HS)
DSR Function
Mixture Design Parameters
Mixture Fatigue Resistance
Mixture Characteristics
Thermal Loading
Pavement Structure
Traffic Loading
Pavement Durability
(Fatigue Resistance, Permanent Deformation)
CA
Time (Days)
62.1 C
69.5 C
78.7 C
86.8 C
97.2 C
Alon 64-22
SEM 64-22
Lion 64-22
Valero-H 64-22
Martin 64-22
Alon 76-22
SEM 70-22
Lion 70-22
R²=0.9437
CJG, Delft-9-17-2014

27

# Background: Pavement Oxidation Model

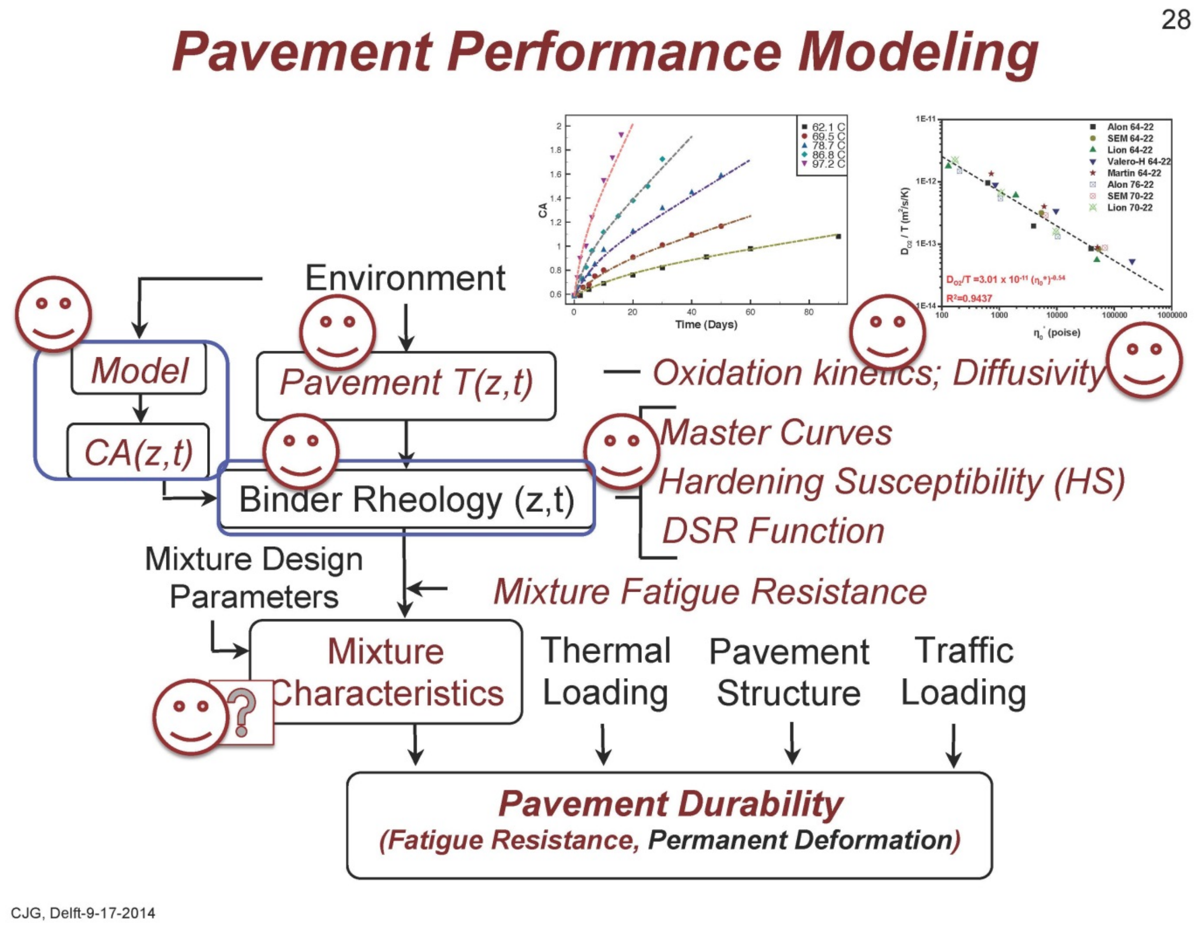



Prapaitrakul et al. (2009)
Glover et al. (2012)
Jin et al. (2013)

Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of Chemical Engineering


28
Pavement Performance Modeling
CA
Time (Days)
62.1 C
69.5 C
78.7 C
86.8 C
97.2 C
Alon 64-22
SEM 64-22
Lion 64-22
Valero-H 64-22
Martin 64-22
Alon 76-22
SEM 70-22
Lion 70-22
$D_{O2}/T$ (m²/s/K)
$\eta_0^*$ (poise)
$D_{O2}/T = 3.01 \times 10^{-11} (\eta_0^*)^{-0.54}$
$R^2=0.9437$
Environment
Model
CA(z,t)
Pavement T(z,t)
Oxidation kinetics; Diffusivity
Master Curves
Hardening Susceptibility (HS)
DSR Function
Binder Rheology (z,t)
Mixture Design Parameters
Mixture Fatigue Resistance
Mixture Characteristics
?
Thermal Loading
Pavement Structure
Traffic Loading
Pavement Durability
(Fatigue Resistance, Permanent Deformation)
CJG, Delft-9-17-2014

29

# So, the Design Procedure (and Aging test) is:

- Using ***original*** binder:
  - Kinetics measurements: POV (3 mos)
  - HS and M measurements
  - Site climate data/characteristics
  - Model calcs of temp history and profile
  - Model calcs of CA growth and hardening
  - Mixture response to hardening
- But, with no original binder, all is lost, right? **NO!**

Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

30

# And the Forensics Procedure (on an interesting aged pavement) is:

- Using ***extracted and recovered*** binder:
  - Kinetics measurements: POV (3 mos)
  - HS and M measurements
  - Site climate data/characteristics
  - Model calcs of temp history and profile
  - Model calcs of CA growth and hardening
  - Mixture response to hardening
- But **what about the POV 3 mos procedure**?

Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

31

# Oxidation Kinetics Problem: It Takes Time to Determine the Parameters – 3 months! Oxidation Kinetics Solution (?): Measurements in the PAV

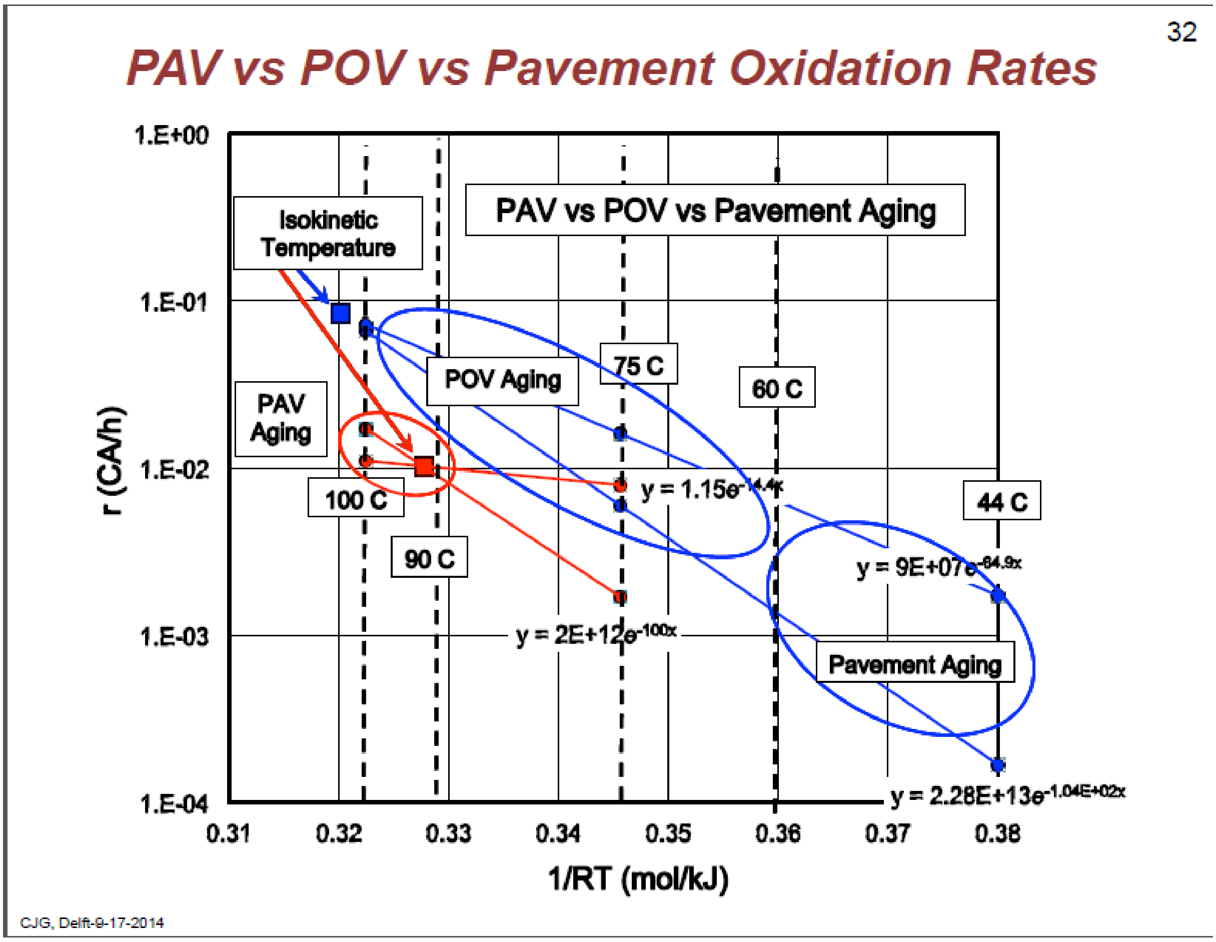
- Accelerate aging with higher air pressure
- **Big Question**: Are the kinetics at 1 atm air comparable to kinetics at 20 atm air?

van Oort, *Durability of Asphalt, 1956*
Herrington, P.R. *Petroleum Science and Technology, Vol.16, 1998*

Texas A&M Transportation Institute

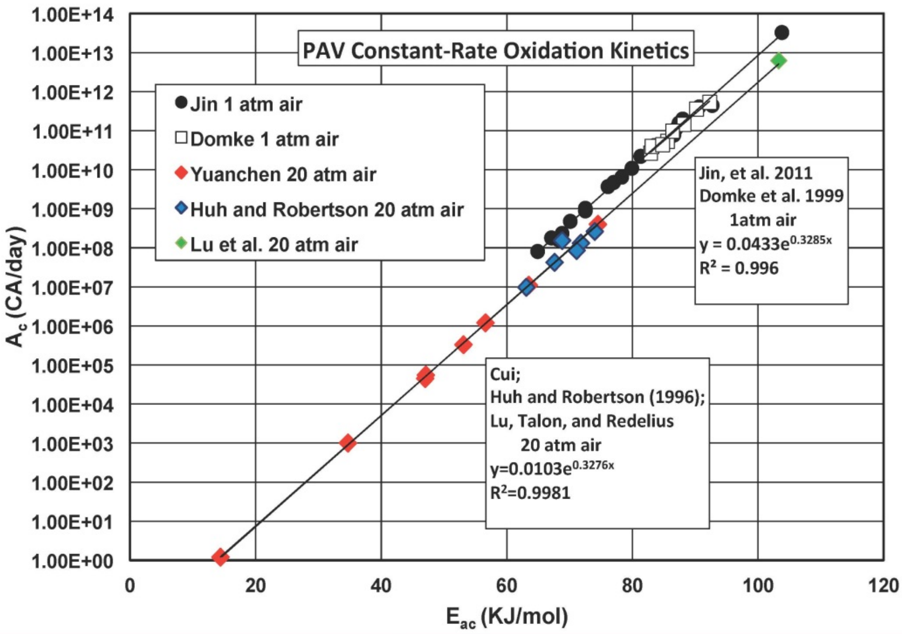
*Charles J. Glover*
*Symposium on Aging of Bituminous Materials*
*Delft, Netherlands*
*September 17, 2014*

Artie McFerrin Department of CHEMICAL ENGINEERING


32
PAV vs POV vs Pavement Oxidation Rates
PAV vs POV vs Pavement Aging
Isokinetic Temperature
PAV Aging
POV Aging
100 C
90 C
75 C
60 C
44 C
Pavement Aging
y = 1.15e-14.4x
y = 9E+07e-64.9x
y = 2E+12e-100x
y = 2.28E+13e-1.04E+02x
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
r (CA/h)
0.31
0.32
0.33
0.34
0.35
0.36
0.37
0.38
1/RT (mol/kJ)
CJG, Delft-9-17-2014

33

# PAV Ac versus Eac Correlation

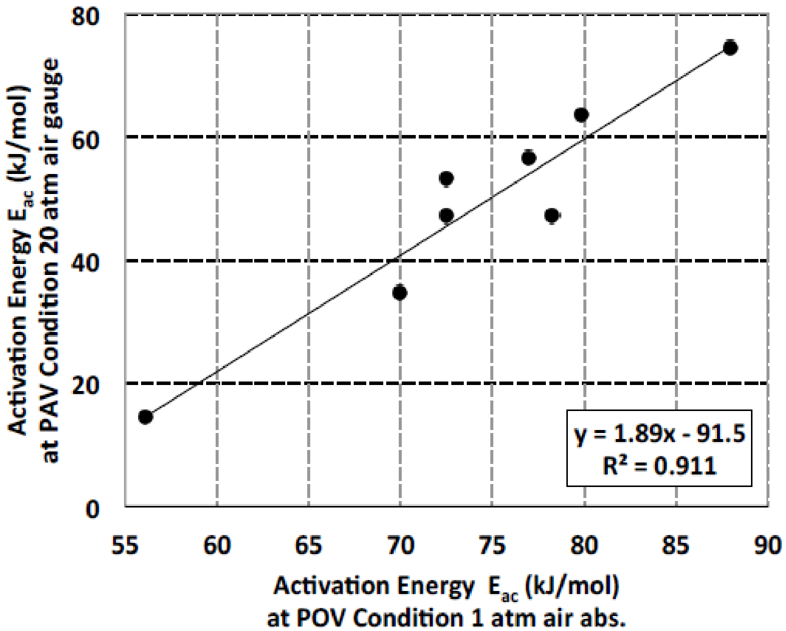



Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

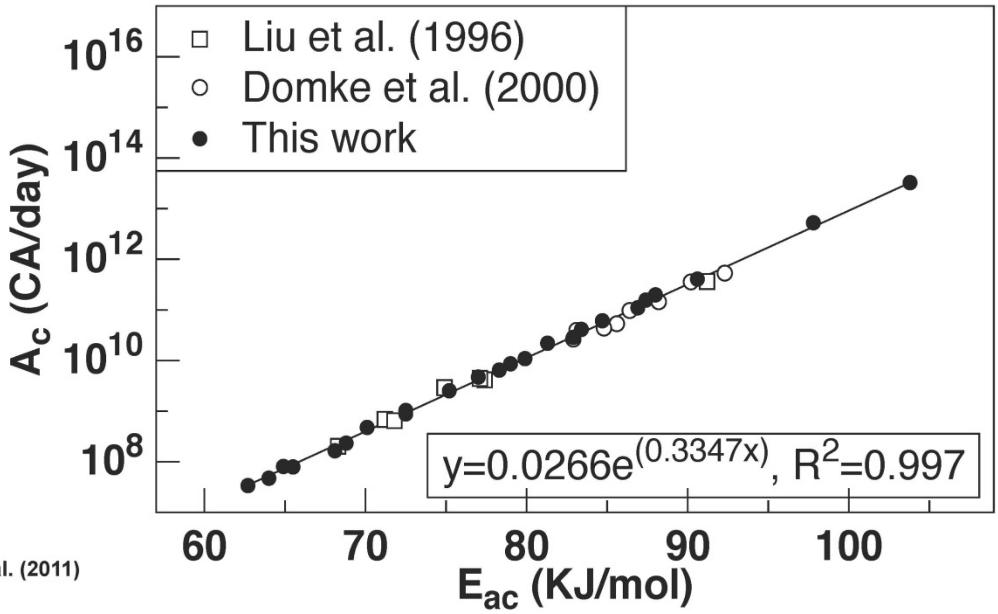
# PAV vs POV Activation Energies




Cui et al. (2014)

35

# Overview: Kinetics Correlations




Jin et al. (2011)

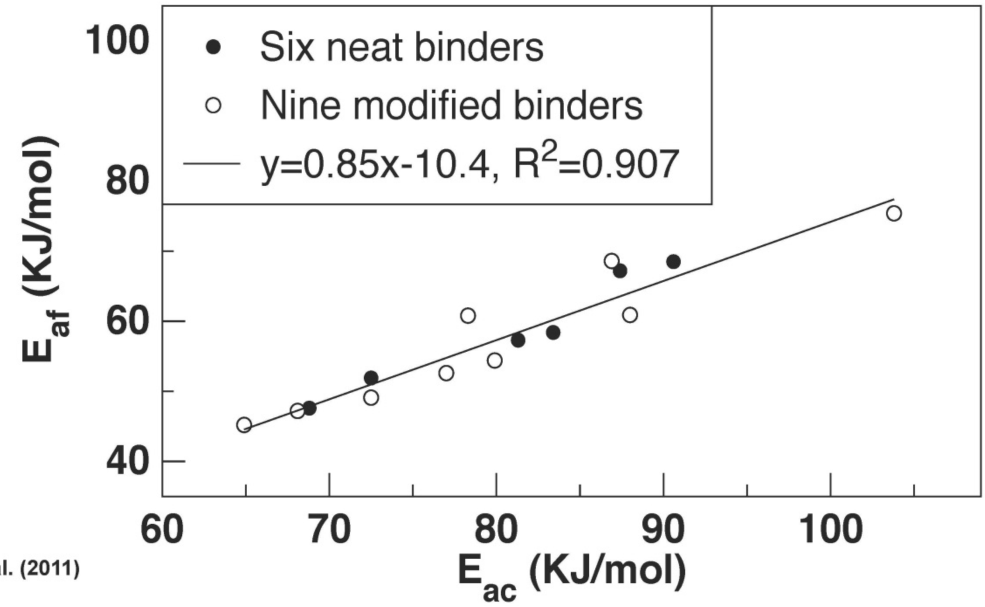
Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

36

# Overview: Kinetics Correlations




Jin et al. (2011)

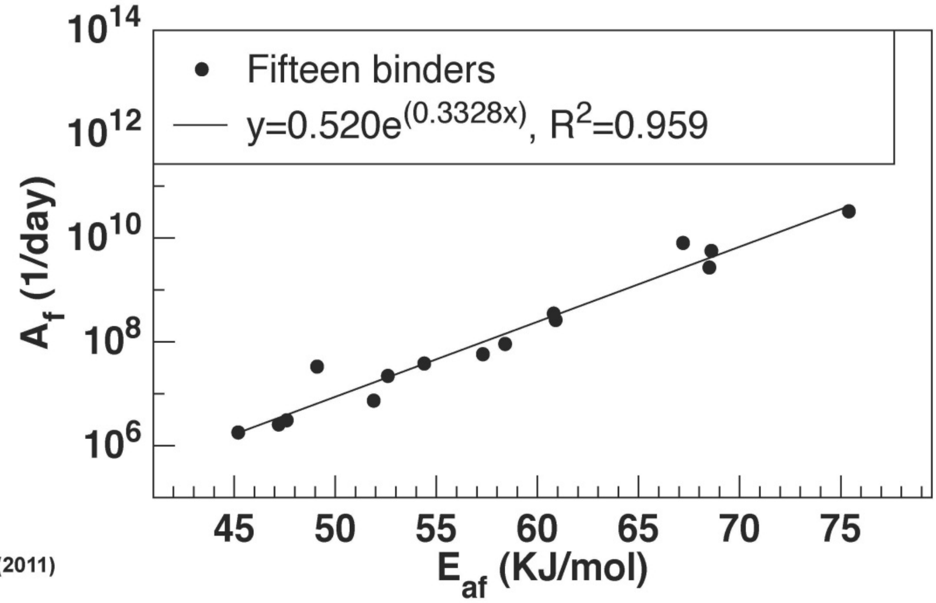
Texas A&M Transportation Institute

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

Artie McFerrin Department of CHEMICAL ENGINEERING

37

# Overview: Kinetics Correlations




Jin et al. (2011)

Charles J. Glover
Symposium on Aging of Bituminous Materials
Delft, Netherlands
September 17, 2014

# So: A strategy to estimate 1 atm kinetics parameters from PAV!

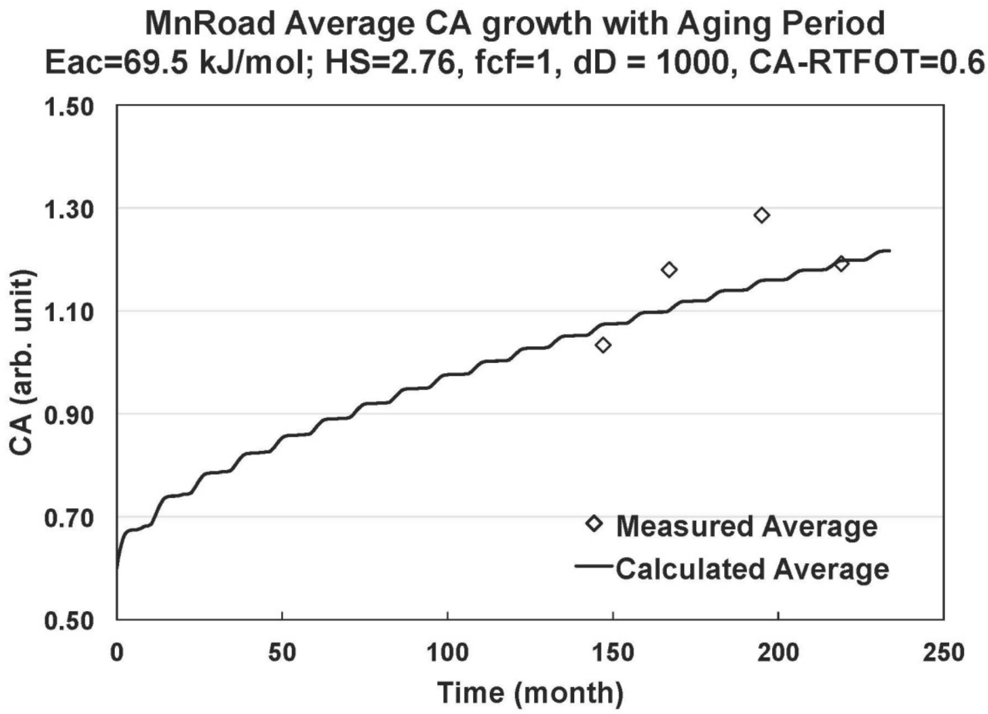
- Measure $E_{ac}$, $A_c$ in PAV; verify their fit to the existing correlation (data consistency check)
- Using $E_{ac}$ (1 atm) vs $E_{ac}$ (20 atm), determine 1 atm $E_{ac}$
- Using 1 atm correlations, use $E_{ac}$ to determine other parameters at 1 atm: $A_c$, $E_{af}$, $A_f$
- Determine M separately from 1 atm data
- Time: approximately 1 week!

39

# So, the Forensics Procedure (on an interesting pavement) is:

- Using ***extracted and recovered*** binder:
  - Kinetics measurements: PAV (1 week)
  - HS and M measurements
  - Site climate data/characteristics
  - Model calculations of temp history and profile
  - Model calculations of CA growth and hardening
  - Mixture response to hardening

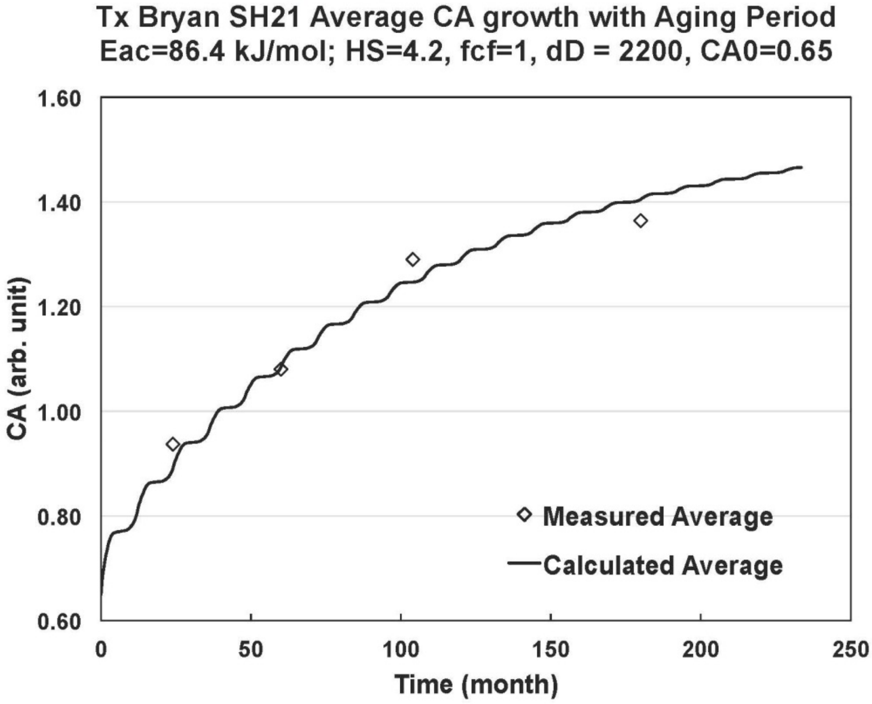
# Example Oxidation Modeling - MnRoad Cell 1 -



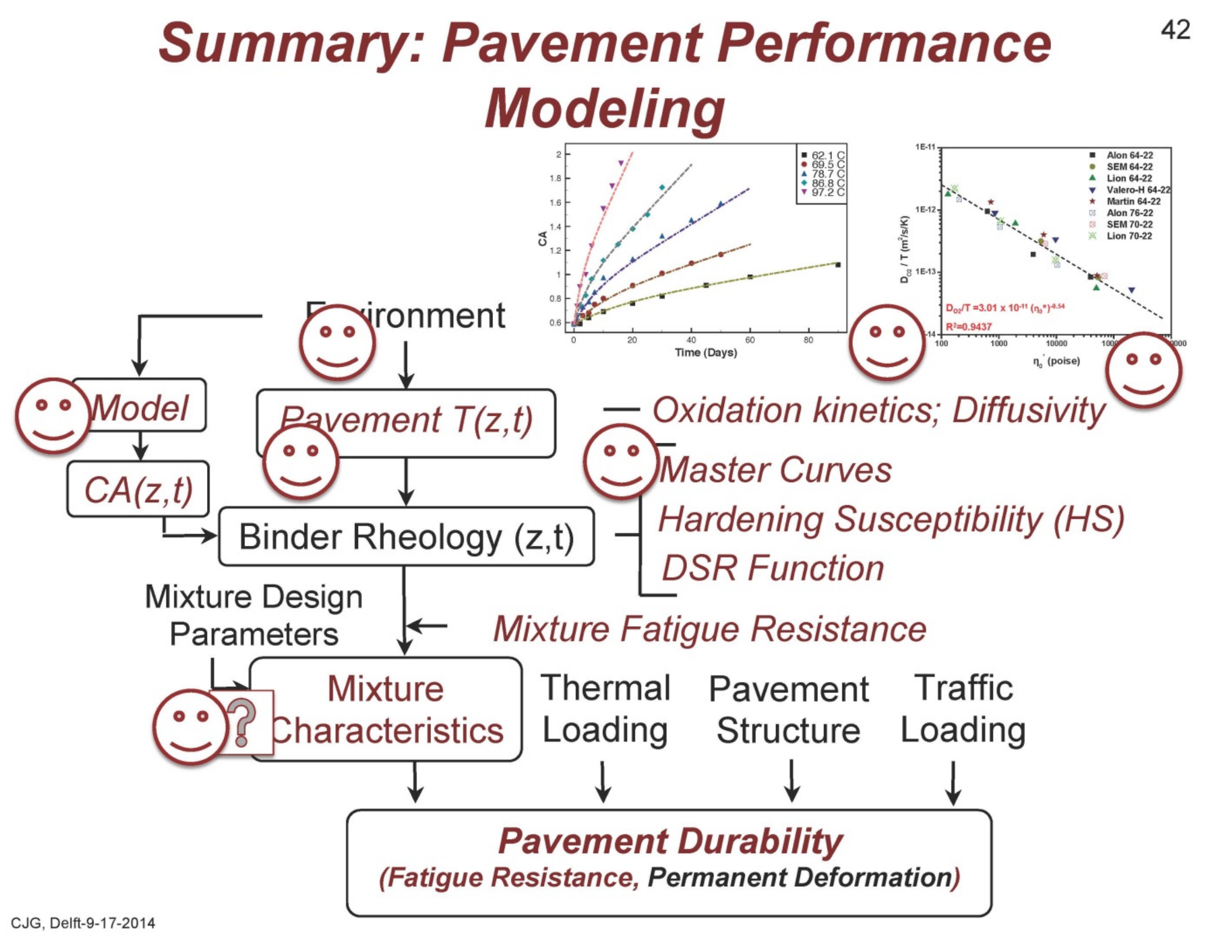

CJG, Delft-9-17-2014

41

# Example Oxidation Modeling - Bryan, Tx SH 21 -




CJG, Delft-9-17-2014


Summary: Pavement Performance Modeling
42
62.1 C
69.5 C
78.7 C
86.8 C
97.2 C
CA
Time (Days)
Alon 64-22
SEM 64-22
Lion 64-22
Valero-H 64-22
Martin 64-22
Alon 76-22
SEM 70-22
Lion 70-22
R²=0.9437
Environment
Model
CA(z,t)
Pavement T(z,t)
Oxidation kinetics; Diffusivity
Master Curves
Binder Rheology (z,t)
Hardening Susceptibility (HS)
DSR Function
Mixture Design Parameters
Mixture Fatigue Resistance
Mixture Characteristics
Thermal Loading
Pavement Structure
Traffic Loading
Pavement Durability
(Fatigue Resistance, Permanent Deformation)
CJG, Delft-9-17-2014

# Conclusions

- Pavement binders ***oxidize and harden over time***
  - A ***relentless*** process
  - Occurs ***well below the pavement surface***
  - Hardening results in ***binder embrittlement***: fracture at a lower strain; "March to Death"
- ***Long-term goal has been to understand this process*** quantitatively and its impact on pavement durability
- These ***fundamentals can be used for***:
  - ***design*** that is specific to pavement site
  - ***forensics*** studies of in-service pavements
  - ***fast oxidative aging test of binders***, specific to each pavement site

44

# Thank You!

- *TxDOT for multiple projects over many years leading up to and including pavement oxidation modeling and binder kinetics*
- *The FHWA and the Asphalt Research Consortium for support of elements of the pavement model*
- *Tom Scarpas and Sandra Erkens for the invitation to this symposium*

Texas A&M Transportation Institute

*Charles J. Glover*
*Symposium on Aging of Bituminous Materials*
*Delft, Netherlands*
*September 17, 2014*

Artie McFerrin Department of CHEMICAL ENGINEERING

# References

45


- Cui, Yuanchen, Jin, Xin, Liu, Guanlan, and Glover, C.J., "An Accelerated Method for Determining Asphalt Oxidation Kinetics Parameters for use in Pavement Oxidation and Performance Modeling," Petroleum Science and Technology. 32:22,2691-2699 (2014).
- Glover, C. J., Prapaitrakul, N., Han, R. Jin, X., Cui, Y., Rose, A., Lawrence, J.J., Padigala, M., Park, E.S., Arambula, E., Martin, A.E., "Evaluation Of Binder Aging And Its Influence In Aging Of Hot Mix Asphalt Concrete: Technical Report," Texas Dept. of Transp. Research Report No. 0-6009-2, 522 pages, October, 2012.
- Han, Rongbin, Jin, Xin., and Glover, C. J., "Modeling Pavement Temperature for Use in Binder Oxidation Models and Pavement Performance Prediction," Journal of Materials in Civil Engineering, 23(4), 351-359 (2011).
- Han, R., Jin, X., and Glover, C.J., "Oxygen Diffusivity in Asphalts and Mastics," Petroleum Sci. and Technol., 31(15), 1563–1573 (2013).
- Huh, J.-D. and Robertson, R. (1996). Modeling of Oxidative Aging Behavior of Asphalts from Short-Term, High-Temperature Data as a Step Toward Prediction of Pavement Aging. *Transportation Research Record* 1535:91-97.
- Jin, X., Cui, Y., and Glover, C.J., "Modeling Asphalt Oxidation in Pavement with Field Validation," Petroleum Sci. and Technol., 31(13), 1398-1405 (2013).
- Jin, X., R. Han, Y. Cui, and C.J. Glover, "A Fast-rate – Constant-rate Oxidation Kinetics Model for Asphalt Binders," Industrial and Engineering Chemistry Research, 50(23), 13373-13379 (2011).
- Lu, X., Talon, Y., and Redelius, P. (Date?). Aging of Bituminous Binders – Laboratory Tests and Field Data. http://www.nynas.com/Global/Bitumen%20for%20paving%20applications/UK/25341.pdf
- Prapaitrakul N., Jin X., Han R., and Glover, C. J. "A Transport Model of Asphalt Binder Oxidation in Pavements," Road Materials and Pavement Design, 10 (Special Issue), 95-113 (2009).
- Ruan, Y., Davison, R.R., and Glover, C.J., "An Investigation of Asphalt Durability: Relationships between Ductility and Rheological Properties for Unmodified Asphalts," Petroleum Science and Technology, 21(1&2), 231-254 (2003).


- Ruan, Y., Davison, R.R., and Glover, C.J., "An Investigation of Asphalt Durability: Relationships between Ductility and Rheological Properties for Unmodified Asphalts," Petroleum Science and Technology, 21(1&2), 231-254 (2003).


CJG, Delft-9-17-2014

## *8.2 Ron Glaser, WRI, Advances in asphalt binder oxidation understanding with practical implications: Chemical and rheological behavior.*

Western Research Institute

## Oxidation, Rheology, and Durability

Ron Glaser
Fred Turner
J.P Planche
Western Research Institute
Laramie, Wyoming
USA

**TU Delft 2014**

Western Research Institute

Oxidation, Rheology, and Durability

# An overview of the primary effects of oxidation on pavements

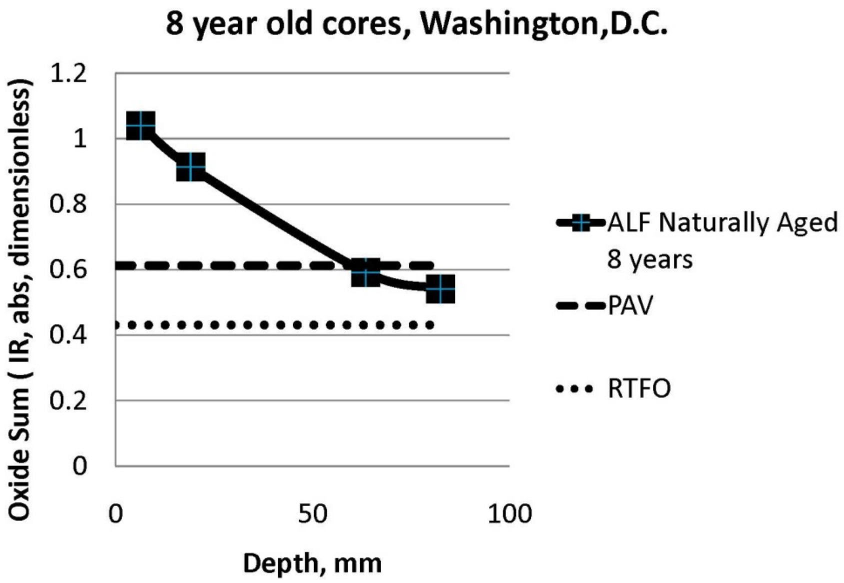
WesternResearch INSTITUTE

## Oxidation, Rheology, and Durability

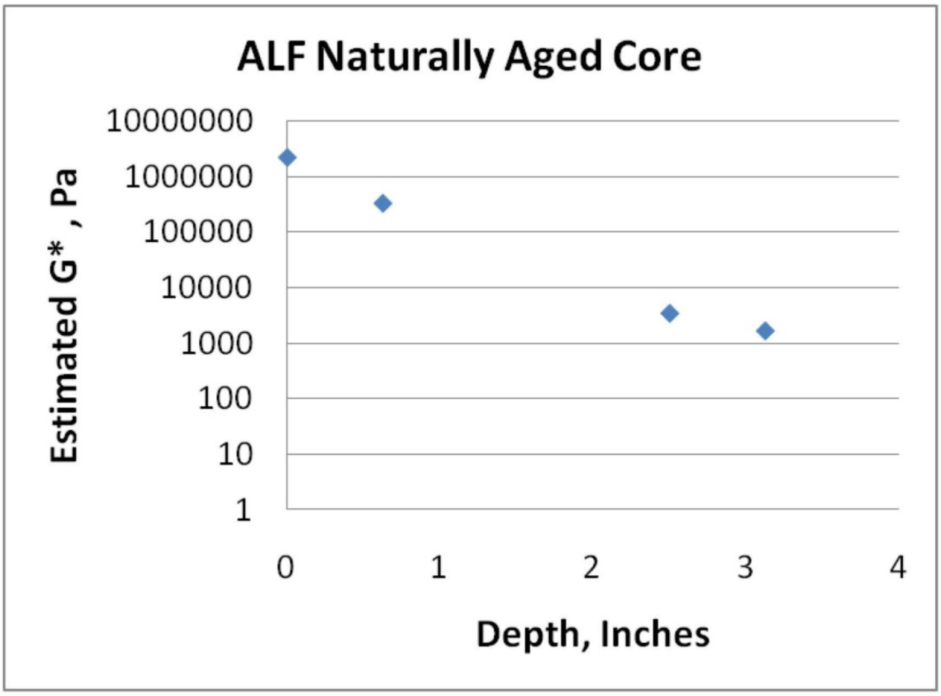
- **Oxidation gradients form in pavements**
- **Extreme stiffness gradients are the result**

WesternResearch INSTITUTE

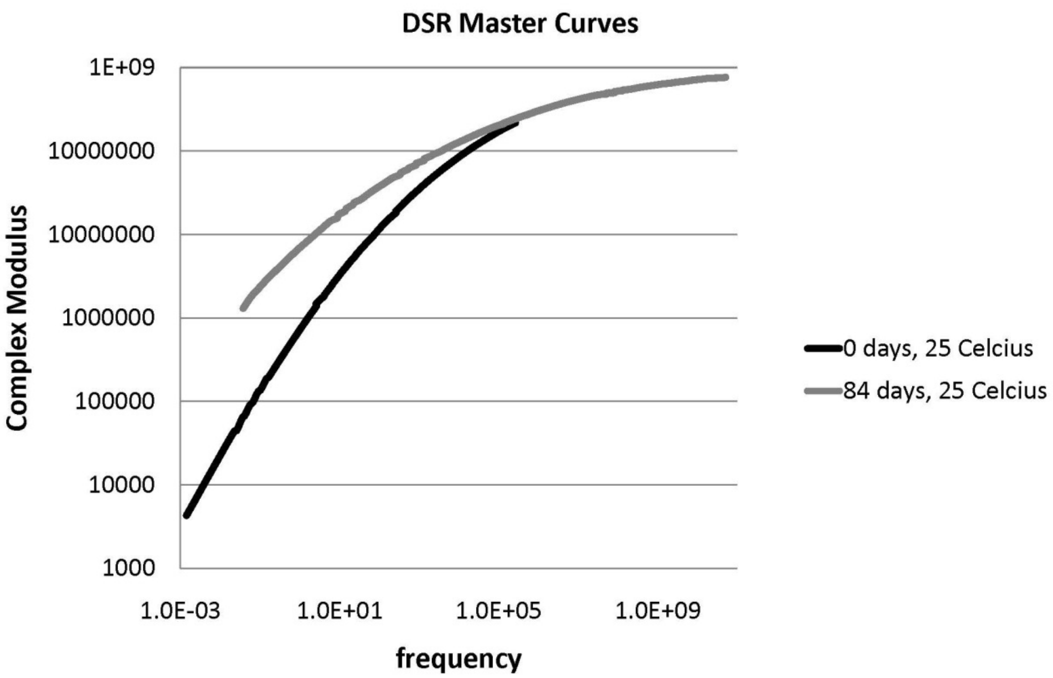
## Oxidation in Pavements



## Complex Modulus with Depth



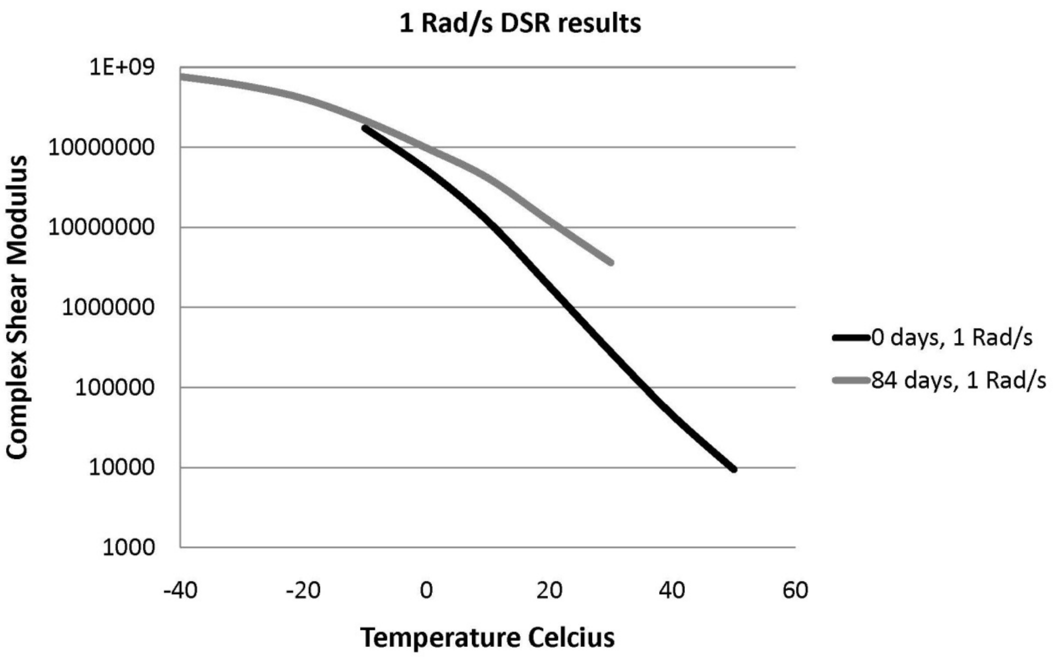

## Master Curve changes with oxidation



ISBN 978-94-6186-524-3

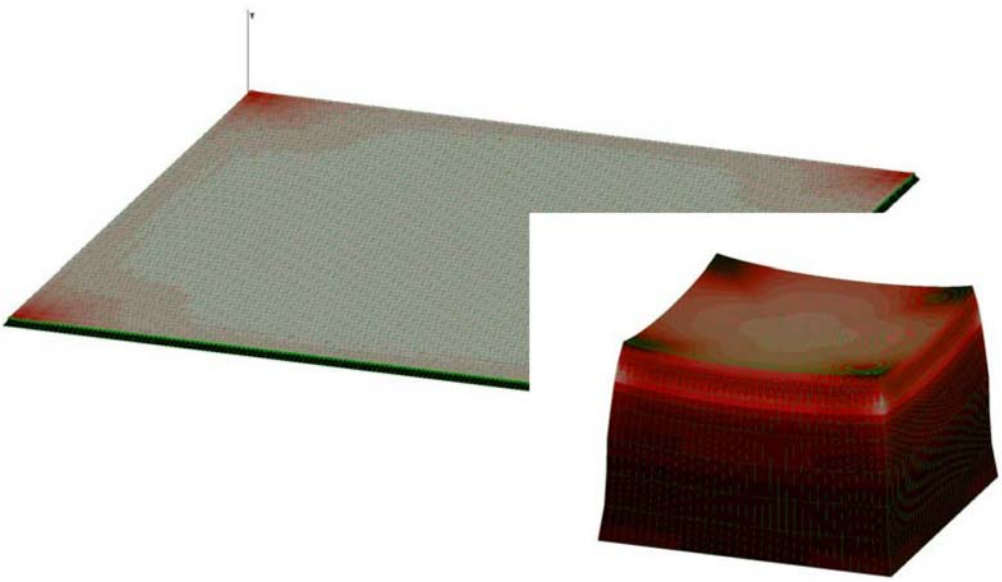

WesternResearch INSTITUTE

## *Master Curve changes with oxidation*



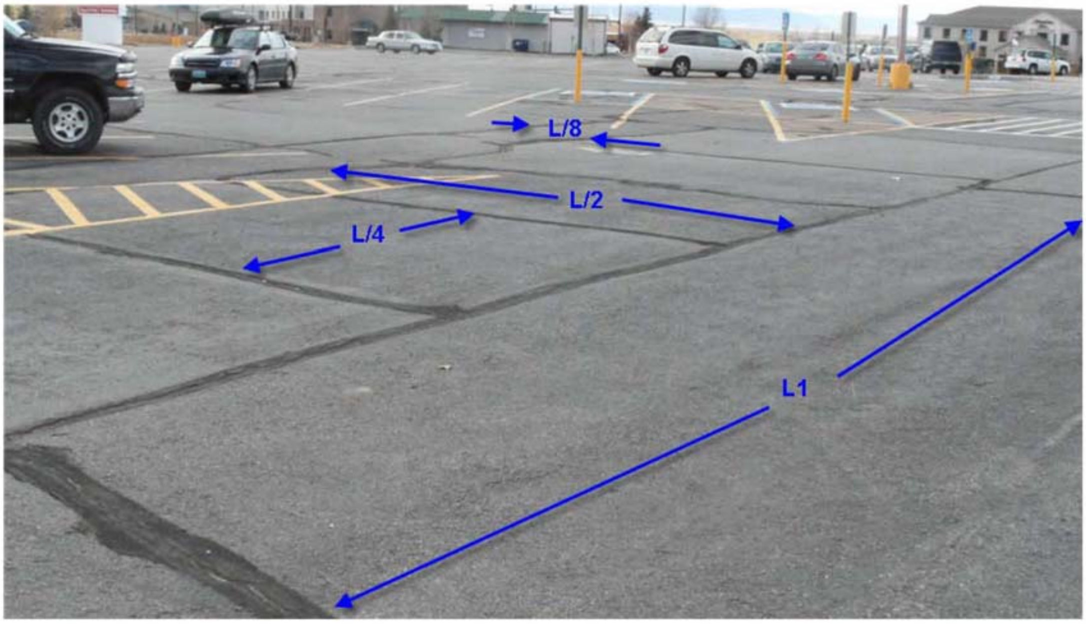

WesternResearch INSTITUTE

## *Static-Elastic Modeling of Thermal Stresses… Aging and Block Cracking*



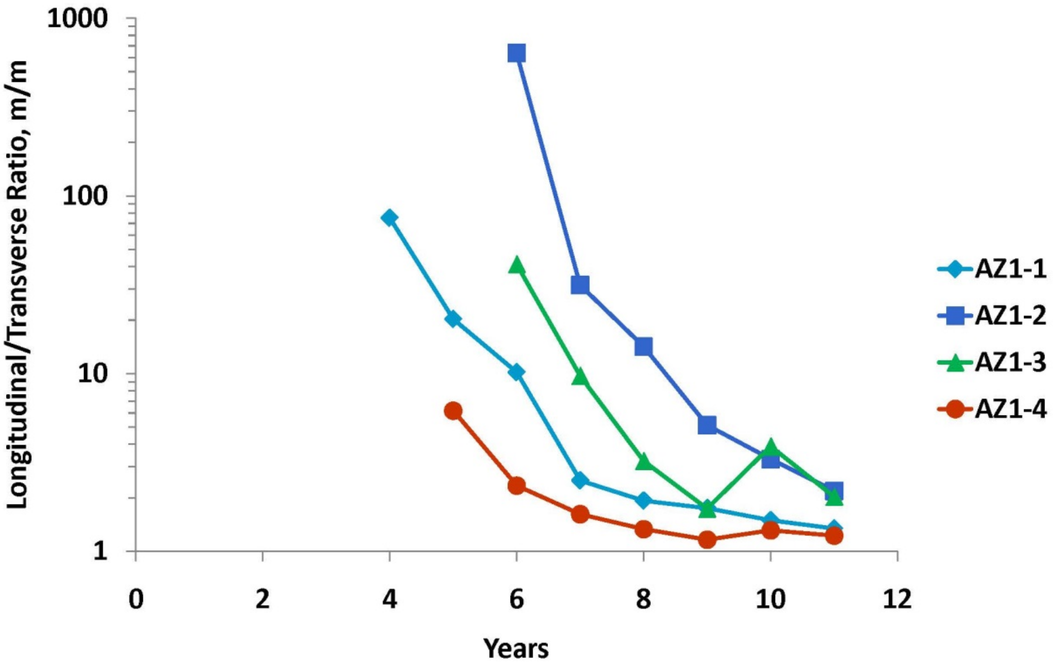
Western Research INSTITUTE

## *Static-Elastic Modeling of Thermal Stresses… Aging and Block Cracking*




Western Research INSTITUTE

## *AZ1 Distress Data*



WesternResearch INSTITUTE

## *Pavement Performance Prediction*

- **Knowing this gradient, mechanical deflection and fracture models for pavement can predict it's performance**

WesternResearch INSTITUTE

## *Why Gradients*

- **The rate of oxidation at any point in the pavement depends on temperature and oxygen concentration.**
- **Daily temperature extremes are greatest at the surface, so rates are fastest at the surface.**
- **Access to oxygen is greatest at the surface as well.**

Western Research INSTITUTE

## *Can we predict the stiffness gradient?*

- The physics of heat transfer are well known. Very good transient temperature models exist.
- The physics of mass transfer (diffusion, permeation, capillary flow, thermal pumping) are also well known.
- These must be coupled with the oxygen consumption to predict the concentration of oxygen in each point in the pavement section.
- The chemistry of asphalt oxidation(oxygen consumption) is less well known, but is understood well enough get a rate calculation ←
- The relationship between mechanical properties (rheology) and oxidation must also be understood. ←

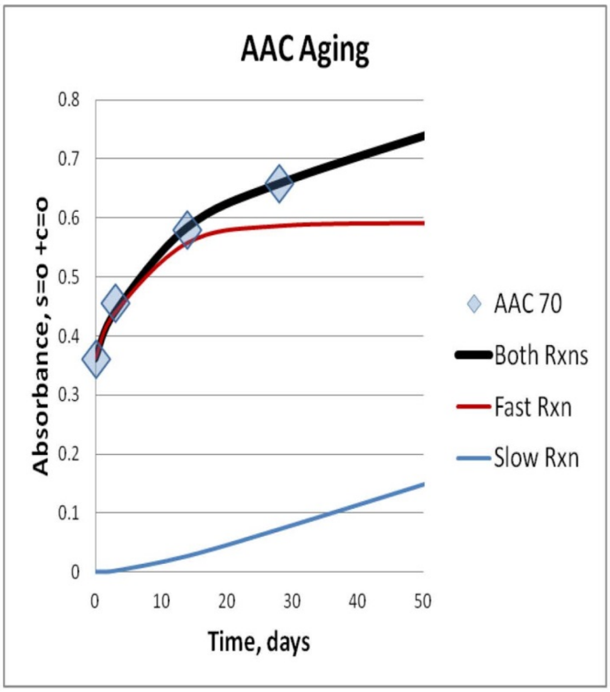
Western Research INSTITUTE

## *Fundamental Approach Oxidation Rate*

- "Fast and Slow Reaction" Dual Reaction Mechanism (Petersen) rate limiting steps

WesternResearch INSTITUTE

## Dual Reaction Model




Fast Reaction:

**RM+$O_2$→Products +FR***

Slow Reaction:

**BC+FR*→BC*+$O_2$→Products +FR***

RM is reactive material

$O_2$ is molecular oxygen

FR* generic free radical

BC is benzyl carbon

BC* is benzyl carbon radical

WesternResearch INSTITUTE

## Universal Rate Equation ?

$$\left[P(t)\right] = M\left(1-\frac{k_2}{k_1}\right)(1-e^{-k_1 t}) + k_2 M t + \left[P_{1,0}\right]$$

$$[sulfoxide + carbonyl] =$$

$$M\left(1-\frac{k_2}{k_1}\right)(1-e^{-k_1 P_{O_2}{}^{n} t}) + k_2 P_{O_2}{}^{m} M t$$

$$+\left[sulfoxide + carbonyl\right]_{rtfo}$$

Western Research INSTITUTE

## One Adjustable parameter

- 34 binders fit with fit qualities exceeding 0.9 (r-squared)
- Also works with RAP-Virgin Binder Blends using simple volumetric blending rules
- Also works with PMA

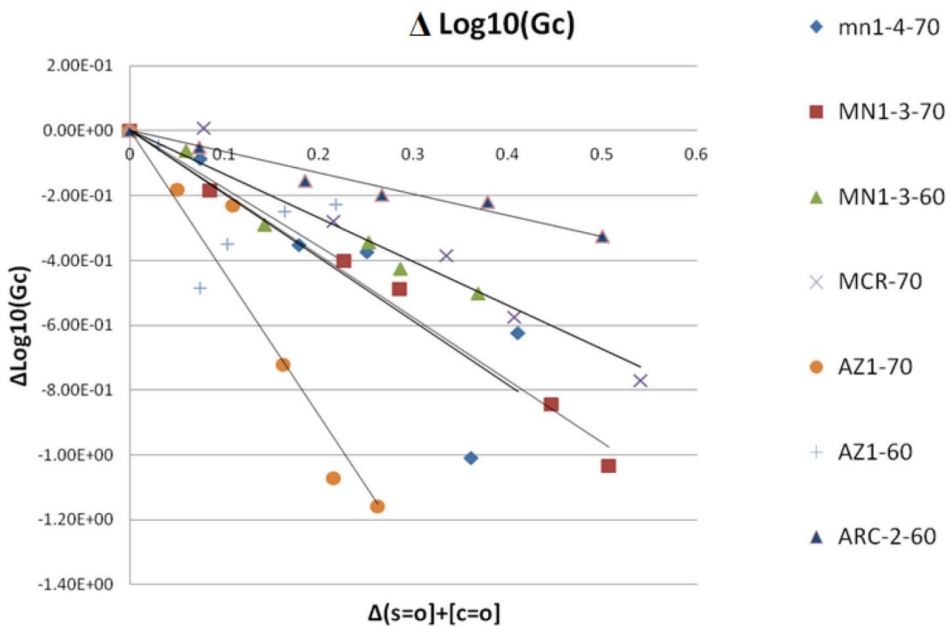
Western Research INSTITUTE

## Complete Picture

- Chemical rate information alone is useless to the pavement designer
- We also need the relationship to rheology
- Empirical data fits suggest a log-linear relationship exists between asphalt binders and rheological master curves
- These relationships depend upon the source, but only two oxidation condition samples are needed to find the relationship. If pressure acceleration is used, a four sample matrix is required.

WesternResearch INSTITUTE

## Example rheology correlations




WesternResearch INSTITUTE

## Moving Forward

- Long oxidation tests are not practical for routine characterization
- A good deal of our work focuses on this issue, developing practical tests for specification and mechanical model inputs.
- We also look carefully at detailed chemistry for material design solutions/opportunites

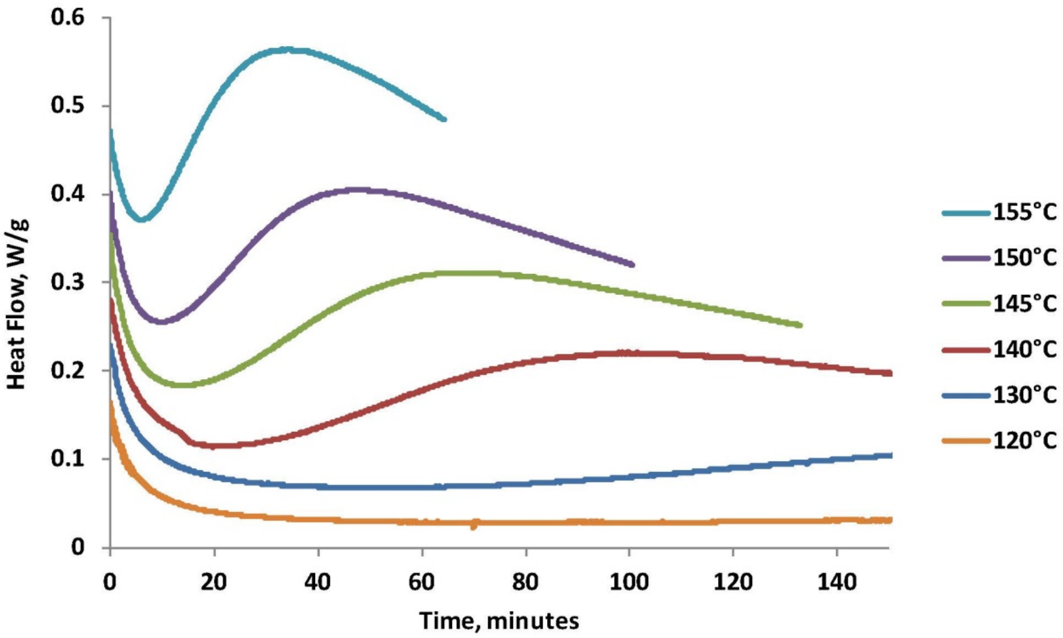
Western Research Institute

## Accelerate the reaction

- The reactive material can be found from the y intercept and slope with a bit of algebra from the long term data.
- But, we need to do the test quickly
- Pressurized Differential Scanning Calorimetry (PDSC) is being studied to investigate acceleration options.
- We have found the mechanism is more complex at elevated temperature and pressure
- We have a preliminary model that fits the available data
- Once validated ( and perhaps improved) , the rate expression for a binder could be determined in a day, not 2 months.
- We are also looking at direct chemical methods to eliminate oxidation tests and rheology altogether.

Western Research Institute

## Heat flow overlay at 550 psia $O_2$




2

WesternResearch INSTITUTE

## Extended Model

$$M + O_2 \xrightarrow{k_1} P_1 + F_1 ; P_1 \xrightarrow{k4} F_3$$

$$F_1 + C_3 \xrightarrow{fast} C_3^* + O_2 \xrightarrow{k_2} F_1 + nF_2 + P_2$$

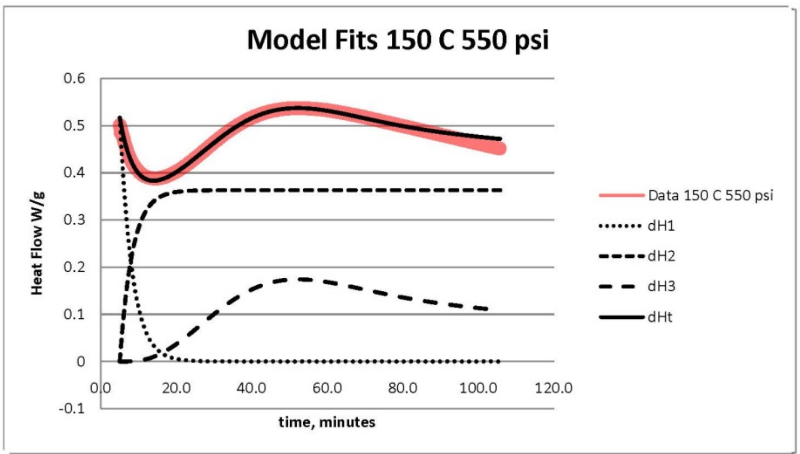
$$F_2 + F_3 \xrightarrow{k_3} \xrightarrow{fast\ oxidation\ steps} P_3$$

- **$F_1$ is small and mobile**
- **$F_2$ and $F_3$ are big and have some steric hindrance**
- **$k_3$ should be independent of pressure**

23

WesternResearch INSTITUTE

## Fits




24

Western Research INSTITUTE

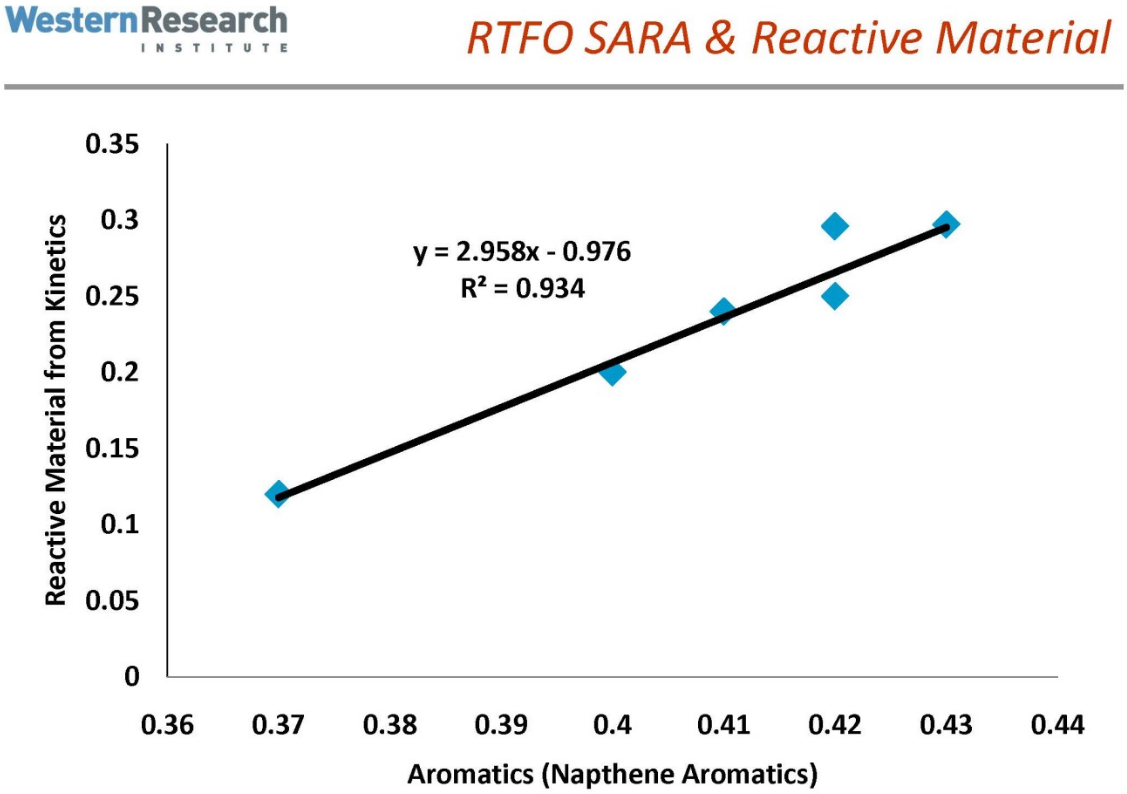
## Direct chemical methods

- IR
- SAR-AD
- GPC (SEC)

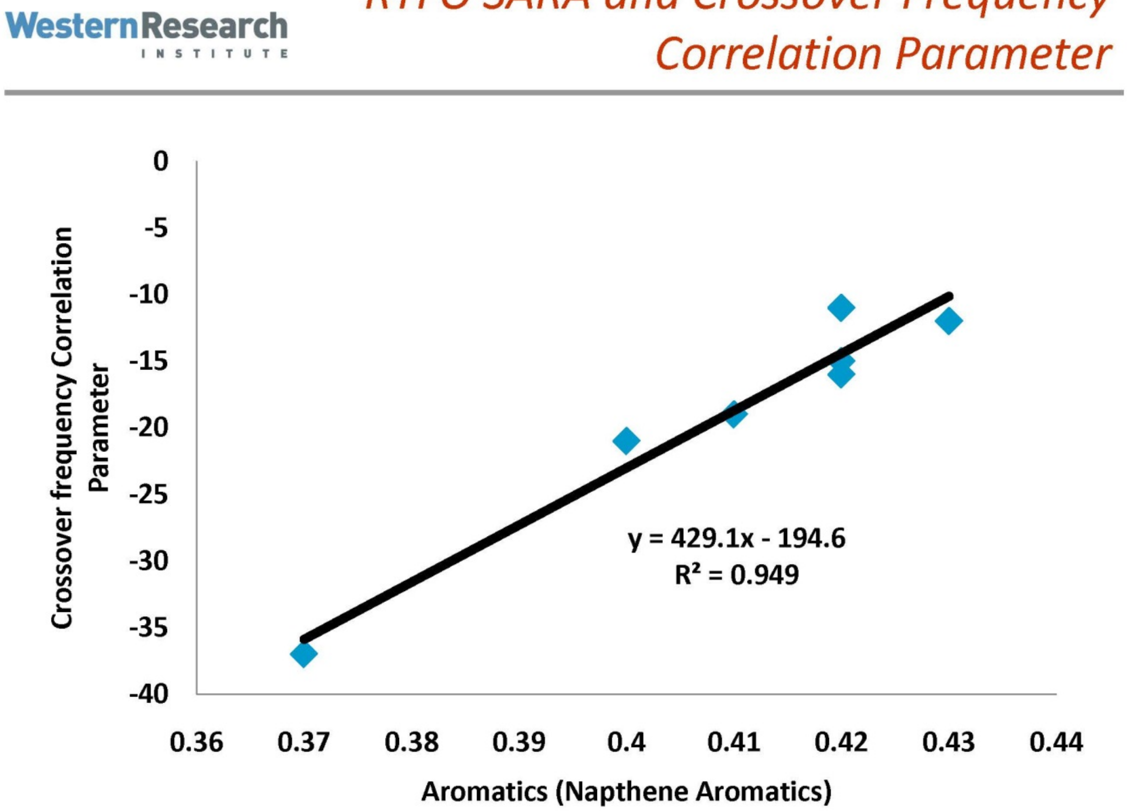
Western Research INSTITUTE

- Best results for directly obtaining reactive material and the rheology response has been from SARA data

## RTFO SARA & Reactive Material

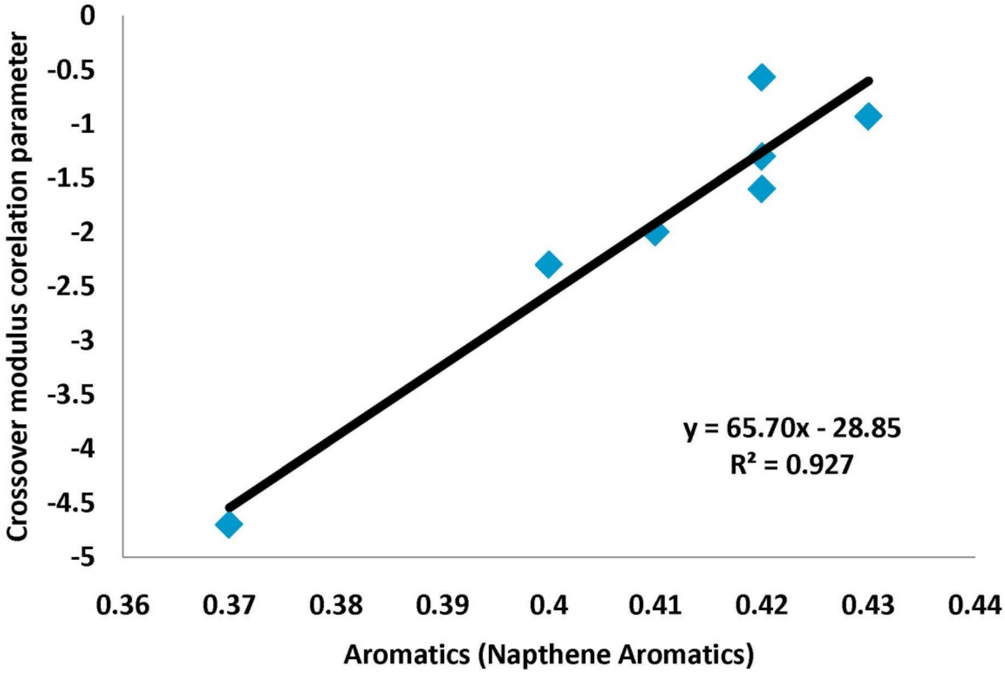



## RTFO SARA and Crossover Frequency Correlation Parameter



WesternResearch INSTITUTE

## RTFO SARA and Crossover Modulus Correlation Parameter




WesternResearch INSTITUTE

## Near Term Approaches

- Generated samples from PAV and extended PAV at 2 pressures can be analyzed with IR and DSR to get the reaction rate and rheological behavior.
- This approach would take about a week, perhaps a little less.

Western Research INSTITUTE

## Conclusions

- **Much better oxidation characterization information suitable for specification and/or model predictions can be obtained with some minor modifications to accepted methods (will need to be validated).**
- **Very rapid methods are on the horizon and appear to be feasible.**

Western Research INSTITUTE

## Selected References


- Fundamental Properties Final Report Drafts. Available by request from WRI.
- Glaser, R. R., J. F. Schabron, T. F. Turner, J-P. Planche, S. L. Salmans, and J. L. Loveridge, 2013, Low-Temperature Oxidation Kinetics of Asphalt Binders. *Transportation Research Record, Journal of the Transportation Research Board, No. 2370, 63-68.*
- Boysen, R. B., and J. F. Schabron, 1993, The Automated Asphaltene Determinator Coupled with Saturates, Aromatics, and Resins Separation for Petroleum Residua Characterization. *Energy & Fuels, 27: 4654-4661; http://pubs.acs.org/doi/pdf/10.1021/ef400952b*
- Schabron, J. F., R. B. Boysen, E. W. Kalberer, and J. F. Rovani, 2012, Automated Asphaltene Determinator and Saturates, Aromatics, and Resins Integrated Separation. *Preprints, Div. of Petroleum Chemistry, American Chemical Society, 57 (1): 1-3.*
- Huang, S.C., R. Glaser, and F. Turner, 2012, Impact of Water on Asphalt Aging. *Transportation Research Record 2293, 64-72.*
- Glaser, R. R, and J. L. Loveridge, 2012, Low Temperature Oxidation Kinetics of Asphalt Binders. *Preprints, Div. of Petroleum Chemistry, American Chemical Society, 57 (1): 9-11.*
- Petersen, J. C., and R. Glaser, 2011, Asphalt Oxidation Mechanisms and the Role of Oxidation Products on Age Hardening Revisited. *Road Materials and Pavement Design, 12 (4): 795-819.*

## *8.3 Hilde Soenen, Nynas, What happens during aging and where is aging happening?*


Outline | Accelarated aging | Field aging studies | Binder films

# Outline

- **PART 1:** Accelarated aging in RTFOT+PAV:
  - -Rheological and chemical changes during standard accelarated aging tests
  - -How important is the aging temperature ?
- **PART 2:** Field aging, using recovered binders
  - -Unmodified (& pmbs)
- **PART 3:** Field aging, leaving a bitumen film outside
  - -To avoid the recovery step, bitumen films were left outside

2

ISBN 978-94-6186-524-3


# PART I: Accelarated aging

NYNAS

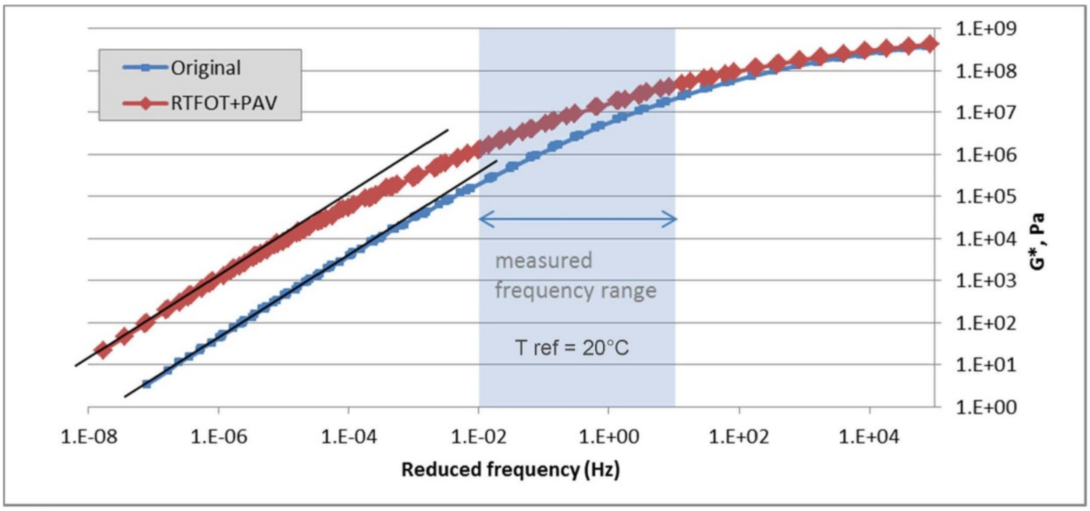
| | | Pen | R&B | PI | melting enthalpy (J/g) |
|---|---|---|---|---|---|
| B1 | SR + oxidation | 5 | 104.5 | 2.57 | 0.0 |
| B2 | solvent deasphalted | 5 | 74.2 | -0.74 | 0.0 |
| B3 | | 12 | 65 | -0.86 | 1.4 |
| B4 | VB | 15 | 64.2 | -0.64 | 5.6 |
| B5 | | 15 | 62.6 | -0.90 | 2.1 |
| B6 | SR | 20 | 62.2 | -0.49 | 0.0 |
| B7 | SR + air rectified | 25 | 61.5 | -0.21 | 0.0 |
| B8 | Blend: solvent deasphalted + B160/220 | 27 | 55.5 | -1.22 | 2.7 |
| B9 | | 27 | 61.5 | -0.06 | 3.5 |
| B10 | VB | 38 | 54.3 | -0.80 | 5.4 |
| B11 | | 42 | 51.3 | -1.27 | 2.8 |
| B12 | | 51 | 49.1 | -1.39 | 6.0 |
| B13 | VB | 52 | 49 | -1.37 | 6.8 |
| B14 | VB + air rectified | 52 | 49.8 | -1.17 | 6.2 |
| B15 | | 53 | 49.9 | -1.10 | 5.0 |
| B16 | | 61 | 47.7 | -1.34 | 4.9 |
| B17 | | 62 | 50 | -0.69 | 6.3 |
| B18 | SR | 64 | 47.7 | -1.23 | 0.0 |
| B19 | VB | 67 | 46.8 | -1.36 | 7.6 |
| B20 | | 70 | 46.1 | -1.46 | 3.8 |
| B21 | VB | 80 | 45.8 | -1.20 | 7.1 |
| B22 | | 81 | 45.5 | -1.25 | 2.4 |
| B23 | | 107 | 43.5 | -1.09 | 4.0 |
| B24 | VB | 187 | 38.5 | -1.03 | 5.4 |
| B25 | SR | 187 | 36.9 | -1.80 | 0.0 |
| B26 | VB | 190 | 39.2 | -0.63 | 9.6 |
| B27 | | 200 | 37.7 | -1.11 | 6.1 |

VB: Visbroken
SR: Straight-run or distilled

3

# Accelarated aging

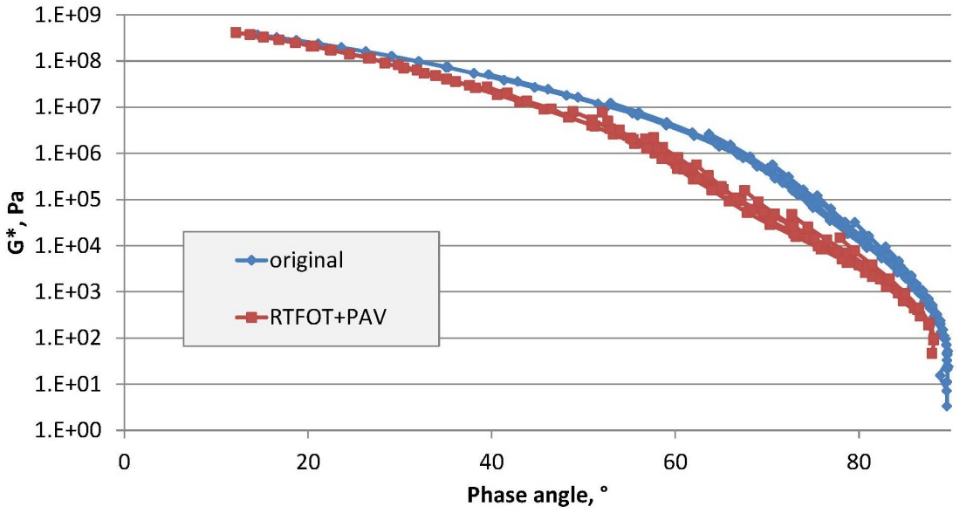
1. Mechanical changes in the linear visco-elastic region:




4

# Accelarated aging

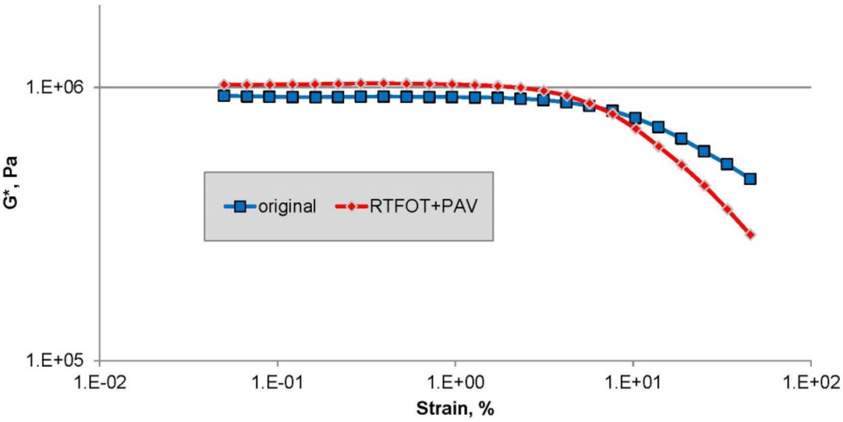
1. Mechanical changes in the linear visco-elastic region:




5

# Accelarated aging

2. Mechanical changes in the non-linear visco-elastic region:

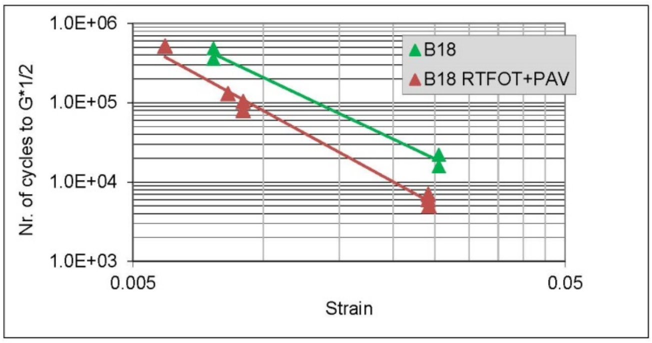


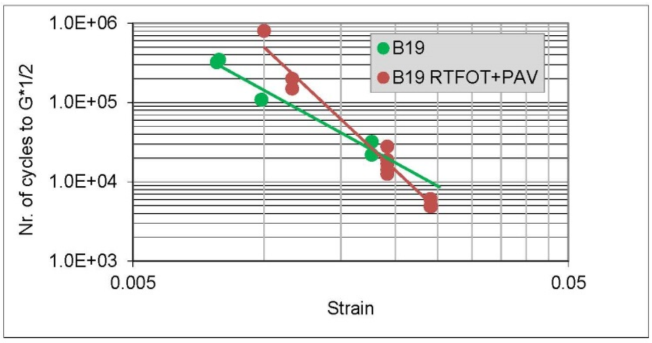

6

# Accelarated aging

3. Mechanical changes in the fatigue behavior:

(Controlled strain test in DSR, 10°C, 10Hz)



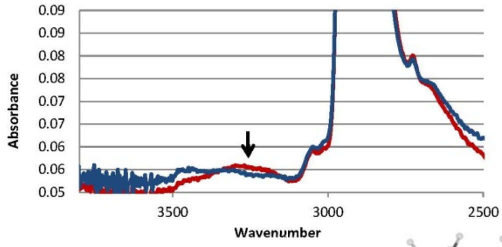

Upper figure: SR
Lower figure: VB

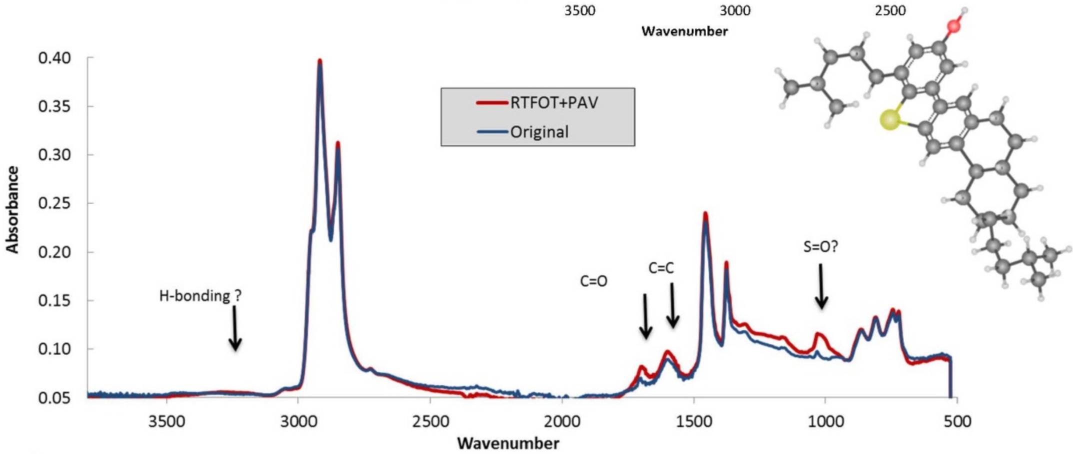
7

 ISBN 978-94-6186-524-3 

# Accelarated aging

4. Chemical changes, FT-IR:



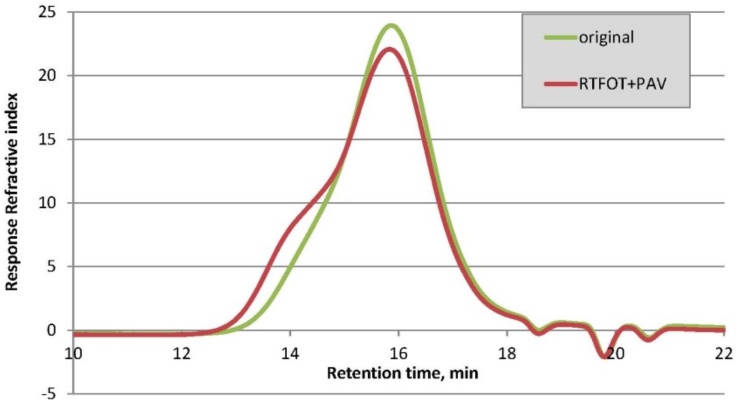



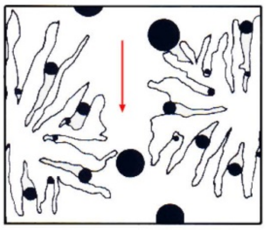

8

 ISBN 978-94-6186-524-3 

# Accelarated aging

5. Chemical changes, GPC:



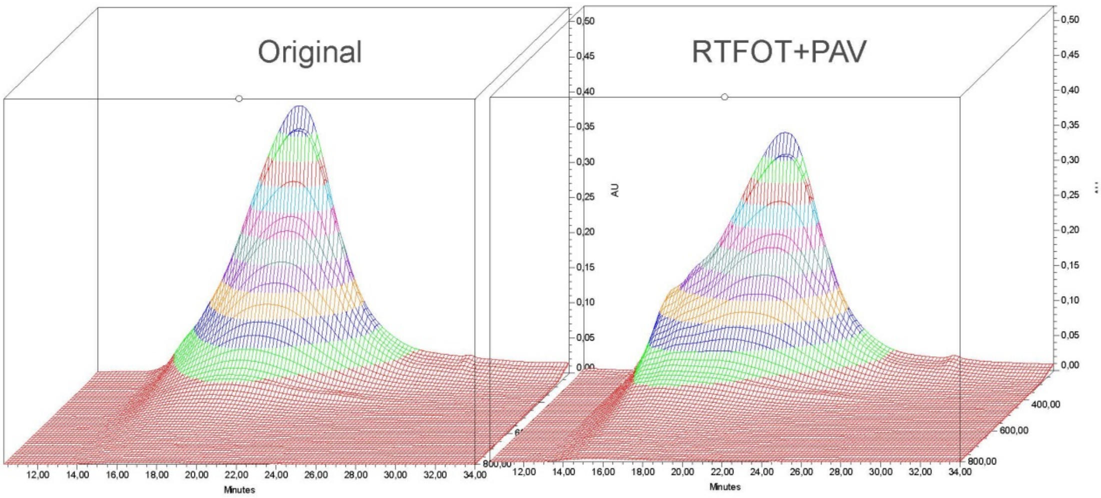



Separation based on molecular size (ideally)

9

# Accelarated aging

6. Chemical changes, GPC: uv-vis absorptions

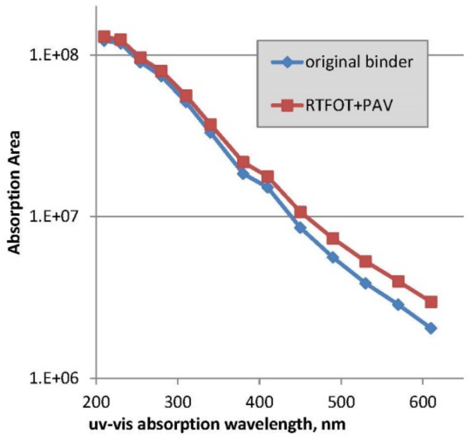



10

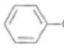
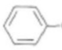
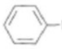
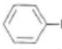
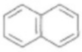
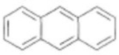
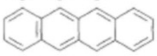
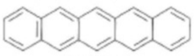
ISBN 978-94-6186-524-3


# Accelarated aging

6. Chemical changes; uv-vis absorptions




Effects of Structure on Electronic Absorption Corresponding to the Benzenoid Band

| Compound | $\lambda_{max}$, nm* | $\epsilon_{max}$ |
|---|---|---|
|  | 255 | 230 |
|  —$CH_3$ | 261 | 300 |
|  —CH=$CH_2$ | 282 | 450 |
|  —I | 256 | 800 |
|  —$NH_2$ | 280 | 1,430 |
|  | 314 | 316 |
|  | 380 | 7,900 |
|  (naphthacene) | 480 | 11,000 |
|  (pentacene) | 580 | 12,600 |

*Mostly in ethanol solution

11

# Accelarated aging

NYNAS

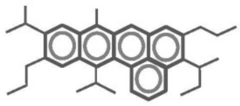
**Conclusions accelarated aging (RTFOT+PAV):**

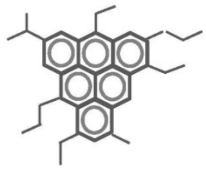
Mechanical:

-decreased temperature sensitivity, more structured black curve
-decreased LVE region at the same stiffness level
-changes in fatigue behavior

Chemical:

-more C=O, more C=C, more S=O, some hydrogen bonding
-increase in (apparent) molecular weight
-increase in larger conjugated aromats
-higher total acid number (TAN)





**Ongoing activities:**

Difference between RTFOT and PAV, aging temperature
Low temperature fracture properties
Aging index – how to quantify

12

# Aging temperature

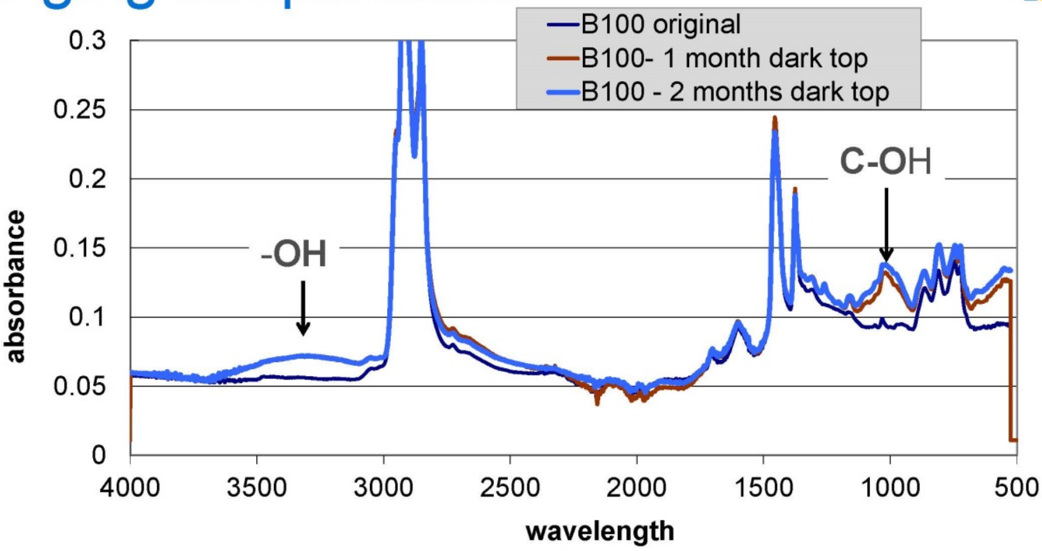
Qualitative measurements mainly using FT-IR:

1. Straigth disstilled binder v/s an oxidized binder (obtained in a refinery process, temp. is 240°C)
2. An original binder aged during PAV 60°C - 10 days
3. An original binder that is dark aged at room temperature (20°C) (2 years)

13

 ISBN 978-94-6186-524-3 

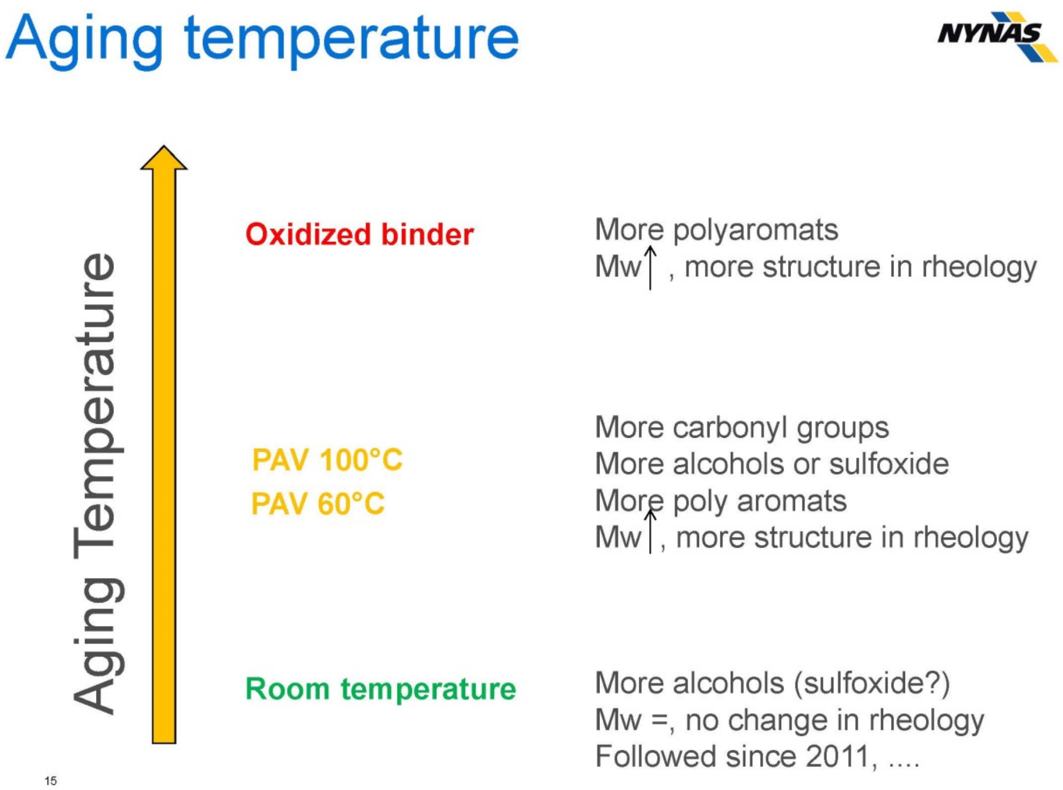
# Aging temperature




Dark aging - room temperature:
no formation of carbonyl groups, no increase in aromaticity;
increased hydrogen bonding and an increased signal at 1000 $cm^{-1}$

14

ISBN 978-94-6186-524-3

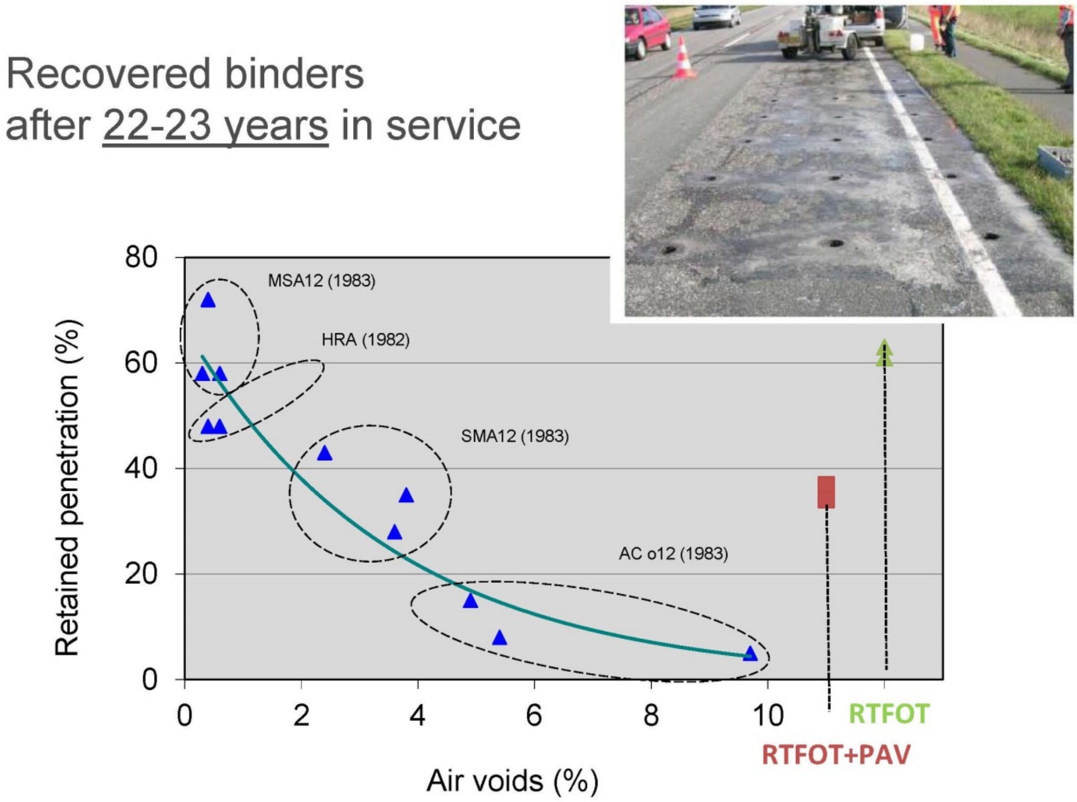
NYNAS

# PART II: Field aging & recovered binders:

- **Long Lasting Asphalt Pavements and Bitumen Ageing** *Xiaohu Lu , Per Redelius , Hilde Soenen , Mikael Thau,* E&E conference 2012

- **Durability of Polymer Modified Binders in Asphalt Pavements**, *Xiaohu Lu, Hilde Soenen, Serge Heyrman, Per Redelius,* ISAP conference 2014

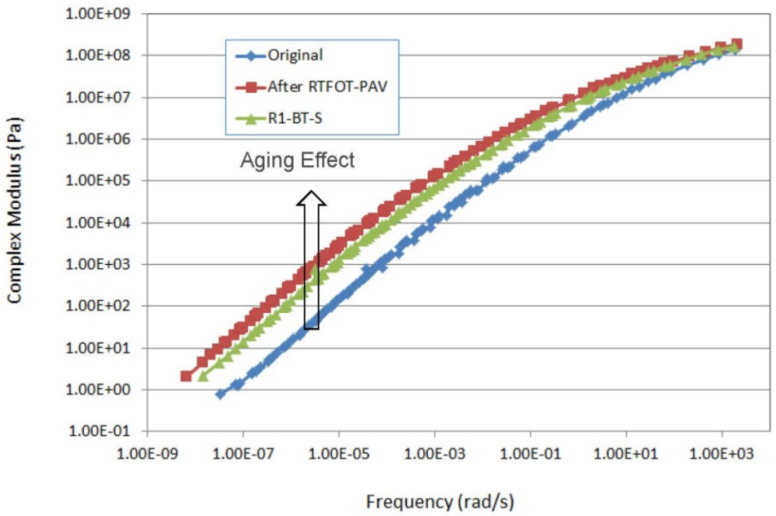
16


Recovered binders
after 22-23 years in service
80
60
40
20
0
0
2
4
6
8
10
Retained penetration (%)
Air voids (%)
MSA12 (1983)
HRA (1982)
SMA12 (1983)
AC o12 (1983)
RTFOT
RTFOT+PAV

# Recovered binders – 6 years in the field (air voids ~ 1%)

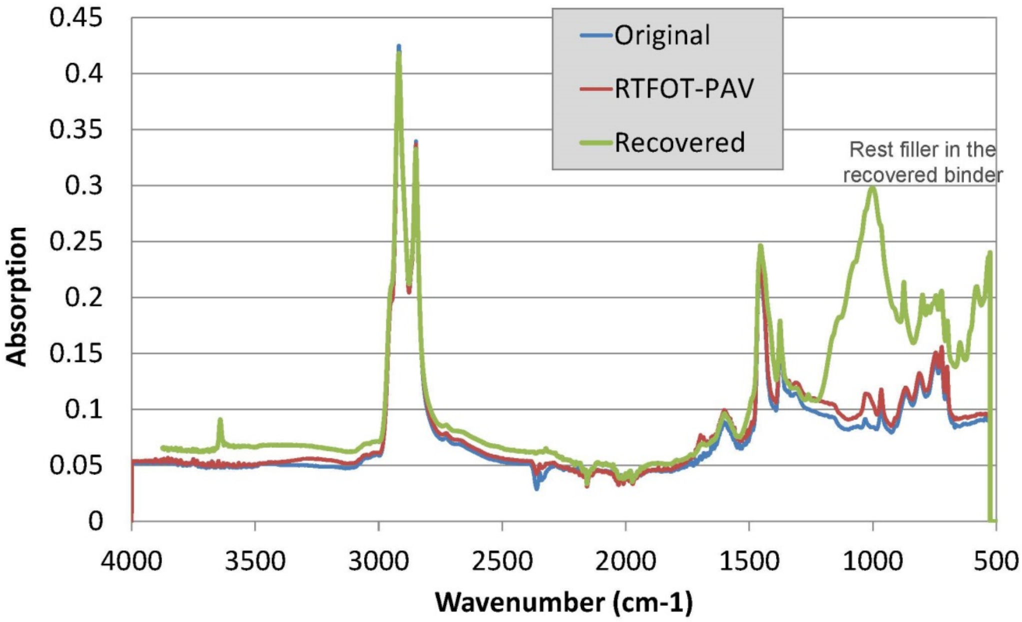
## DSR Master Curve at 10°C

*Wearing Course, Bitumen 70/100*




18

# Further analysis of recovered binders:



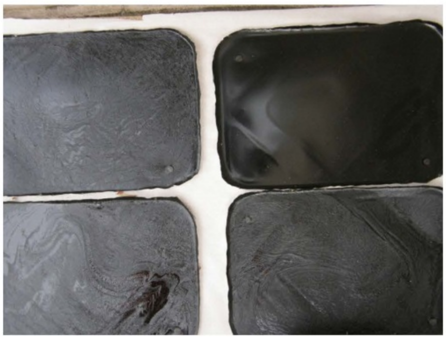

19

# PART III: Bitumen films left outside:

Two sets of bitumen samples were placed outside for 1 year:

- One set got as much sun as possible
- Another set without direct sun light

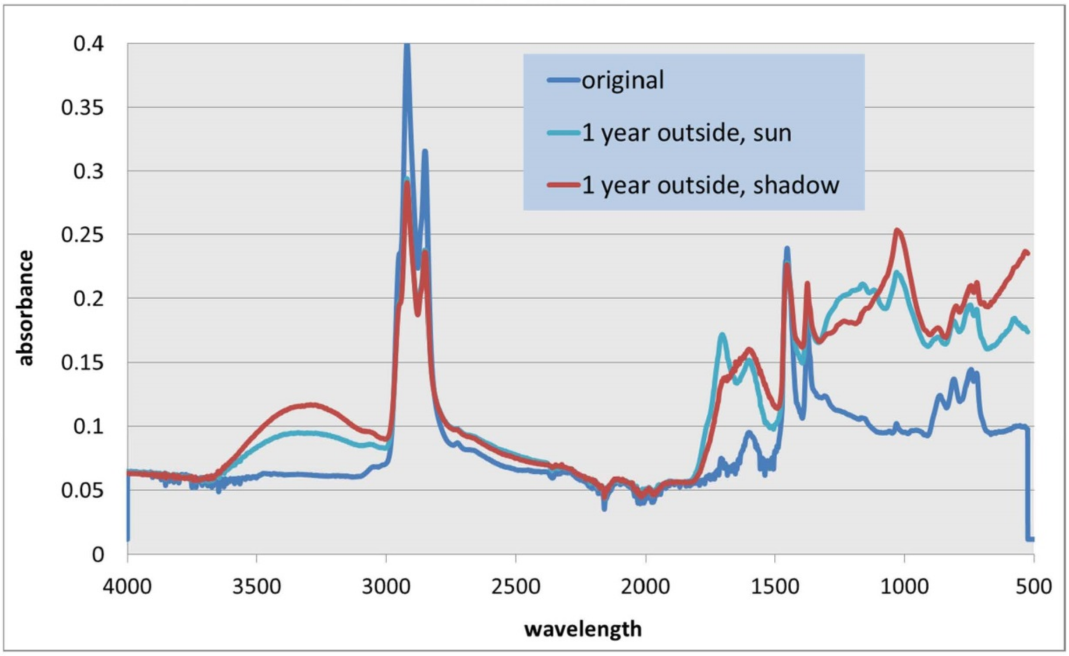
After 1 week:



After 1 year:

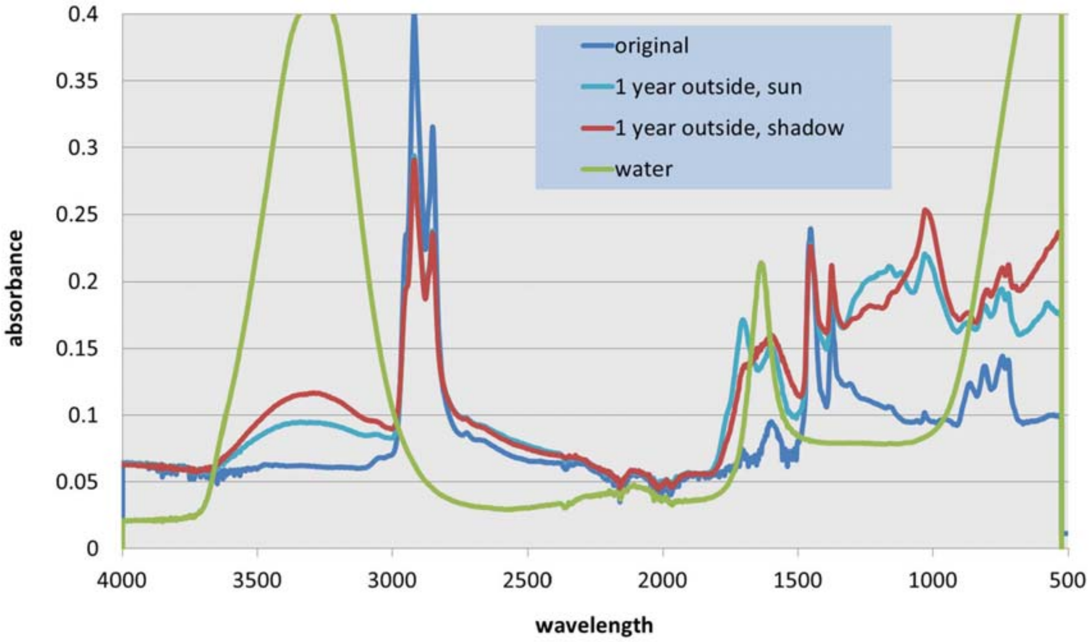
20

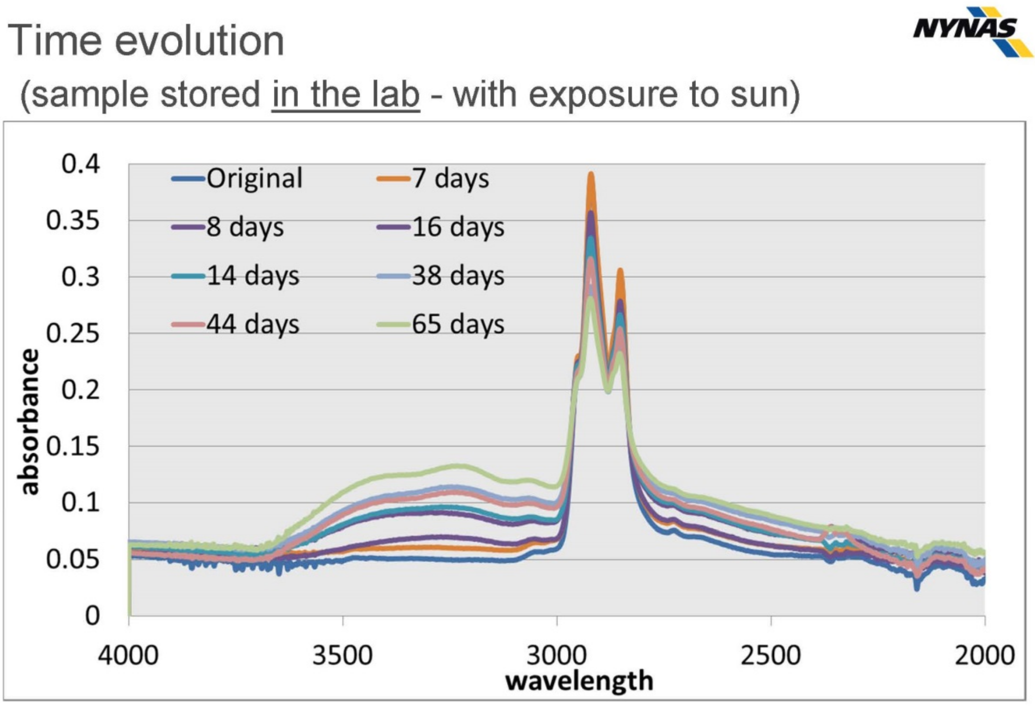
# Bitumen films left outside :

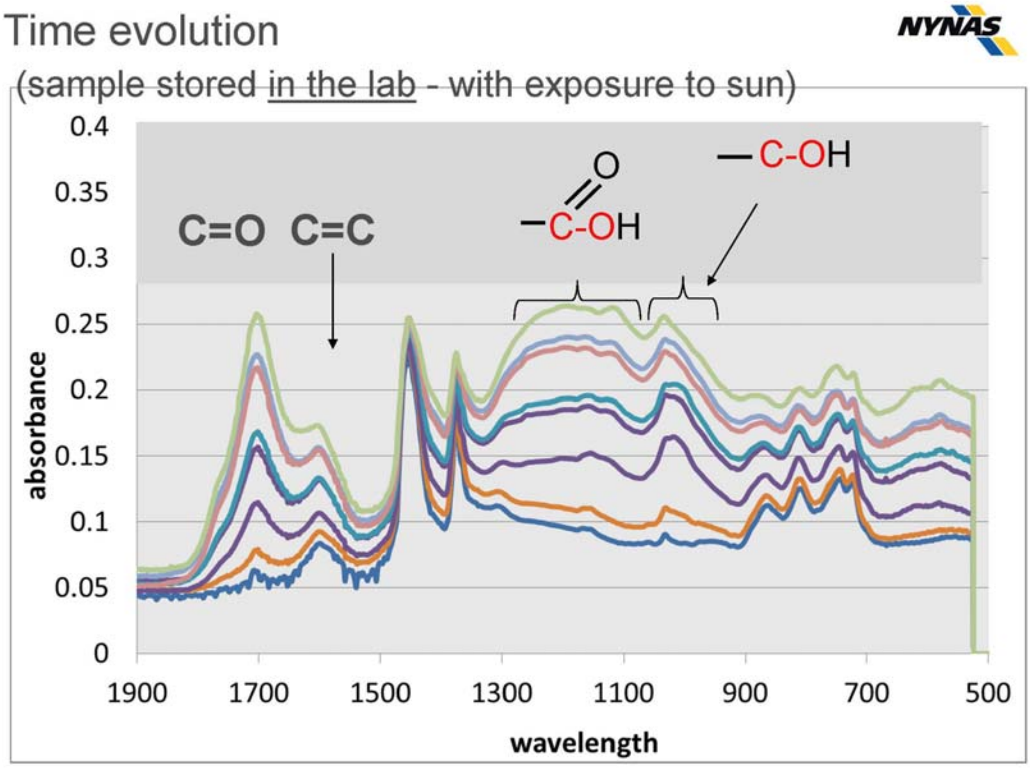



21

## Water?

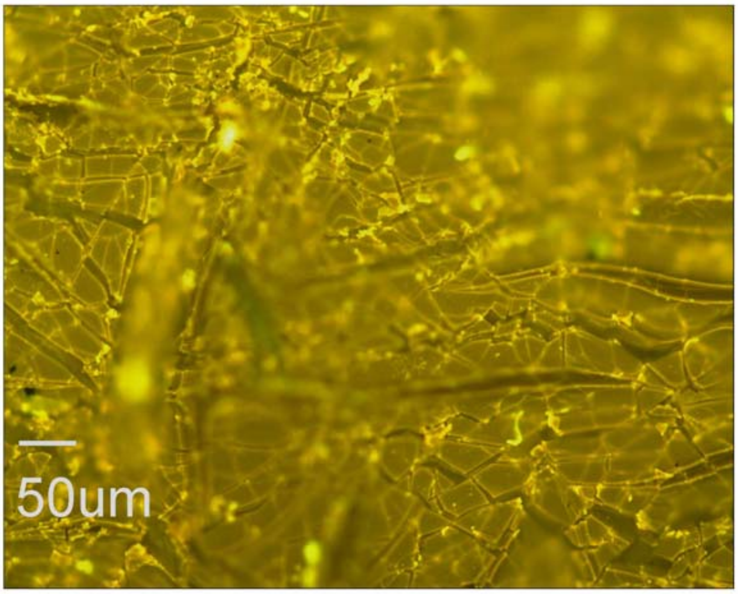

original
1 year outside, sun
1 year outside, shadow
water
absorbance
wavelength
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
4000
3500
3000
2500
2000
1500
1000
500


Time evolution
(sample stored in the lab - with exposure to sun)
NYNAS
Original
7 days
8 days
16 days
14 days
38 days
44 days
65 days
absorbance
wavelength
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
4000
3500
3000
2500
2000



Time evolution
NYNAS
(sample stored in the lab - with exposure to sun)
C=O C=C
O
—C-OH
—C-OH
absorbance
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
1900
1700
1500
1300
1100
900
700
500
wavelength

## Microscopy, lab aged after 8 months
## 200x magnification

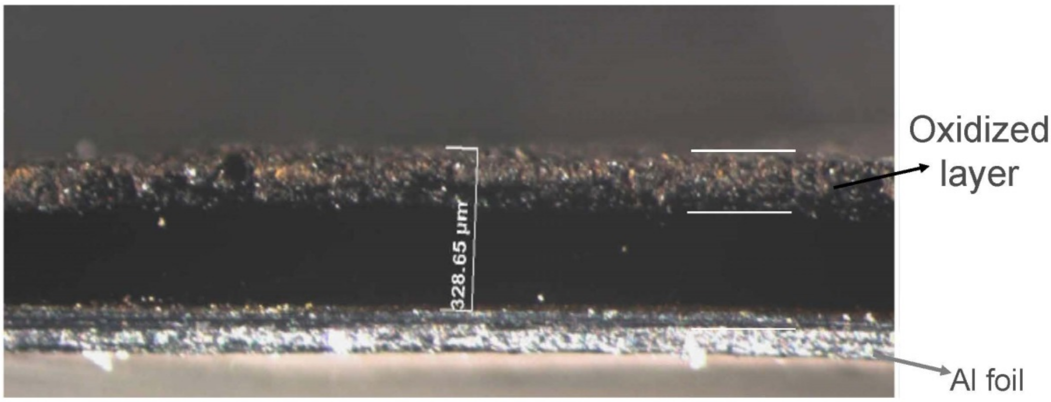



-No loading
-No temp. fluctuations

## Macrotome & microscopy measurements:

Made at Ansers, Louvain La Neuve, Belgium

Visual observations: Color change after oxidation,
Thickness indication of aged layer is ≥ 120 um. (1 year outside)



## Conclusions:

RTFOT + PAV: Similar changes in rheolgical properties
Chemical reactions seem similar as in field aging
Can predict aging for low airvoids (2-4%) pavements

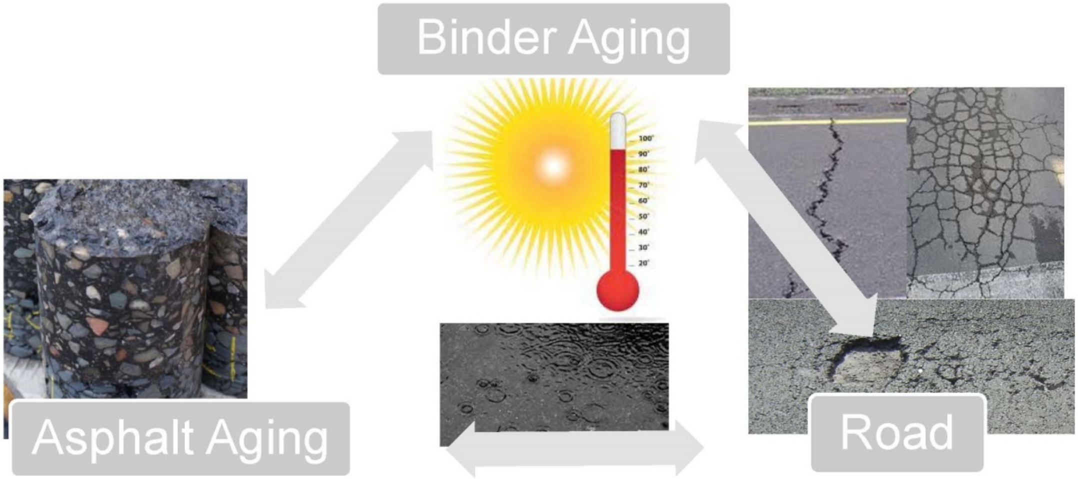
PAV: Open pavements need longer PAV tests
Aging index – what parameter?
Influence of UV light? (raveling, crack initiation top down?)
Influence of aging on adhesion stone-bitumen and water sensitivity?

27

ISBN 978-94-6186-524-3


## Aging :

Which asphalt property deteriorates (first) due to binder aging:
Low temperature cracking? Raveling? Fatigue cracking?
Perform asphalt tests, on aged asphalt specimen (aged in compacted form).




28

## *8.4 Ronald Blab, University of Vienna, How to understand field aging of bitumen - recent experimental and modeling efforts*

TECHNISCHE UNIVERSITÄT WIEN
Vienna University of Technology

### HOW TO UNDERSTAND FIELD AGEING OF BITUMEN - RECENT EXPERIMENTAL AND MODELING EFFORTS

Ronald Blab, Bernhard Hofko, Lukas Eberhardsteiner,
Josef Füssl, Daniel Steiner,
Florian Handle, Markus Hospodka, Hinrich Grothe

Workshop on Bitumen Ageing,
TU Delft, September 2014

---

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

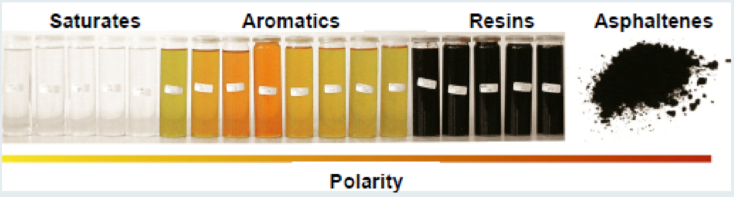
### Outline

- **Bitumen Microstructure & Field Ageing Mechanism**
- Micromechanical Modeling of Binder (Ageing)
- Comparison of Field and Lab Ageing

 ISBN 978-94-6186-524-3 

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

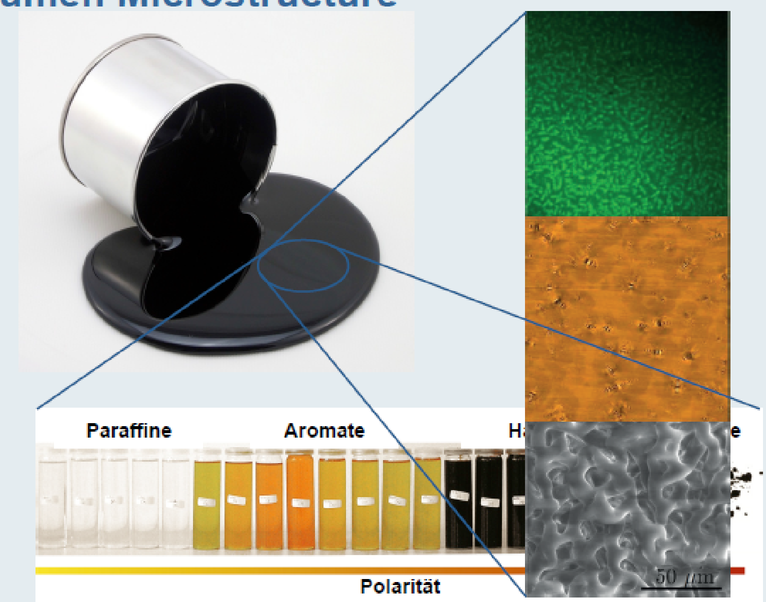
## Bitumen Composition - SARA




- Most common concept to identify constituents of bitumen = **SARA**
- **Asphaltenes** → n-heptane non soluble
- **Maltenes** → n-heptane soluble
- Further separation of Maltenes by chromatographic separation → Saturates, Aromatics, Resins

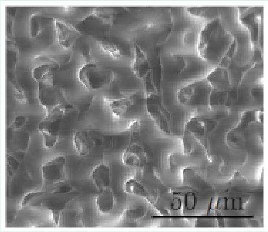
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

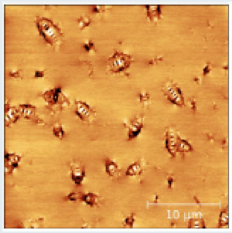
## Bitumen Microstructure

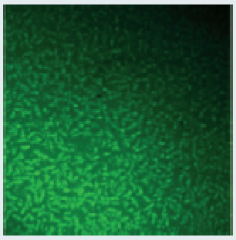


INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Bitumen Microstructure





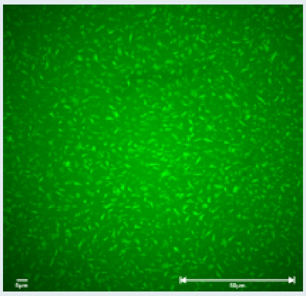
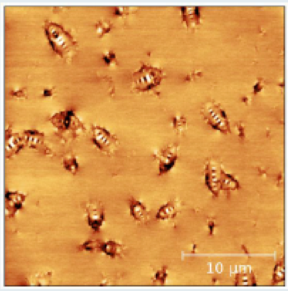


Source: Sayeda Nahar, TU Delft

- Imageing methods to detect microstructure
  - Environmental Scanning Electron Microscopy (ESEM)
  - Atomic Force Microscopy (AFM)
  - Confocal Laser Scanning Microscopy (CLSM)
  - …
- **Micelle structures embedded within a matrix** – different thesis

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Bitumen Microstructure

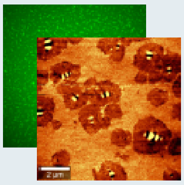

Source: Sayeda Nahar, TU Delft

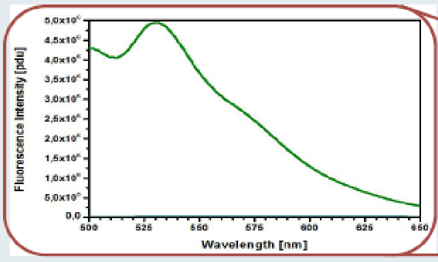
Micro Phase: **2 respective 3 phases distinguishable**
Catana Phase (bees)
Mantle Phase
Matrix

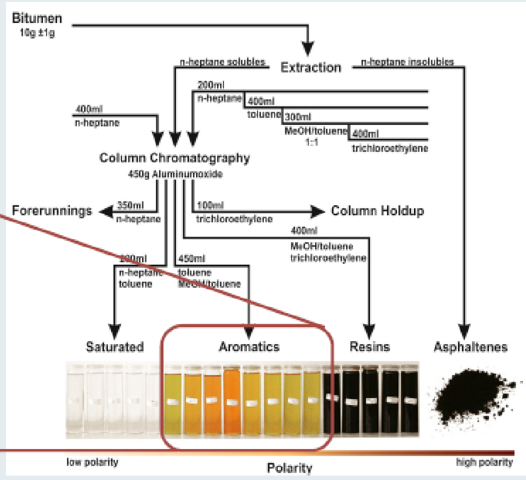
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Bitumen Microstructure

### Identification of phases






**spectroscopy & chromatography**

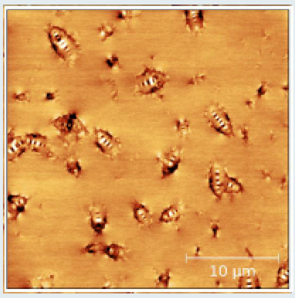
**fluorescence comes from „Aromatics“**

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

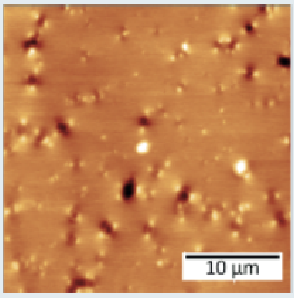
## Bitumen Microstructure

### Identification of phases

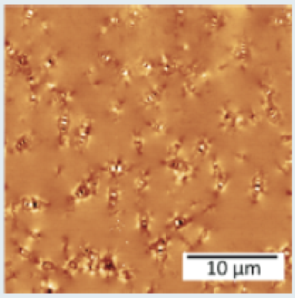
- chromatographic separation of distillation bitumen 70/100 by **n-Heptan-precipitation**
- seperation of asphaltens (non soluble) and maltens (soluble)
- AFM analysis of origin and artificial bitumen with different asphalten content



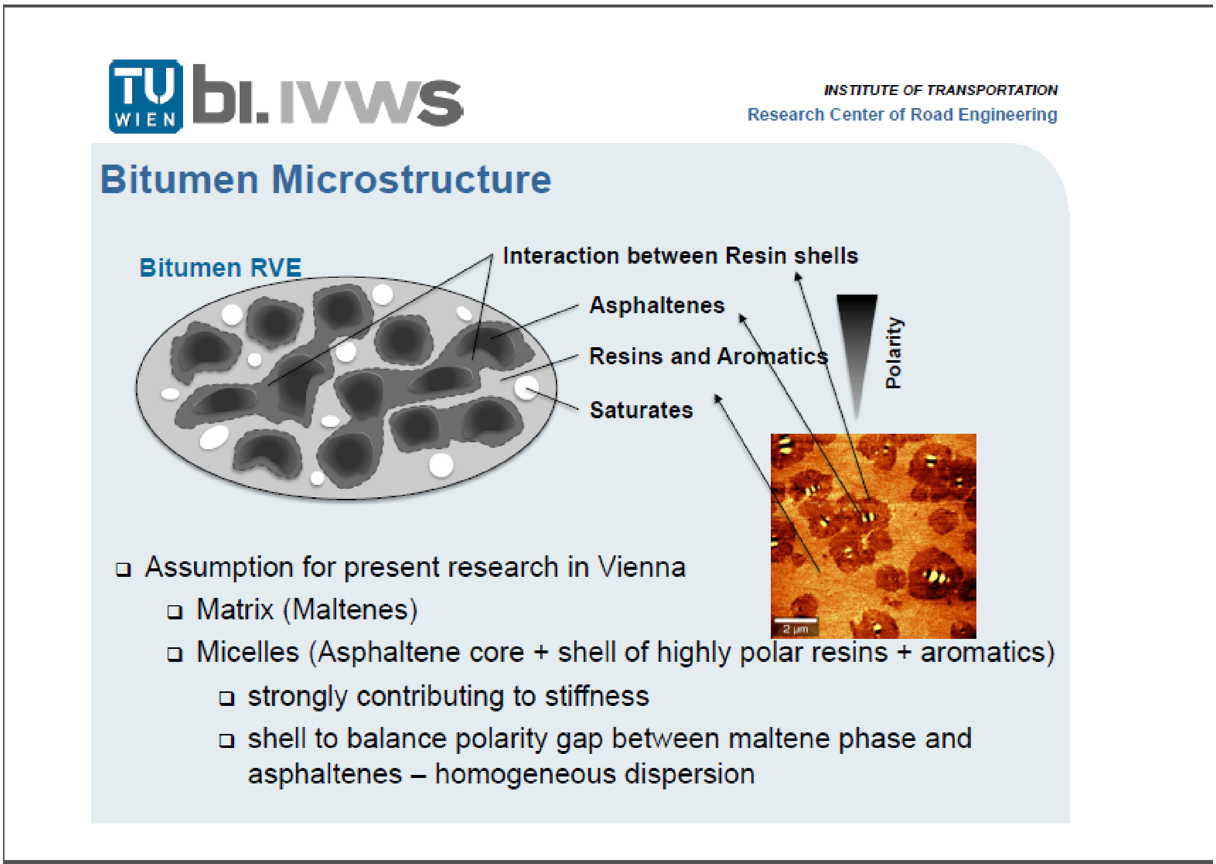

**origin bitumen 10,2% asphaltens**

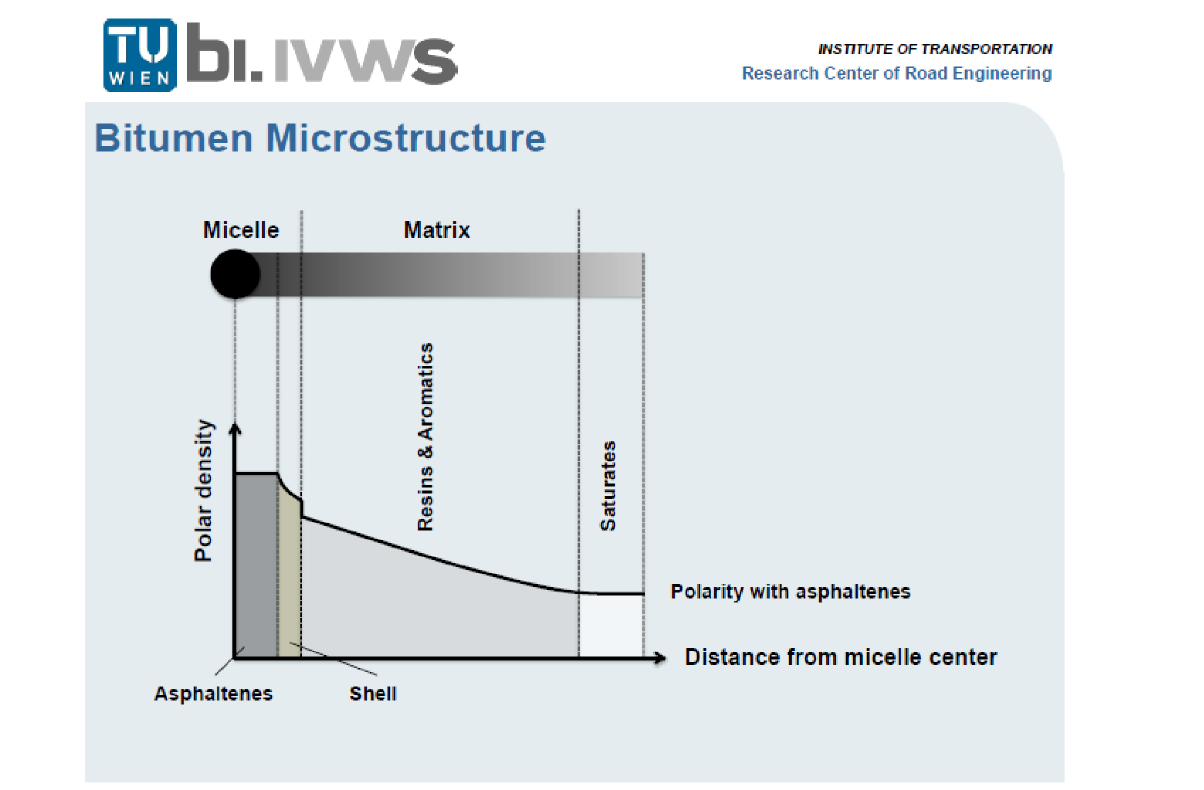



**malten phase without asphaltens**




**artificial bitumen 10 % asphaltens**

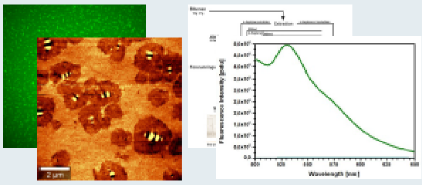

TU WIEN bi.IVWS
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering
Bitumen Microstructure
Bitumen RVE
Interaction between Resin shells
Asphaltenes
Resins and Aromatics
Saturates
Polarity
2 µm
Assumption for present research in Vienna
Matrix (Maltenes)
Micelles (Asphaltene core + shell of highly polar resins + aromatics)
strongly contributing to stiffness
shell to balance polarity gap between maltene phase and asphaltenes – homogeneous dispersion

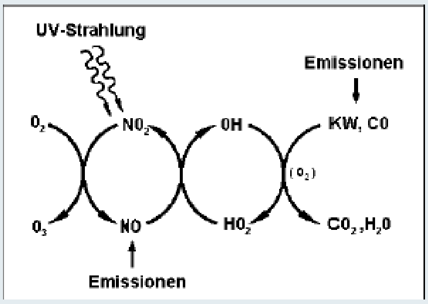

TU WIEN bi.IVWS
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering
Bitumen Microstructure
Micelle
Matrix
Resins & Aromatics
Saturates
Polar density
Polarity with asphaltenes
Distance from micelle center
Asphaltenes
Shell

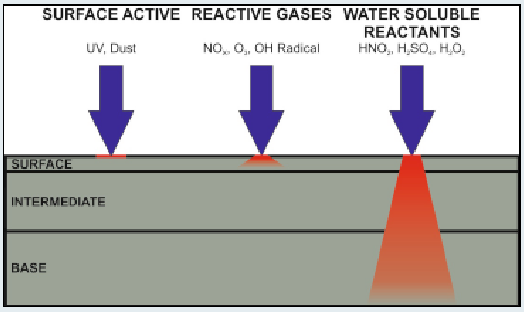
ISBN 978-94-6186-524-3


*INSTITUTE OF TRANSPORTATION*
Research Center of Road Engineering

## Field ageing of Bitumen – influence factors



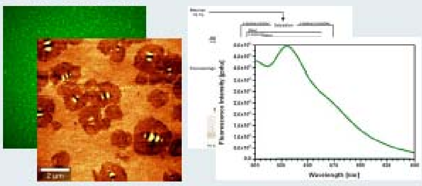


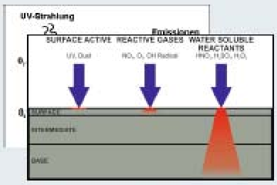




3 types of ageing species (agents):
surface active, gasiform und water-soluble oxidants

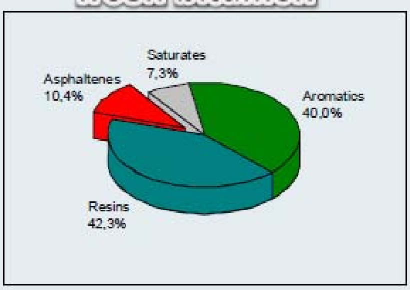
*INSTITUTE OF TRANSPORTATION*
Research Center of Road Engineering

## Microstructural ageing model
### Mechanism

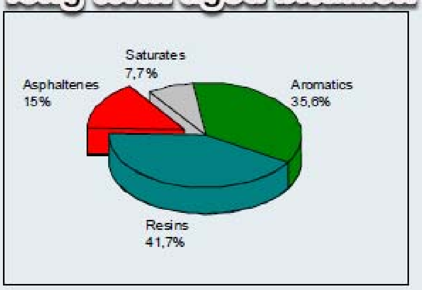





fresh bitumen



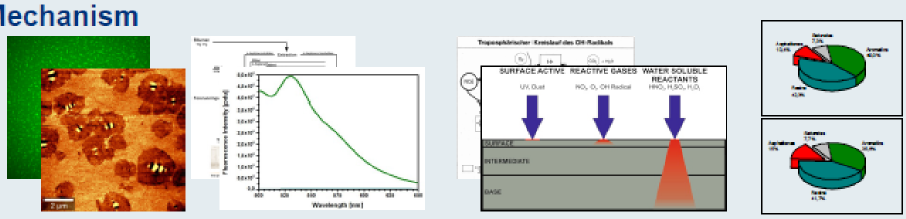

long term aged bitumen

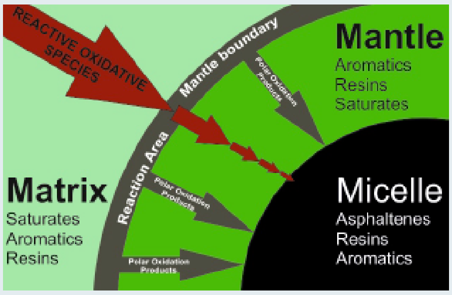


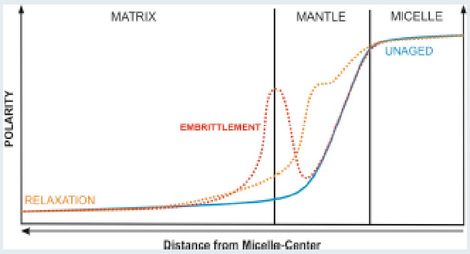

ageing: shift from aromatics to asphaltens: chemical change – increase of polar material!

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Microstructural ageing model
### Mechanism




**oxidative species reacts at the mantel boundary and leads to embrittlement (ageing), polar oxitation products can be transported to the micelle in dependence of temperature (healing)**

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Conclusion

- Improved **model of the bitumen micro structure** based on combined chemical and modern image analyzing procedures
- Identification of different **field ageing species**
- **Field ageing mechanism**: reactive oxidative species lead to an embrittlement of bitumen due to a shift of the polarity gradient in the mantle boundary between micelle and matrix (shell structure)
- „**Healing“- effects** result from a re-organization of the polar oxidation products from the mantle into the micelle

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## References

Hofko B., Blab R., Eberhardsteiner L., Füssl J., Grothe H., Handle F., Hospodka M., S. Nahar, A. Schmets, A. Scarpas: *Microstructure and Rheology of Bitumen - Friends or Foes?*, Materials and Structures, 2014 (submitted)

Handle F., Eberhardsteiner L., Füssl J., Hofko B., Hospodka M., Blab R., Grothe H.: *The Bitumen Microstructure – A Fluorescent Approach, Materials and Structures*, 2014 (submitted)

Hofko B., Blab R., Eberhardsteiner L., Füssl J., Grothe H., Handle F., Hospodka M.: *Recent Developments in the Field of Ageing of Bitumen and Asphalt Mixes*, Transport Research Record, 2015 (submitted)

Handle F., Eberhardsteiner L., Füssl J., Hofko B., Hospodka M., Blab R., Grothe H.: *Understanding the Microstructure of Bitumen: a CLSM and Fluorescence Approach to Model Bitumen Ageing Behavior*, 12th ISAP International Conference on Asphalt Pavements, Raleigh, 2014

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Outline

- Bitumen Microstructure & Field Ageing Mechanism
- **Micromechanical Modeling of Binder (Ageing)**
- Comparison of Field and Lab Ageing

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Motivation for Multiscale Modeling

- macroscopic material models
  identified material parameters applicable to *one* specific mixture consisting of *one* specific bitumen (e.g., B70/100), *one* specific filler (e.g. limestone dust) and *one* specific aggregate
- (bottom-up) multiscale models
  material parameters as functions of composition (mix design), morphology, and the properties of the material phases (e.g., bitumen, filler, ...)

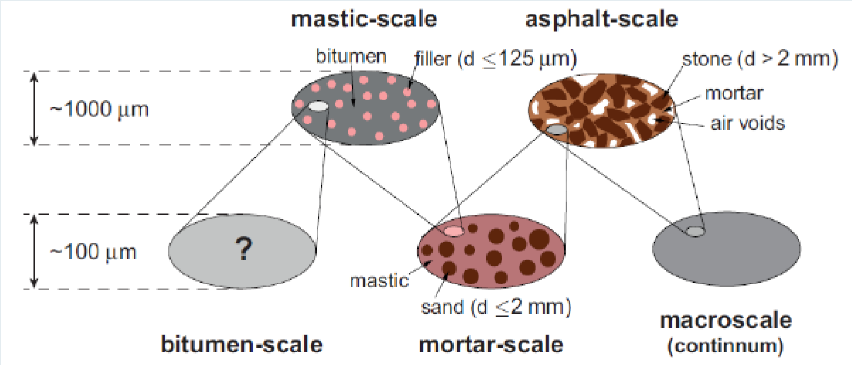
  ⇨ applicable to several asphalt mixes
  ⇨ consideration of changes in material behavior at respective scale of observation

TU WIEN bi.ivws

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Multiscale Model for Asphalt

Five Scales of observation:



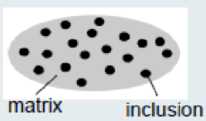

- **Volumetric** composition
- Identification of **mechanical properties** and **morphology**
- Phase **interaction** (Mori Tanaka)
- **Homogenization** and **Upscaling** (Viscoelasticity – Transformation to Laplace Carson Space)

TU WIEN bi.ivws

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

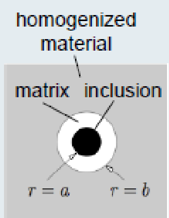
## Homogenization Strategy used for Asphalt

- Mori-Tanaka (MT) scheme:



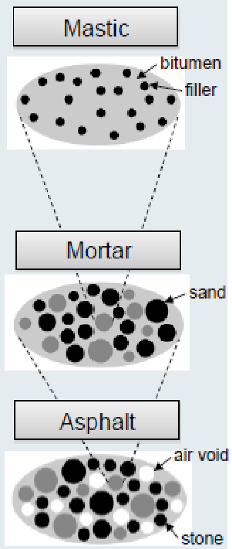

  - suitable for matrix/inclusion type morphologies with low volume fractions of inclusions
  - particle interactions insufficiently taken into account

- Generalized self-consistent (GSC) scheme:




$f_i = \frac{a^3}{b^3}$ ...volume fraction of inclusions

  - for highly filled composite materials with matrix/inclusion type morphologies
  - inclusion interactions taken into account
  - applicable when volume fraction of inclusions exceeds 50 %



INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

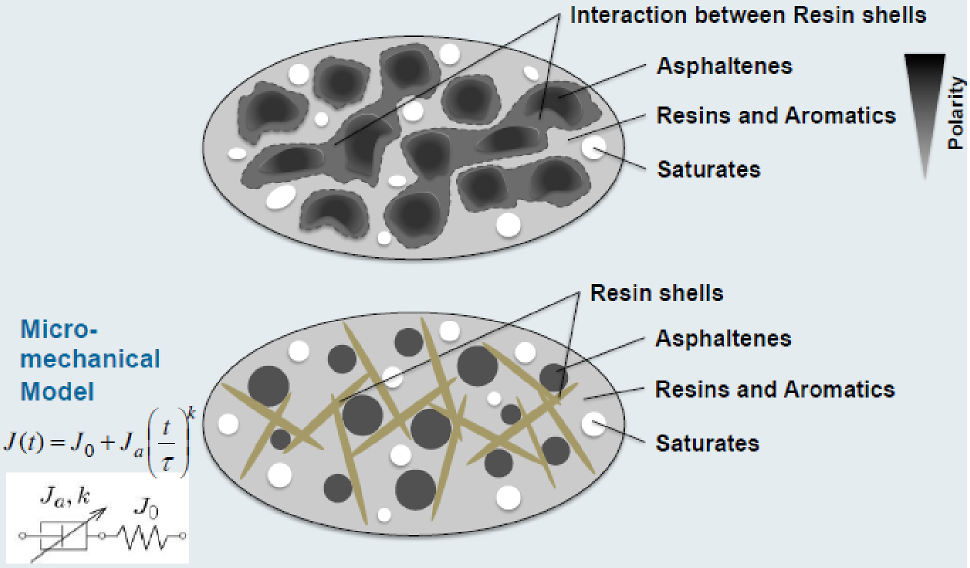
## Micromechanical Modelling of Binder Ageing

- **Set-up** of micromechanical model
- **Identification** of mechanical behavior of material phases
  - Maltenes
  - Asphaltenes + Shell
- **Validation** of model for un-aged binder

- Mechanical behavior of **lab-aged binder** (RTFOT+PAV)
- **Validation** of model for lab-aged binders

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Micromechanical Model



TU WIEN bi.IVWS

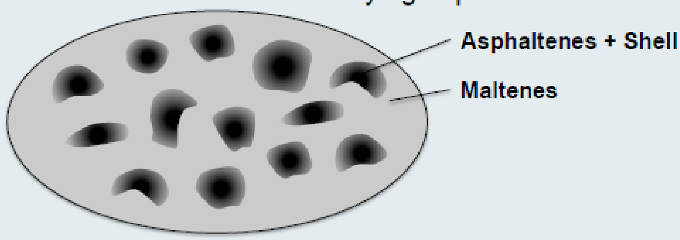
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Identification experiments

- Binder: 70/100 pen

| Parameter | 70/100 pen |
|---|---|
| Penetration [1/10 mm] | 90.9 |
| Softening Point Ring & Ball [°C] | 46.7 |
| SHRP PG [°C] | 58-22 |

- Artificial bitumens with varying asphaltene contents




- Creep-Recovery tests at different temperatures

TU WIEN bi.IVWS

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Experimental Layout

Identification Maltenes
+ Effect of Temperature (Arrhenius)

| Asphaltene content | | Test temperature | | |
|---|---|---|---|---|
| | | -5 °C | +5 °C | +15 °C |
| 0 wt. % | 0 vol-% | • | • | • |
| 5 wt. % | 4.18 vol-% | • | • | • |
| 10 wt. % | 7.77 vol-% | | • | |
| 15 wt. % | 12.32 vol-% | | • | • |
| 20 wt. % | 17.36 vol-% | | • | |
| 30 wt. % | 26.71 vol-% | | • | |

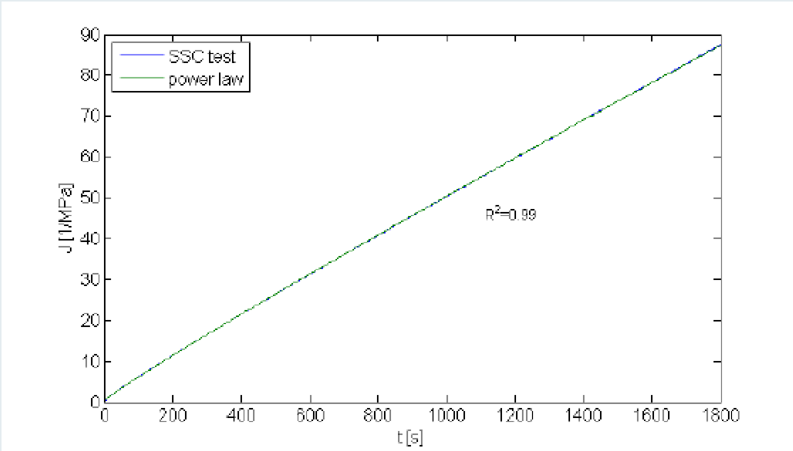
Validation

Identification Asphaltenes

Identification Interaction Shell

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

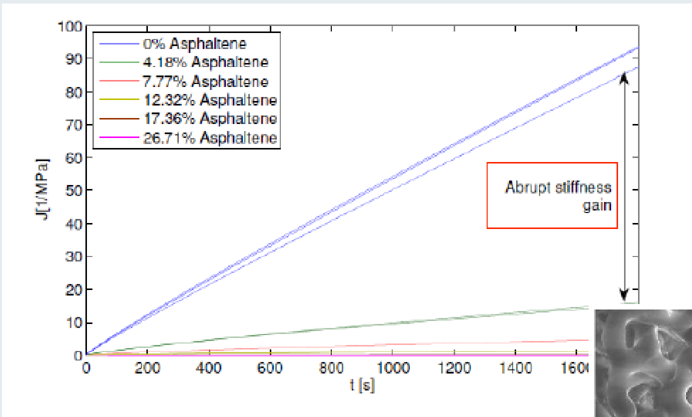
## Identification Maltenes

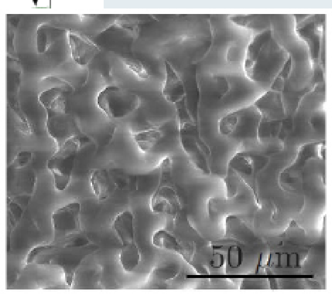



| | -5 °C | +5 °C | +15 °C |
|---|---|---|---|
| $J_{0,malt}$ [1/MPa] | 0.0980 | 0.2652 | 2.433 |
| $J_{a,malt}$ [1/MPa] | 0.0076 | 0.0766 | 1.205 |
| $k_{malt}$ [-] | 0.8124 | 0.9386 | 1.027 |
| $R^2$ | 0.99 | 0.99 | 0.99 |

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Identification Asphaltenes + Shell

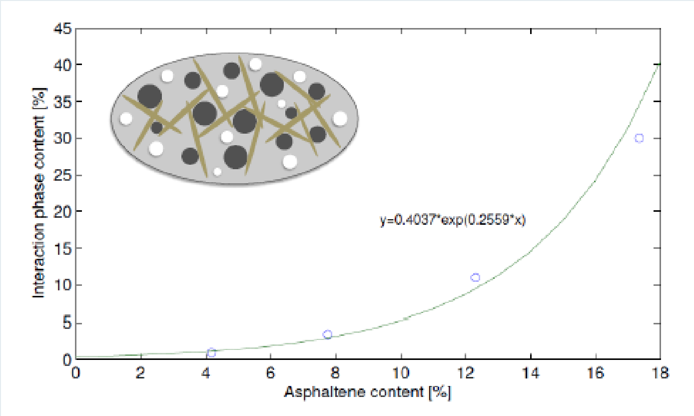


ISBN 978-94-6186-524-3

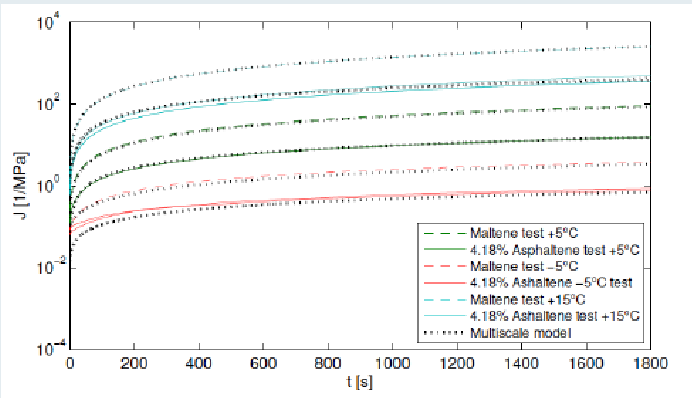

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Identification Asphaltenes + Shell




INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Model Validation



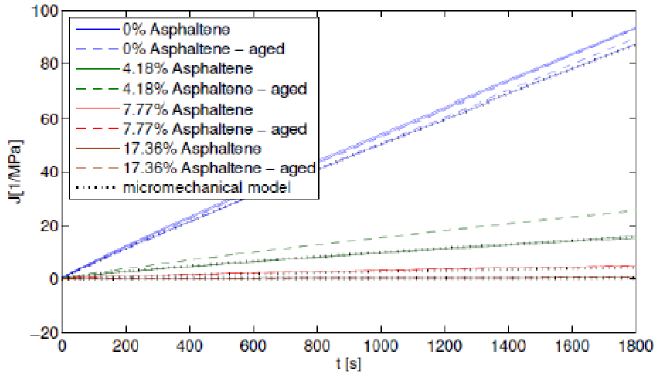
 ISBN 978-94-6186-524-3 

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Mechanical Behavior of Lab-aged Binders

| Asphaltene content | Test temperature | | |
|---|---|---|---|
| | -5 °C | +5 °C | +15 °C |
| 0 % | •/○ | •/○ | •/○ |
| 4.18 % | •/○ | •/○ | •/○ |
| 7.77 % | ○ | •/○ | ○ |
| 12.32 % | | • | • |
| 17.36 % | ○ | •/○ | ○ |
| 26.71 % | | • | |

tumen, ○ . . . tests on aged bitumen




INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Conclusion

- **Power-law model** describes viscoelastic behavior of bitumen constituents well
- **Identification** of mechanical behavior of maltenes, asphaltenes and interaction of micelle shells **successfully**
- Abrupt gain in stiffness with addition of asphaltenes to maltene phase → **Micelle-Matrix Model including interacting shells**
- **Correlation** between interaction of micelle **shells** (needles) and **asphaltene** content
- No difference between un-aged and lab-aged binder
  - in maltene/asphaltene behavior
  - in interaction of micelle shells
- **Change in asphaltene content sufficient** to explain change in mechanical behavior due to **ageing**

TU WIEN bi.IVWS — INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## References


Eberhardsteiner L., Füssl J., Hofko B., Handle F., Hospodka M., Blab R., Grothe H.: *Influence of asphaltene content on mechanical bitumen behavior – Experimental investigation and micromechanical modeling*. Materials and Structures, 2014, DOI: 10.1617/s11527-014-0383-7

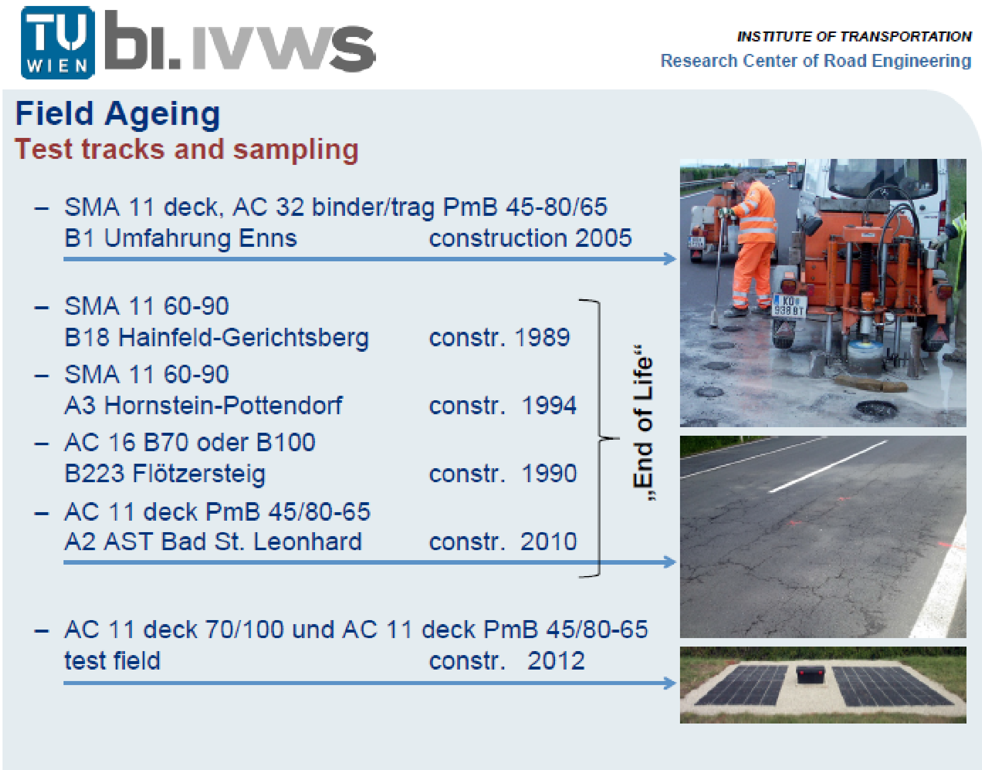
Eberhardsteiner L., Füssl J., Hofko B., Handle F., Hospodka M., Blab R., Grothe H.: *Towards a microstructural model of bitumen aging behavior*. International Journal of Pavement Engineering, 2014

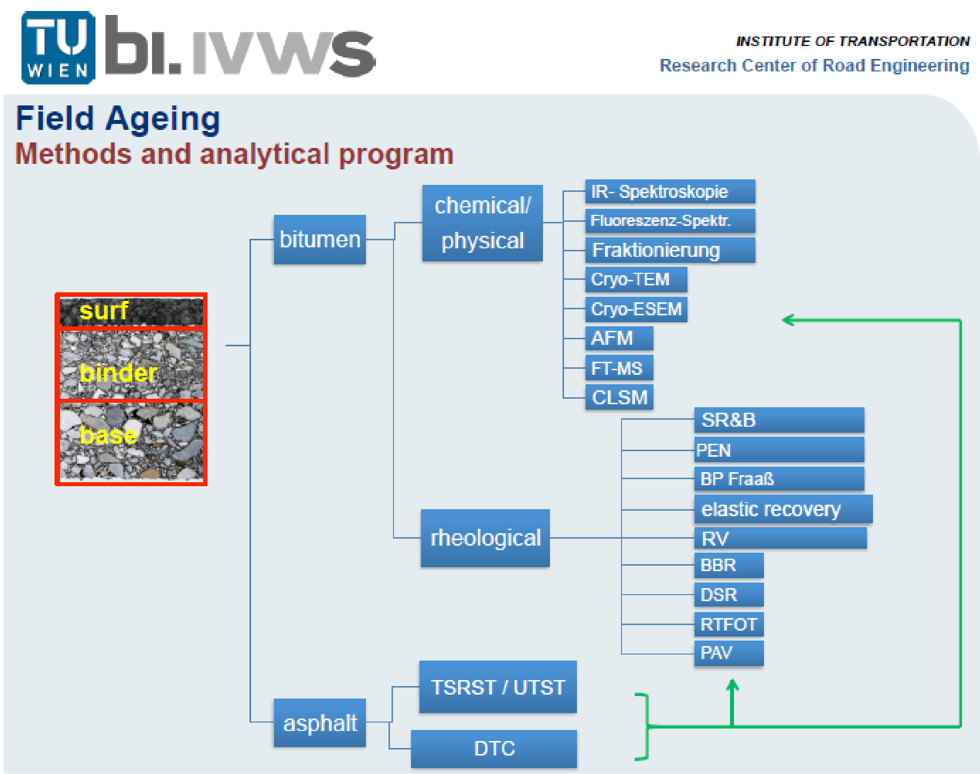
Eberhardsteiner L., Füssl J., Hofko B., Blab R. and Lacker, R.: *Prediction of Hot Asphalt Stiffness – A Multiscale Approach*. Transport Research Record, 2015 (submitted)


TU WIEN bi.IVWS — INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Outline

- Bitumen Microstructure & Field Ageing Mechanism
- Micromechanical Modeling of Binder (Ageing)
- **Field and Lab Ageing**


TU WIEN
bi.ivws
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering
Field Ageing
Test tracks and sampling
– SMA 11 deck, AC 32 binder/trag PmB 45-80/65
B1 Umfahrung Enns construction 2005
– SMA 11 60-90
B18 Hainfeld-Gerichtsberg constr. 1989
– SMA 11 60-90
A3 Hornstein-Pottendorf constr. 1994
– AC 16 B70 oder B100
B223 Flötzersteig constr. 1990
– AC 11 deck PmB 45/80-65
A2 AST Bad St. Leonhard constr. 2010
„End of Life“
– AC 11 deck 70/100 und AC 11 deck PmB 45/80-65
test field constr. 2012


TU WIEN
bi.ivws
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering
Field Ageing
Methods and analytical program
surf
binder
base
bitumen
chemical/ physical
IR- Spektroskopie
Fluoreszenz-Spektr.
Fraktionierung
Cryo-TEM
Cryo-ESEM
AFM
FT-MS
CLSM
rheological
SR&B
PEN
BP Fraaß
elastic recovery
RV
BBR
DSR
RTFOT
PAV
asphalt
TSRST / UTST
DTC

ISBN 978-94-6186-524-3


TU WIEN bi.ivws

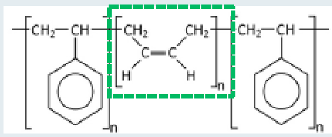
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Field ageing
### Results bitumen

- Bitumen recoverd from base and binder course show almost identical rheological parameter after 10 years → recycling!
- Long term ageing of bitumen is very much restricted to surface course
- Comparison of field and lab ageing indicates

| | | |
|---|---|---|
| • RTFOT | rheological | ☑ |
| | chemical | ☑ |
| • RTFOT+PAV | rheological | ☑ |
| | chemical | ☒ |
| | SBS-degeneration | ☒ |

- Butadien binding is sensitive to UV-radiation



TU WIEN bi.ivws

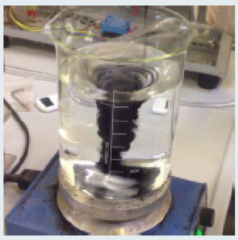
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Field Ageing
### Bitumen - alternative Lab Test for long term ageing

**PAV:** high pressure (21 bar) and temperatures (100°C) do not simulate field ageing mechanism

**Liquid phase ageing**
high concentration of OH radicals
(3-6 vol.%- $H_2O_2$ solution)

- **treatment of R&B specimens**
  → uneven bitumen surface
- **dropping and steering of hot bitumen in $H_2O_2$ solution**
  → clumping of bitumen sample



under construction

ISBN 978-94-6186-524-3


TU WIEN bI.IVWS

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Field ageing

### HMA - Alternative Lab Test for long term ageing

Existing lab-ageing procedures

**handicaps**

- Loose HMA
- High pressure
- High temperature

**objective:**

- compacted HMA specimen
- field surface temperature and pressure
- high concentrations of highly reactant gaseous agents

| Alterungsmethode | Temp. | Dauer | Probeart | DIN EN | Veröffentlichung | Jahr | Alterung durch |
|---|---|---|---|---|---|---|---|
| | [°C] | [h] | | | | | |
| Short-Term Oven Ageing (STOA) | 135 | 8-36 | loses Material | - | NCHRP | 1988 | - |
| Long-Term Oven Ageing (LTOA) | 85 | 120 | verdichtete PK | - | NCHRP | 1988 | - |
| Low-Pressure Oxidation (LPA) | 60, 85 | 120 | verdichtete PK | - | SHRP | 1989 | Sauerstoff (1,9 l/min) |
| Rotating Cylinder Aging Test (RCAT) | 70 - 100 | 144 | Asphaltmastix | 15323 | Verhasselt & Choquet | 1991 | Sauerstoff (4,5 l/h) |
| Long-Term Ageing | 60 | 48 | verdichtete PK | - | NCHRP | 1988 | |
| | 60 | 120 - 240 | verdichtete PK | - | NCHRP | 1988 | Druck (0,7 MPa) Luft |
| | 107 | 72 | verdichtete PK | - | NCHRP | 1988 | |
| Bitutest-Protocol | 135 | 2 | loses Material | - | Scholz (PhD-Thesis) Nottingham | 1995 | - |
| | 85 | 120 | verdichtete PK | - | Scholz (PhD-Thesis) Nottingham | 1995 | - |
| Ottawa Sand Mixtures | 163 | variiert | verdichtete PK | - | AAPT | 1962 | - |
| | 60 | 1200 | verdichtete PK | - | AAPT | 1962 | - |
| Plancher et al. | 150 | 5 | verdichtete PK | - | AAPT | 1976 | - |
| Hugo & Kennedy | 100 | 96, 168 | - | - | AAPT | 1985 | 80 % relative Luftfeuchtigkeit |
| Khalid & Walsh | 60 | bis 600 | verdichtete PK | - | EE Congr. | 2000 | Luft (3 l/min) |
| Kumar & Goetz | 60 | 24-240 | verdichtete PK | - | AAPT | 1977 | Luft Wasser |
| Kim et al. | 60 | 24-120 | verdichtete PK | - | Oregon | 1986 | Druck (0,7 Mpa) Luft |
| Pressure Ageing Vessel | 100 | 72 | verdichtete PK | 14769 | EE Congr. | 1996 | Druck (2,07 Mpa) Luft |
| Saturation Ageing tensile stiffness conditioning Test (SATS) | 85 | 65 | verdichtete PK | 12697-45 | Transport 157 | 2004 | Wasser Druck |
| Modelltopf nach Potschka | 140 | 1 | loses Material | - | FA 07.121 G95 E | | Luft 20%Sauerstoff 80%Stickstoff |
| Braunschweiger Alterung (BSA) | 80 | 96 | loses Material | - | FE 07.208/2004/BGB 2007 | 2007 | Luft |
| Wamboldscher Alterungstisch | 40 | 720 - 1440 | verdichtete PK | - | Diss. Wambold | 1996 | Luft UV Licht |
| Alterung im Wärmeschrank | 135-175 | 4-24 | loses Material | - | Bitumen 2/1999 | 1999 | Luft Stickstoff |
| Bochumer Alterungsverfahren BAV | 100 | 72 | verdichtete PK | - | Cetinkaya (Diss.) Bochum | 2011 | Erwärmte Druckluft |
| Wheatherometer Delft | -20 - +60 | 1,2,3,4, 6,8,10,12 | verdichtete PK | - | Hagos (PhD-Thesis) Delft | 2008 2011 | Weather-Ometer UV Licht Luftfeuchtigkeit NaCl |
| BRRC long term Re road | 60 | 24, 72, 216, 336 | loses Material | - | journal of wuhan university | 2010 | Sauerstoff (15ml/min) |
| UV (LCPC) long term | 60 | 336 | loses Material | - | journal of wuhan university | 2010 | UV Licht |
| Rilem (ISBS - Braunschweig) | 85 | 24, 72, 144, 216 | loses Material | - | journal of wuhan university | 2010 | - |
| Pr.1-van de ven - circular Steelplate - STA | 165 | 2 | Asphaltmastix | - | van de Ven et al: EE congress | 2012 | - |
| Pr.1-van de ven - LTA - PAV | 80 | 168 | Asphaltmastix | - | van de Ven et al: EE congress | 2012 | Druck (21 bar) |
| Pr.1-van de ven - for removal from plate | 150 | 0,5 | Asphaltmastix | - | van de Ven et al: EE congress | 2012 | - |
| Pr.2-van de ven - STA - oven | 135 | 4 | loses Material | - | van de Ven et al: EE congress | 2012 | - |
| Pr.2-van de ven - protocol 2 - heated up and compacted | 165 | | loses Material | - | van de Ven et al: EE congress | 2012 | mechanische Bel. |
| Pr.2-van de ven - LTA - PAV | 70+80 | 72+96 | verdichtete PK | - | van de Ven et al: EE congress | 2012 | Druck (21 bar) |
| AASHTO R302 (nchrp) - STA | 135 | 4 | loses Material | - | RILEM Advances in [...]Testing [...]of Bituminous Materials | 2013 | - |
| c - long-term aging | 85 | 120 | verdichtete PK | - | RILEM Advances in [...]Testing [...]of Bituminous Materials | 2013 | - |
| Braunschweiger Alterung (BSA) | 80 | 96 | loses Material | - | Buchler et al. EE congress | 2008 | Luft |

TU WIEN bI.IVWS

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Field ageing

### HMA - Alternative Lab Test for long term ageing

**Viennese Ageing Procedure VAPro**

**optimize mix design**

- durability
- recyclability

**Long term aged pavements are more prone to failure by**

- low-temperature cracking
- fatigue cracking

INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Ageing Procedure for Hot Mix Asphalt Specimen - SETUP
## Viennese Ageing Procedure VAPro

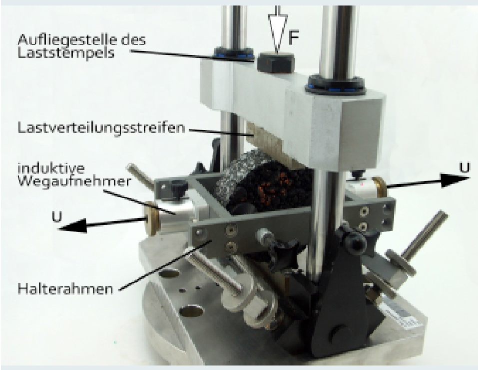
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

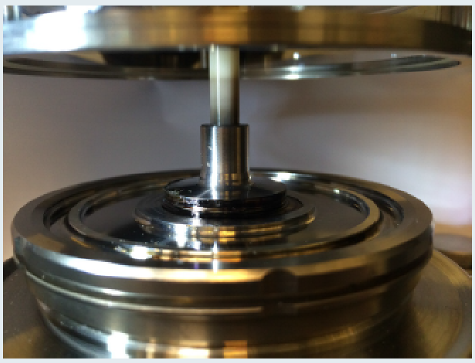
## Field Ageing
### HMA - Alternative Lab Test for long term ageing
### Validation tests - VAPro

**Indirect Tensile Test, Cylindrical Sample (IT-CY)**

Tests before and after ageing

**Recovered bitumen DSR**

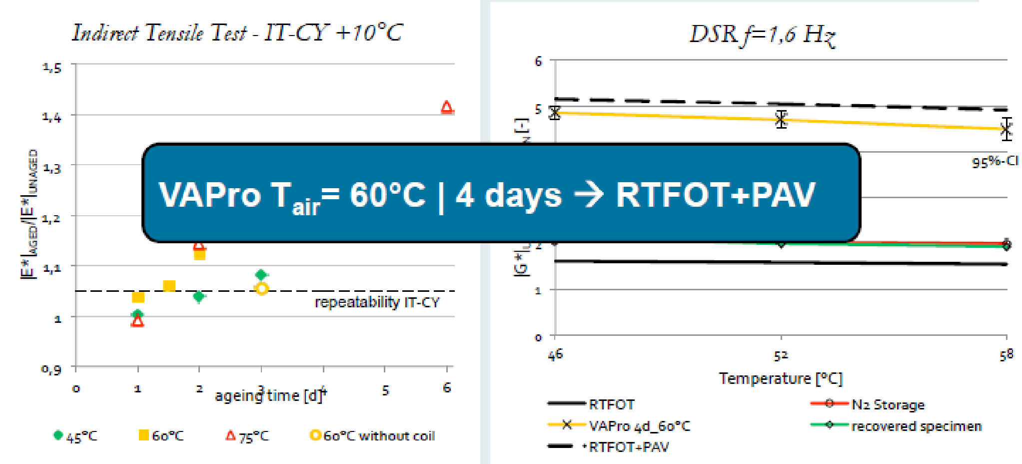


INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Ageing Procedure for Hot Mix Asphalt Specimen - RESULTS
## Viennese Ageing Procedure VAPro

**HOT MIX ASPHALT** | **BINDER**




INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## Conclusion

- long term field ageing of bitumen can not be simulated realistically by RTFOT & PAV procedure in the lab
- **Liquid Phase ageing** as alternative bitumen ageing procedure is not practicably yet
- **modified RTFOT** (1-times @ 230°C, 3-times @ 163°C) is recommended instead of RTFOT & PAV procedure to simulate bitumen field ageing
- **Viennese ageing procedure** (VAPro) is appropriate lab method to simulate field ageing of compacted HMA specimens and will be further developed to carry out performance based tests on lab aged HMA specimens

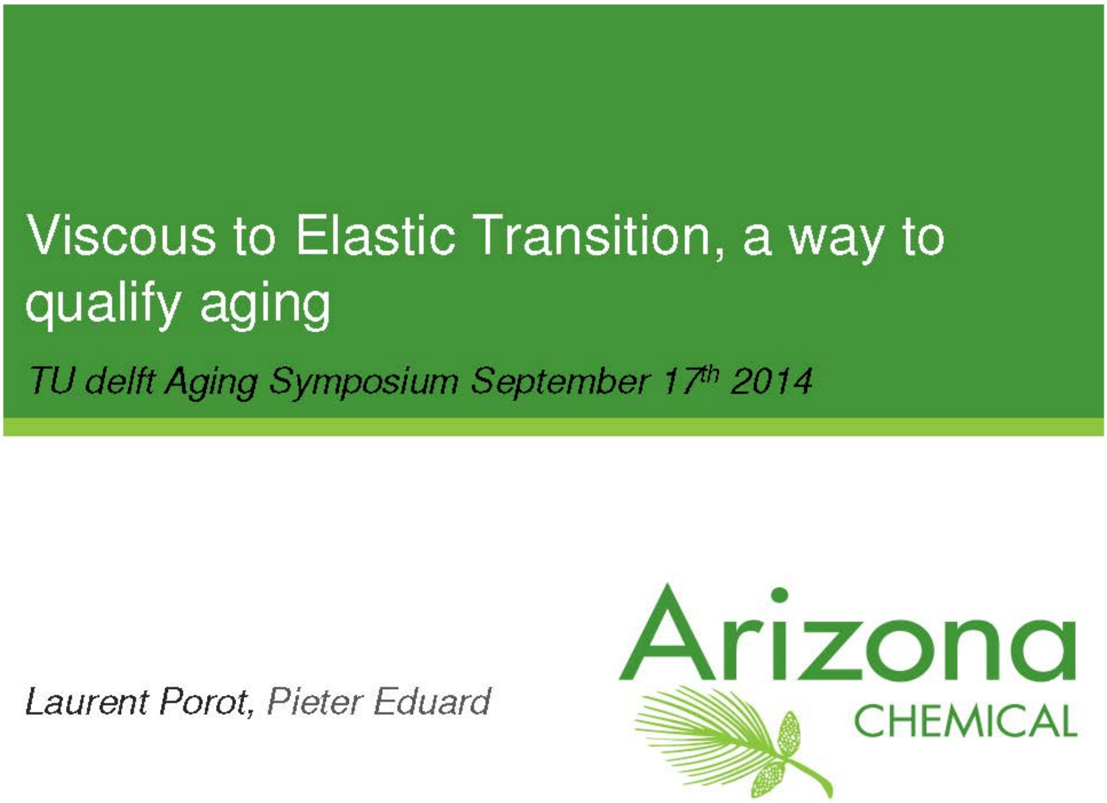
INSTITUTE OF TRANSPORTATION
Research Center of Road Engineering

## References

Hofko B., Blab R., Eberhardsteiner L., Füssl J., Grothe H., Handle F., Hospodka M.: *Impact of Field Ageing on Low-Temperature Performance of Binder and Hot Mix Asphalt*, 12th ISAP International Conference on Asphalt Pavements, Raleigh, 2014

Steiner, D., Hofko B., Blab R., Eberhardsteiner L., Füssl J., Grothe H., Handle F., Hospodka M.: Towards *an efficient laboratory protocol for long-term ageing of compacted asphalt mix specimens*, Transport Research Record, 2015 (submitted)

## 8.5 Laurent Porot, Arizona Chemical, Viscous to Elastic Transition: a way to qualify aging



# Outlines

Arizona CHEMICAL

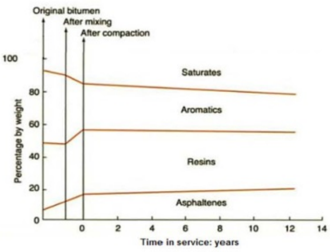
- Background
- Technical approach
- Status & results
  - Chemical structure FTIR
  - Mechanical properties DSR
- Conclusion

# Background

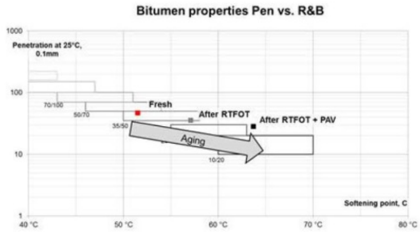
# Aging of asphalt binder

Arizona CHEMICAL

- With aging, an asphalt binder changes
  - in microstructure due to oxidation
  - and in properties with hardening

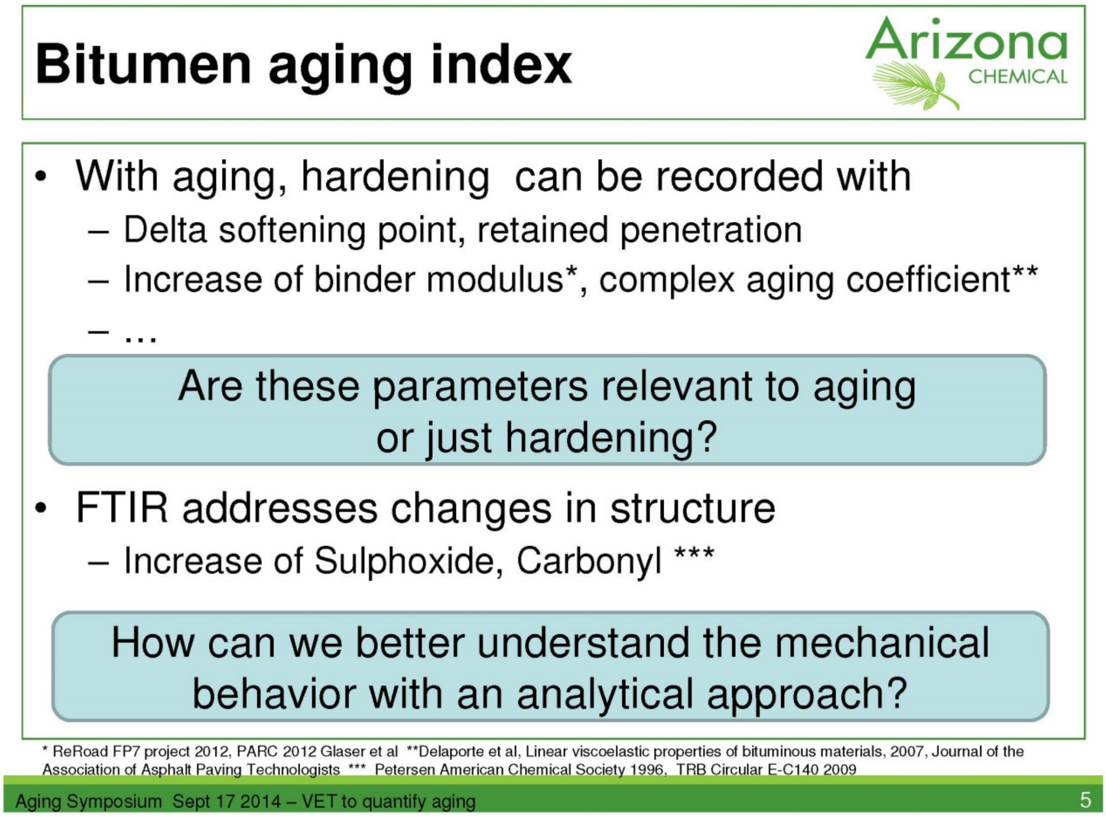



*The Shell Bitumen Handbook fifth edition*




How to define proper parameters to characterize aging?

Aging Symposium Sept 17 2014 – VET to quantify aging 4


Bitumen aging index
Arizona CHEMICAL
• With aging, hardening can be recorded with
– Delta softening point, retained penetration
– Increase of binder modulus*, complex aging coefficient**
– …
Are these parameters relevant to aging or just hardening?
• FTIR addresses changes in structure
– Increase of Sulphoxide, Carbonyl ***
How can we better understand the mechanical behavior with an analytical approach?
* ReRoad FP7 project 2012, PARC 2012 Glaser et al **Delaporte et al, Linear viscoelastic properties of bituminous materials, 2007, Journal of the Association of Asphalt Paving Technologists *** Petersen American Chemical Society 1996, TRB Circular E-C140 2009
Aging Symposium Sept 17 2014 – VET to quantify aging
5

# Viscous to Elastic Transition

Arizona CHEMICAL

- Rheology can address the viscous elastic behavior of asphalt with
  - Complex Modulus → stiffness
  - Phase angle → visco-elastic behavior
- The Viscous to Elastic Transition* concept
  - When the phase angle equal to 45° (tanδ=1)
  - Modulus /temperature at VET, "*useful tool to demonstrate the changes in the properties of bituminous materials*"

*Viscous to Elastic Transition temperature of bitumen and the in-situ performance of asphalts, I. Widyatmoko Asphalt 2005
Mapping crack susceptibility of bituminous materials with binder durability, I. Widyatmoko, Rilem 2004

Aging Symposium Sept 17 2014 – VET to quantify aging 6

Arizona CHEMICAL

# Experimental plan

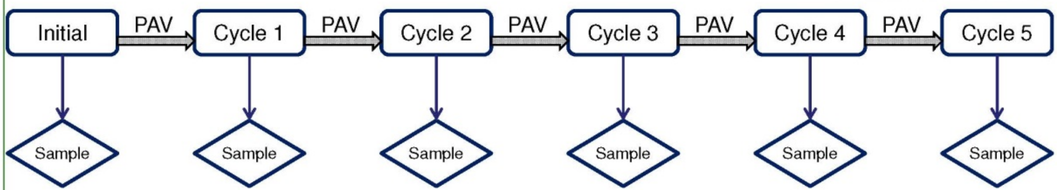
# Technical approach

- Comparing asphalt binders
  - Different binder grades
  - Different binder sources
  - Different binder aging levels through tailored aging cycles
  - Different RA binders recovered from the road
- Looking at the test results from a different angle
  - Basic properties with penetration value and softening point
  - Analytical approach with FTIR
  - Mechanical behavior with DSR

# Aging cycles

Arizona CHEMICAL

- Aging in the laboratory using the PAV
  - Test conditions of 100°C for 40h gave similar hardening effect than from RA coming from road sections
  - Aging through 5 cycles total




Characterization and analysis with FTIR and DSR

PAV, Pressure Aging Vessel

# Quantitative FTIR analysis

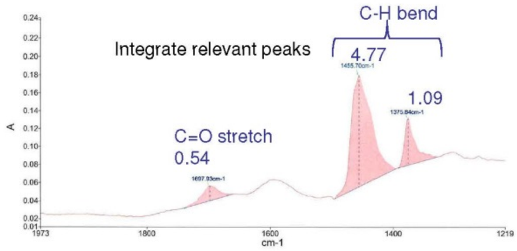
Arizona CHEMICAL

- Quantitative analysis of asphalt binders*
  - Amount of aliphatics → **Unrelated to ageing** 1460 and 1376 $cm^{-1}$
  - Level of oxidation → **Related to ageing** 1700 and 1030 $cm^{-1}$

- Calculated ratio
  - Integrated relevant peaks

$ISO = A_{S=O} / A_{C\text{-}H\ bend}$

$ICO = A_{C=O} / A_{C\text{-}H\ bend}$



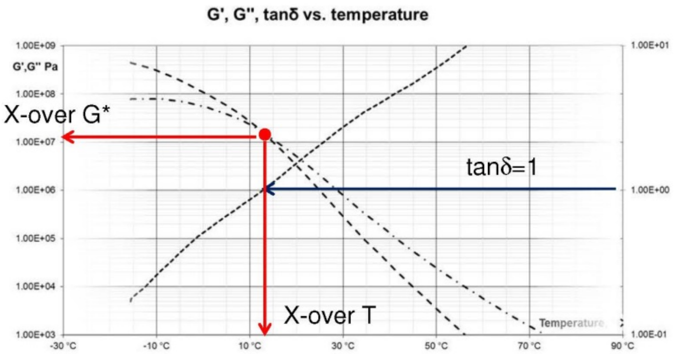

* W. van den Bergh, *The Effect of Ageing on the Fatigue and Healing Properties of Bitumen*, 2011, Petersen American Chemical Society 1996, TRB Circular E-C140 2009

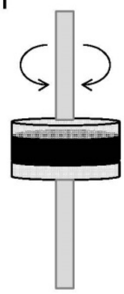
Aging Symposium Sept 17 2014 – VET to quantify aging 10

# Viscous to Elastic Transition

Arizona CHEMICAL

- Rheological properties characterized via DSR
  - In Temperature sweep at 1 fixed frequency (10rad/s)
  - Analysis in the range of $10^3$ to $10^9$ Pa
  - Consider the cross-over properties, G* and T



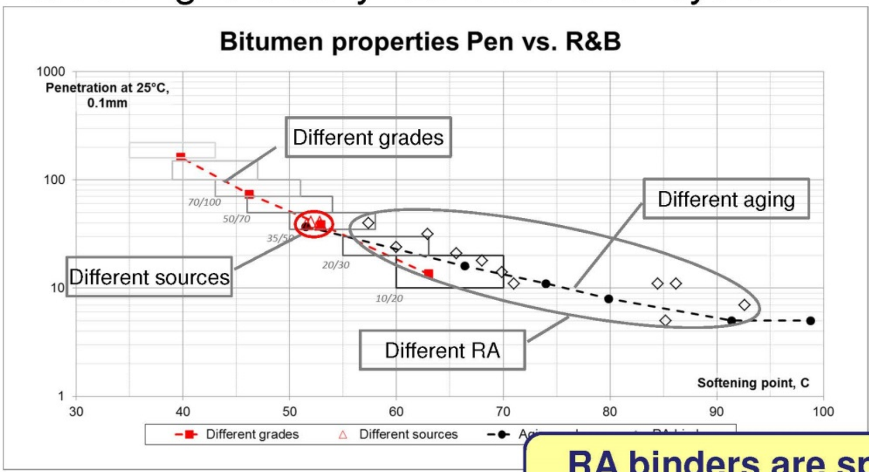



# Results

# Results – basic properties

Arizona CHEMICAL

- Hardening is clearly identified over cycles




**RA binders are spread along aging cycles**

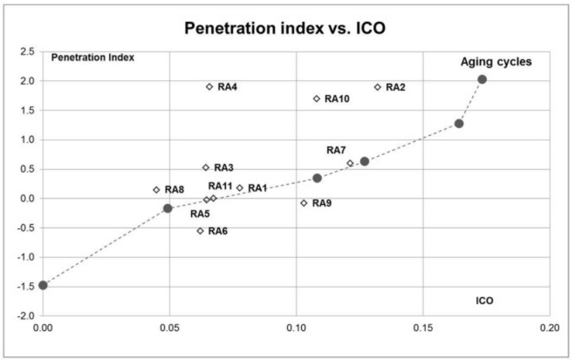
Aging Symposium Sept 17 2014 – VET to quantify aging 13

# Simple analysis

Arizona CHEMICAL

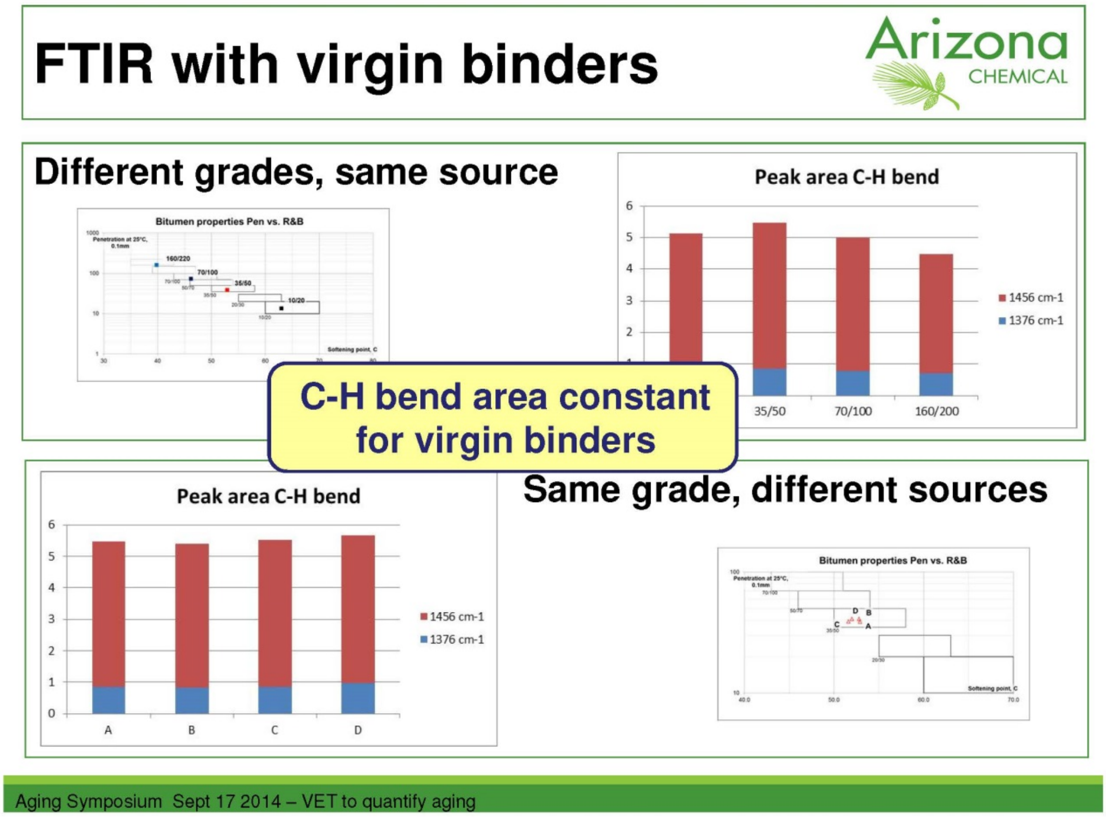
- Penetration Index considered as indicator of oxidation
  - With aging cycles PI increases
  - But PI trend is not obvious compared to ICO

**Something more to address aging**




Aging Symposium Sept 17 2014 – VET to quantify aging 14

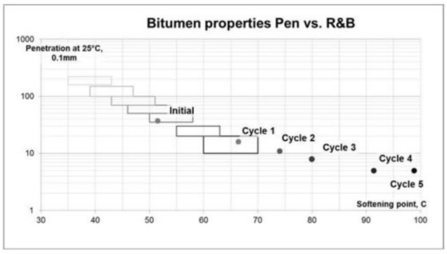
ISBN 978-94-6186-524-3

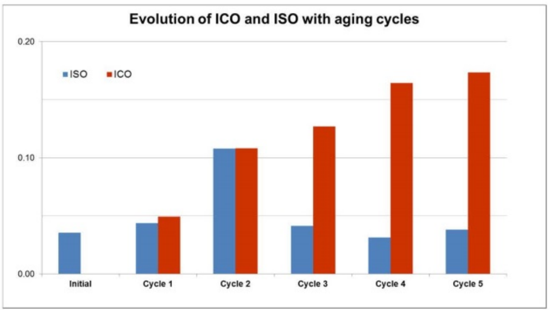



# FTIR with aging cycles

Arizona CHEMICAL

- FTIR data computed for ICO and ISO index
  - ICO increases constantly over aging



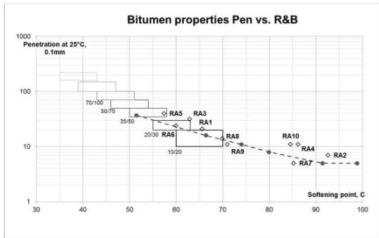

**Both ICO and ISO are measures of aging**

ISBN 978-94-6186-524-3

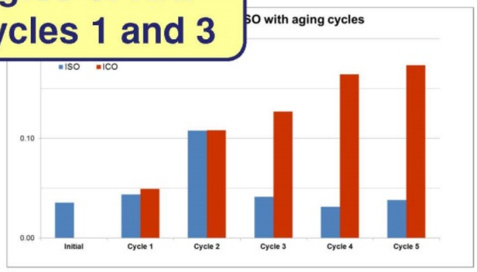

# FTIR with RAP binders

Arizona CHEMICAL

- Different samples from road
  - Different locations, aging levels
  - Unknown initial grades or sources
  - ICO & ISO are in a similar range for all the RA binders




**Ageing degree of RAP between cycles 1 and 3**

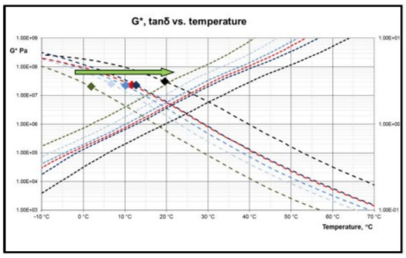



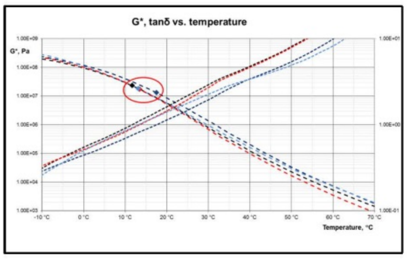
# VET for virgin binder

Arizona CHEMICAL

## Different grades, same source

- Shift in X-over temperature in range of 0 to 20°C
- X-over modulus almost constant above $10^7$ Pa



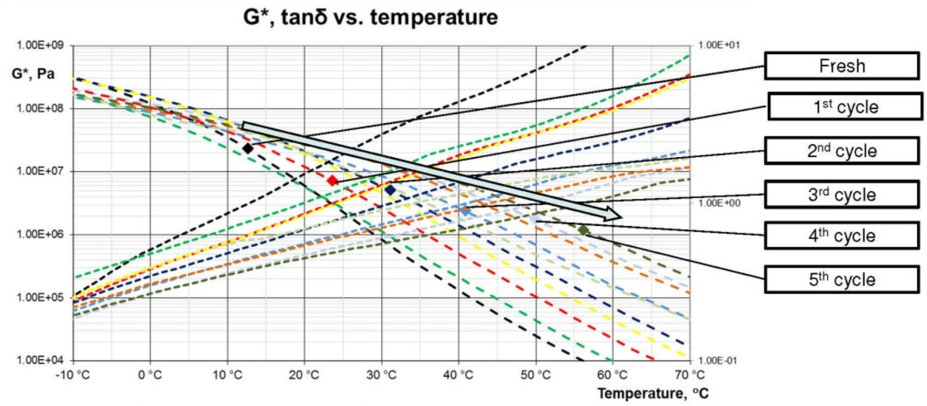

## Same grade, different sources

- Similar DSR profile
- X-over parameters close together

Aging Symposium Sept 17 2014 – VET to quantify aging

# VET for aging cycles

Arizona CHEMICAL



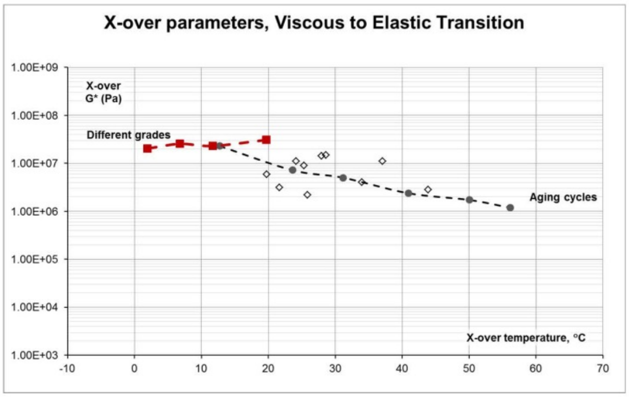

- Increase in cross-over temperature as a result of hardening (same as with different grades)
- Decrease in G* after each cycle from temperature susceptibility

Aging Symposium Sept 17 2014 – VET to quantify aging

# VET for with RA binders

Arizona CHEMICAL

- Different grades
  - Shift in X-over T
- Aging cycles
  - Shift in X-over T (hardening effect)
  - Shift in X-over G*

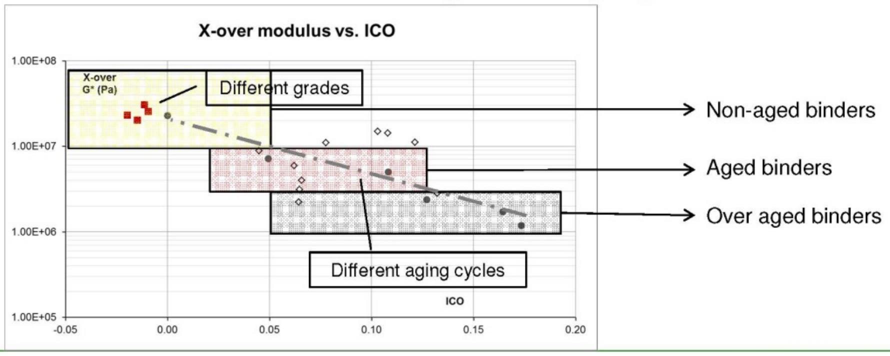



- Aged binders from road
  - Spread along the aging / grading line

Aging Symposium Sept 17 2014 – VET to quantify aging

# X-over G* vs Carbonyl Index

- Non-aged binders are clearly concentrated with Carbonyl Index at 0
- Aging (oxidation) increases carbonyl index and decreases X-over G*
- Possible to estimate the degree of aging



# Conclusion

# Conclusion

- Multi-aging extrapolates the effect of aging
- FTIR ICO relevant parameter for oxidation degree
  - Results are independent of asphalt binder grade or source
- DSR, addresses the change of mechanical behavior
  - Shear modulus alone is not enough to address aging
  - Cross over parameters are good indicators
    - Cross over temperature addressing stiffness with grading
    - Cross-over modulus addressing temperature susceptibility
- DSR and FTIR, a reasonable trend
  - A new approach to qualify the degree of aging

# Questions?

The information presented herein by Arizona Chemical Company, LLC is derived from testing and experience. It is offered for your consideration and verification. Since operating conditions vary significantly, and are not under Arizona Chemical's control, all warranties on the results that may be obtained from the use of Arizona Chemical's products is hereby disclaimed. Arizona Chemical Company, LLC and its subsidiaries cannot be held responsible for any damage or injury occurring as a result of improper installation or use of its products.

Arizona CHEMICAL

# Materials

Arizona CHEMICAL

- Different asphalt binder grades

| Grade | 10/20 | 35/50 | 70/100 | 160/220 |
|---|---|---|---|---|
| Penetration at 25°C | 14 | 39 | 74 | 162 |
| Softening point | 63.0 | 52.9 | 50.4 | 39.8 |
| Penetration Index | -1.00 | -1.06 | -1.29 | -1.04 |

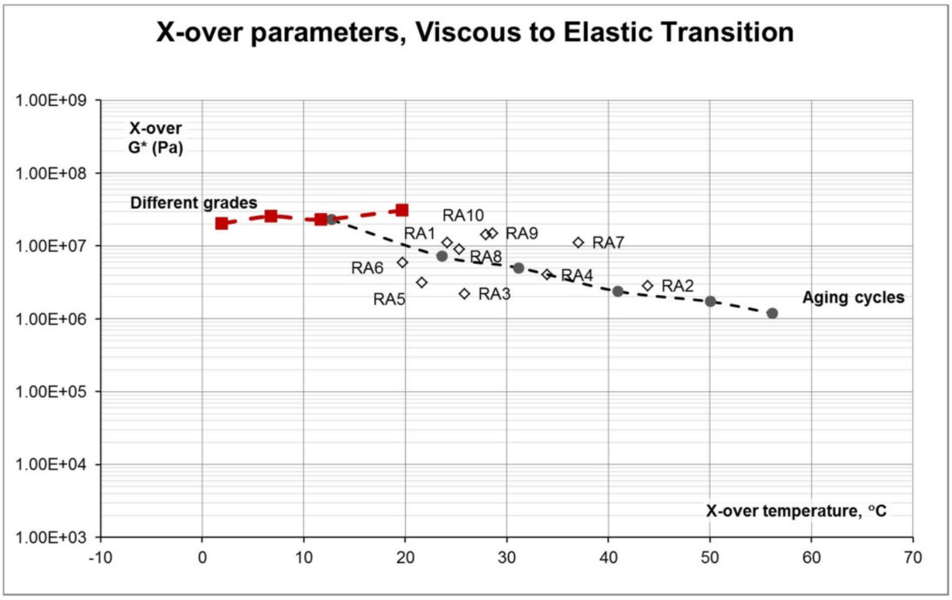
- Different asphalt binder sources

| Source | A | B | C | D |
|---|---|---|---|---|
| Penetration at 25°C | 39 | 41 | 39 | 41 |
| Softening point | 52.9 | 52.8 | 51.6 | 52.0 |
| Penetration Index | -1.06 | -0.97 | -1.35 | -1.15 |

- Different asphalt binder aging levels
  - A pen grade 40/60 aged through 5 cycles
- Different asphalt binder as recovered from the road
  - Various locations, unknown initial source, grade, aging

Aging Symposium Sept 17 2014 – VET to quantify aging 26

# Viscous to Elastic Transition




Aging Symposium Sept 17 2014 – VET to quantify aging 27

## *8.6 Markus Oeser, TU Aachen, TBA*

# Prevention of Asphalt Binder Oxidation using MMT-Particles

Markus Oeser
RWTH Aachen University
Uwe Beginn
UNI Osnabrück

**Delft, 17 September 2014**

## FE 07.0243/LRW/2011
## „NANOASPHALT – Optimization of the Performance Characteristics and the Durability of Asphalt Pavements using Nano-Technology“

Diesem Vortrag liegen Teile des im Auftrag des Bundesministeriums für Verkehr und digitale Infrastruktur, vertreten durch die Bundesanstalt für Straßenwesen, unter FE 07.0243/2011/LRB laufenden Forschungsvorhabens zugrunde.

Die Verantwortung für den Inhalt liegt allein beim Autor.

The presentation is based on parts of the research project carried out at the request of the Federal Ministry of Transport and Digital Infrastructure, requested by the Federal Highway Research Institute, under research project No. 07.0243/2011/LRB.

The author is solely responsible for the content.





## Challenges in Asphalt Pavement Engineering

- Increasing Axle Loads
- Climate Change
- Changing Quality of Resources
- Fewer Resources
- Workability
- Work Safety
- Environment Protection
- Energy Efficiency

etc.

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Improving the Performance of Bitumen through Modification

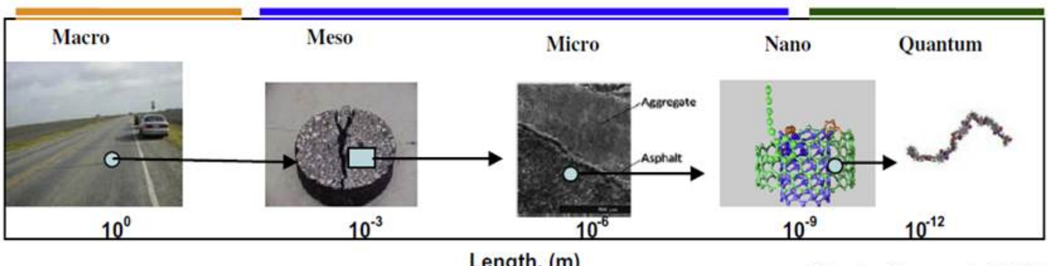
- Polymer Modification
- Rubber Modification
- Wax Modification
- Primer
- Nano Modification

4

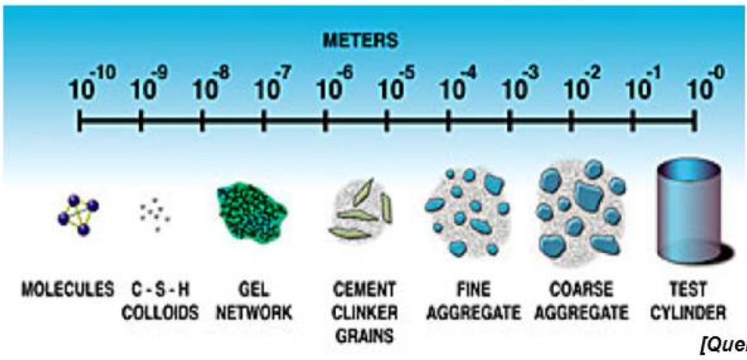
Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Length Scales




[Quelle: You et al. (2011)]




Length of light waves
380 nm to 780 nm

[Quelle: Resperion Whitepaper (2008)]

5

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Asphalt Performance Optimization using Nano-Technology

a) Bound between grains

b) Mastics (Stiffness, Cohesion etc.)

c) Bound between the layers

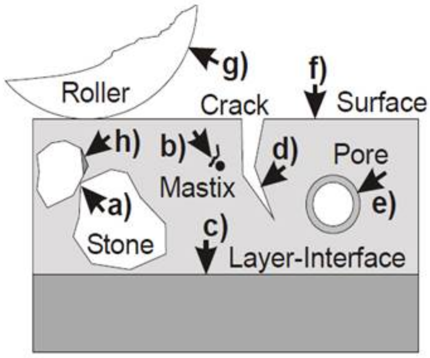
d) Crack healing

e) Binder Oxidation

f) Surface Characteristics

g) Adhesion / Anti-Adhesion Characteristics

h) Grain-Mastics-Adhesion




Source: Partl et al., 2004

6

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Approach

Basic Idea:

- Adding (MMT-Nano-Particles (Montmorillonite) to asphalt bitumen
- Guaranteeing for an exfoliated alignment of the particles

Result:

- Reducing the susceptibility of asphalt bitumen to aging
- Increasing the barrier characteristics of asphalt binder

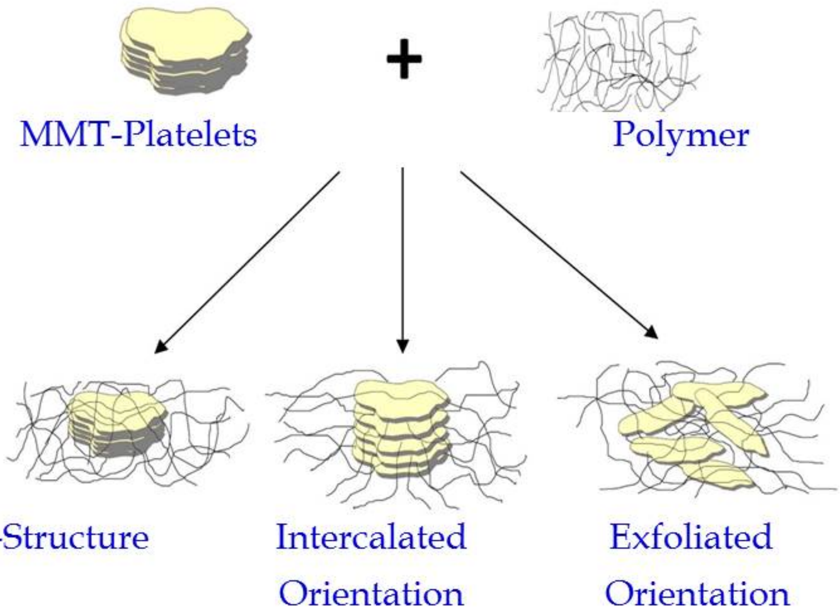
7

Markus Oeser | Delft, 17 September 2014

ISBN 978-94-6186-524-3


Prevention of Asphalt Binder Oxidation using MMT-Particles

## Alignment / Orientation

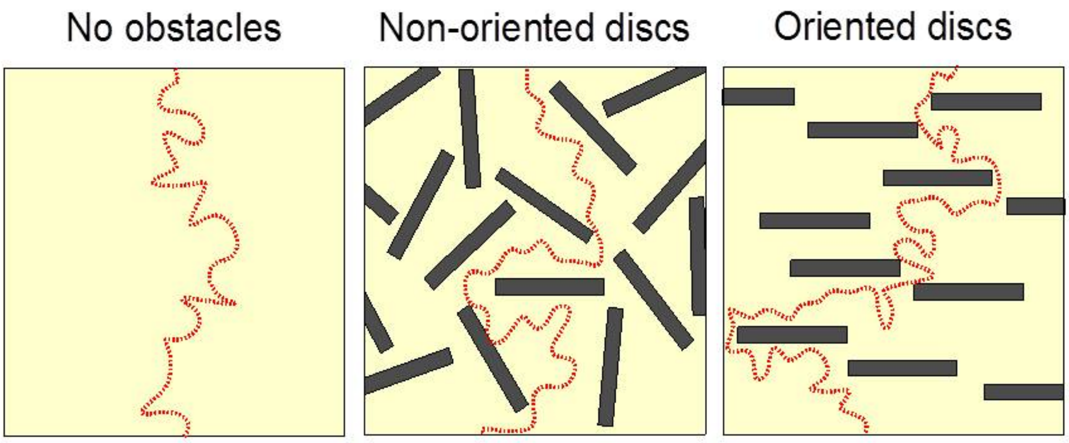



8

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Principle: Reducing the Diffusivity of Asphalt Binder

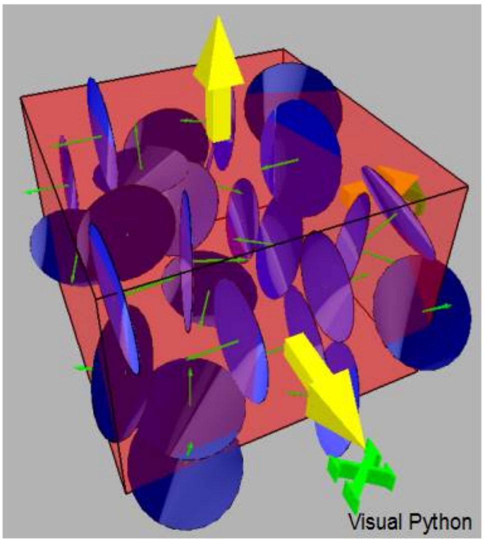



Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

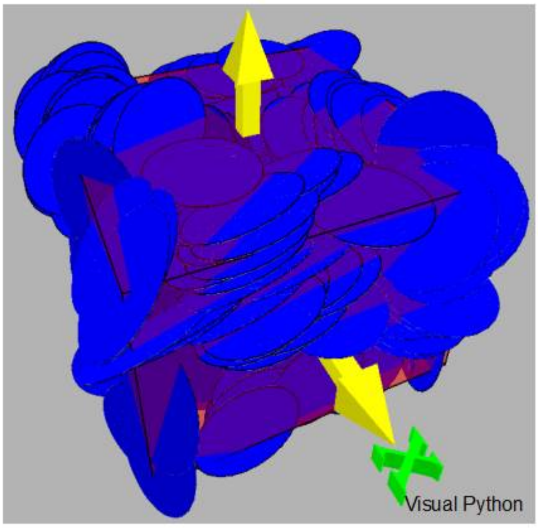
## Principle: Reducing the Diffusivity of Asphalt Binder

$R_D = 1.00$, $H_D = 0.01$




$\Phi_D = 0.005$, $N_{DSC} = 27$

$R_D = 1.00$, $H_D = 0.01$




$\Phi_D = 0.050$, $N_{DSC} = 326$

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Laboratory Shear Mixer L5M

**Capacity**
1 ml to 12 liter
**Engine**
250/750 W , 220 Volt, 50/60 Hz. 8000 R/min (6000 R/min in 12 liters are used).

11

Markus Oeser | Delft, 17 September 2014

ISBN 978-94-6186-524-3


Prevention of Asphalt Binder Oxidation using MMT-Particles

## Sample Preparation

Nano-composite MMT

Breaking the MMT composite

Shear Mixer

Adding MMT

12

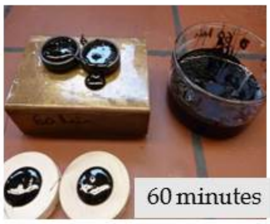
Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Test program (Trials)

- Variants
  - Bitumen 50/70 with 5 M.-% MMT
  - PmB 25/55-55 A with 5 M.-% MMT
- Tests
  - Mixing time: 0, 5, 10, 20, 30 and 60 minutes
  - Characterization: Pen, Softening Point, DSR
  - Visual inspection/observation (Agglomerates? ⇨ **N E I N** <u>but</u> little air bubbles)



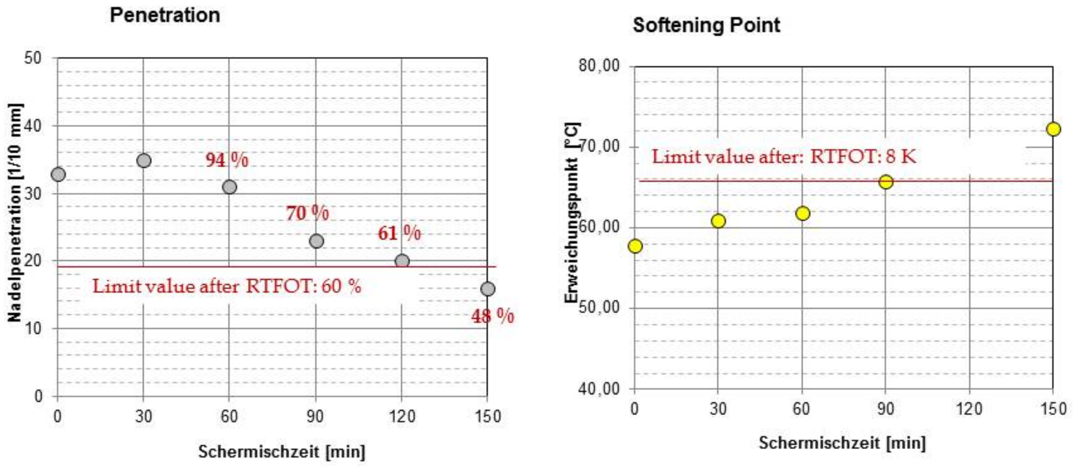

13

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Influence of the Mixing Duration

- Bitumen: PmB 25/55-55 A
- Mixing Parameters: N = 5.000 U/min, T = 160 °C, ohne MMT




14

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Prüfungen an Nanopartikel-Bitumen-Kompositen (NPBK)

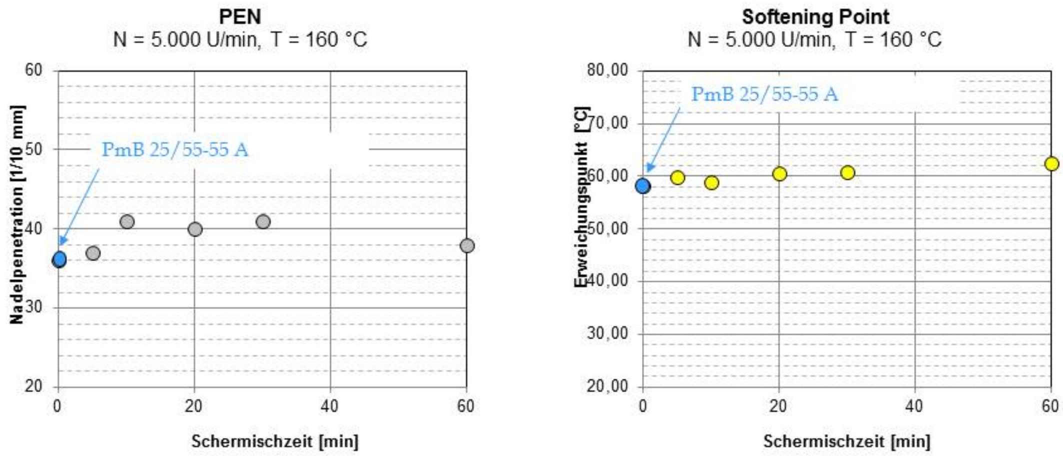
- Materials:
  - Bitumen: PmB 25/55-55 A
  - Nano Particles: Montmorillonite (MMT)
- Tests:
  - Needle Penetration
  - Softening Point
  - DSR-Analytic

15

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Results: PmB 25/55-55 A with 5 M.-% MMT




➲ Small reduction in penetration after MMT has been added

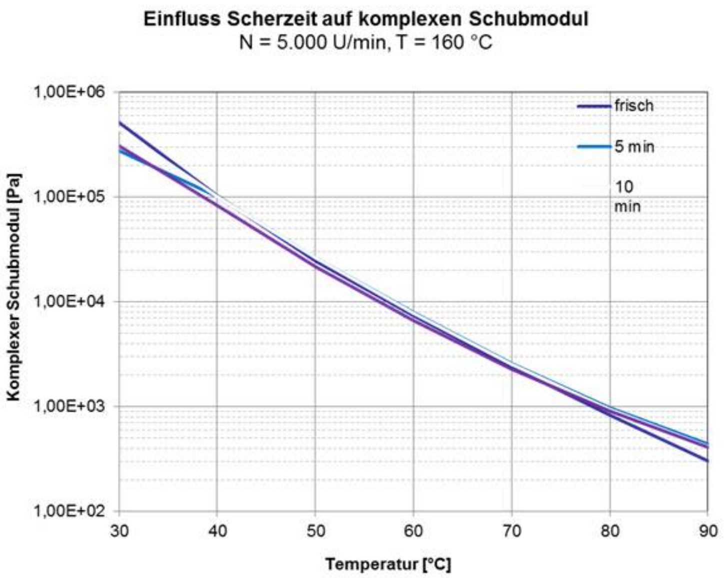
➲ Almost no influence of the Softening Point

16

Markus Oeser Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Results: PmB 25/55-55 A with 5 M.-% MMT



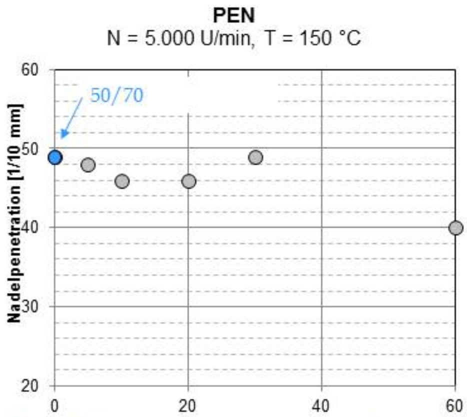

➲ No significant changes

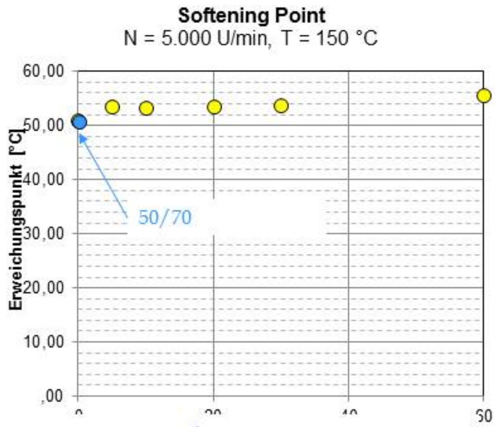
17

Markus Oeser Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Results: 50/70 with 5 M.-% MMT



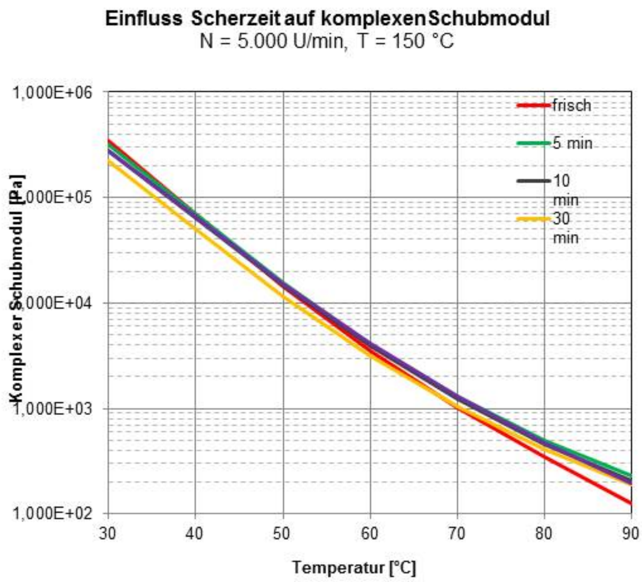

- If the mixing time is less than 30 minutes, changes in PEN and Softening Point can be attributed to the MMT particles added!
- If mixing time exceeds 30 minutes , bitumen becomes significantly harder.

18

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Results: 50/70 with 5 M.-% MMT



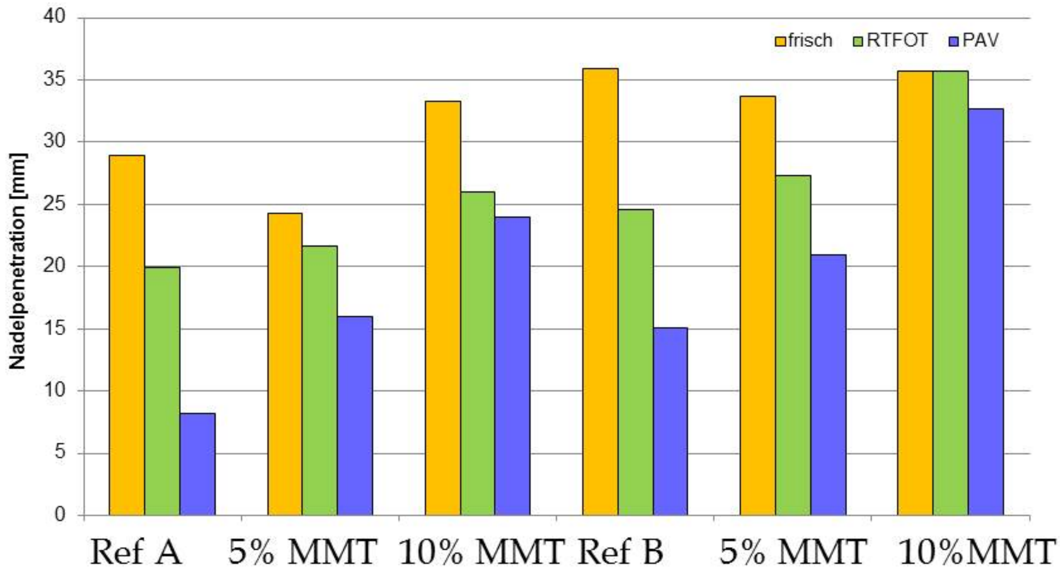

- No significant changes
- Slightly higher module at very high temperatures

19

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## PEN

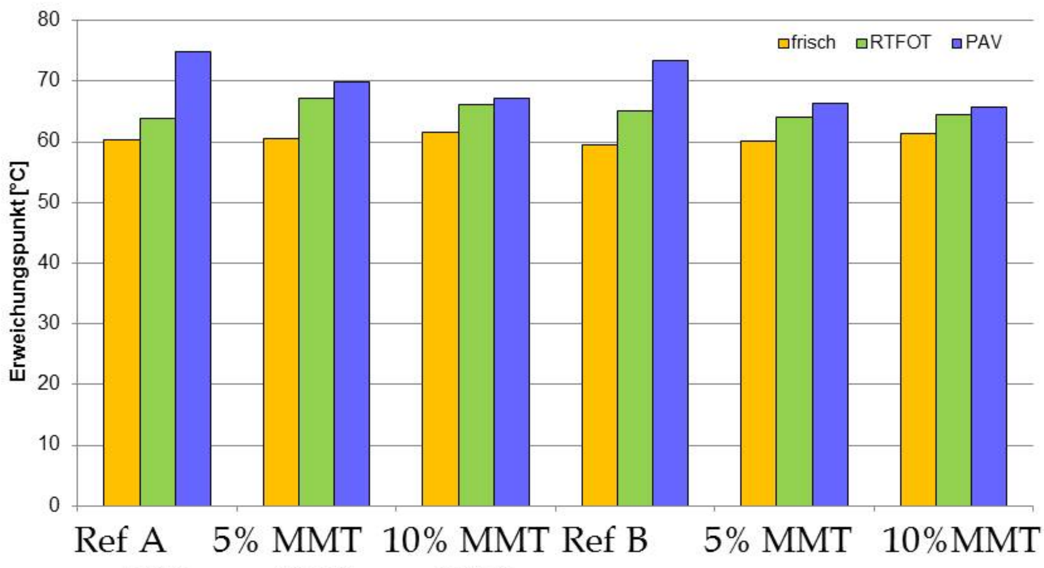



20

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Softening Point

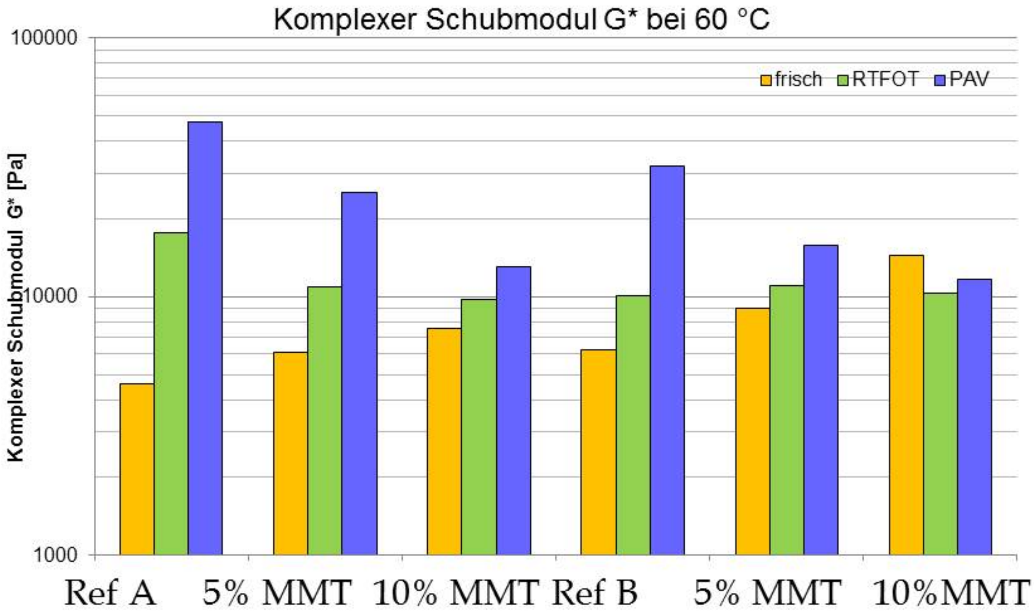



21

Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## DSR-Results




22

Markus Oeser | Delft, 17 September 2014

Prevention of Asphalt Binder Oxidation using MMT-Particles

## Conclusions

- MMT particles can be easily mixed in the binder using a simple shear mixed.
- Even after a mixing time of only 5 minutes (at N = 5.000 R/min) sample appears homogeneous. Dark field microscopy will be carried out to gain further information!
- Influence on PEN and Softening Point is quite low.

23

Markus Oeser | Delft, 17 September 2014

## Conclusions

- Production of larger quantities of MMT-modified bitumen appears to be feasible.
- Technique needs to be up-scaled to be used in mixing plants.
- Rate of oxidation is reduced
- Influence on the adhesion between the grains and the mastics is to be investigated.
- Influence on the cohesion of the bitumen will be studied in future.
- Asphalt tests will be done.



Prevention of Asphalt Binder Oxidation using MMT-Particles

The End!

# 9 References

AASHTO M 320-10, Standard Specification for Performance-Graded Asphalt Binder, standard by American Association of State and Highway Transportation Officials, 2010

AASHTO R 28-12, *Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)*, standard by American Association of State and Highway Transportation Officials, 2012

AASHTO T 315-12, *Standard Method of Test for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)*, standard by American Association of State and Highway Transportation Officials, 2012

AASHTO T 240-13, *Standard Method of Test for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test),*(ASTM Designation: D 2872-04, standard by American Association of State and Highway Transportation Officials, 2013

R.M. Anderson, G.N. King, D.I. Hanson, P.B. Blankenship, AAPT 80, 615 (2011).
Rowe, G.M., Prepared discussion following the Anderson AAPT paper above, AAPT 80, 649-652 (2011)

Asphalt Institute, the, "*Performance graded asphalt binder specification and testing, Superpave series No.1 (SP-1)*"

ASTM D2872 - 12e1, "Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test)", Developed by Subcommittee: D04.46, Book of Standards Volume: 04.03, 2012

Bell, C. A., AbWahab, Y. , Cristi, M. E. and Sosnovske, D., "*Selection of Laboratory Aging Procedures for Asphalt-Aggregate Mixtures*", Oregon State University, Strategic Highway Research Program report SHRP-A-383, National Research Council, Washington, DC 1994

Bahia et.all., "*Classification of asphalt binders into simple and complex binders"*, AAPT, V67, P1, 1998

Besamusca, J., Volkers, A., Water, J. vd.and Gaarkeuken, B." simulating ageing of en 12591 70-100 bitumen at lab cond comp tot PA -5th Eurasphalt & Eurobitume Congress 13-15th June 2012 Istanbul

Besamusca, J., Sörensen , A. and Southwell, Ch., "*Adressing Ageing Characteristics of Bitumninous Binders in Europe*" , 5th Eurasphalt & Eurobitume Congress, 13-15th June 2012, Istanbul, Turkey

Boysen, R. B., and J. F. Schabron, 1993, *The Automated AsphalteneDeterminatorCoupled with Saturates, Aromatics, and Resins Separation for Petroleum Residua Characterization*. Energy & Fuels, 27: 4654-4661; http://pubs.acs.org/doi/pdf/10.1021/ef400952b

Chabron, J. F., R. B. Boysen, E. W. Kalberer, and J. F. Rovani, 2012, *Automated AsphalteneDeterminatorand Saturates, Aromatics, and Resins Integrated Separation*. Preprints, Div. of Petroleum Chemistry, American Chemical Society, 57 (1): 1-3.

Choquet, F., and Verhasselt, A., "*Ageing of bitumen: from the road to the laboratory and vice versa"*, Proceedings of the Conference on the SHRP and Traffic Safety on two continents, The Hague, Netherlands, Sep 22-24, 1993

Cui, Yuanchen, Jin, Xin, Liu, Guanlan, and Glover, C.J., "An Accelerated Method for Determining Asphalt Oxidation Kinetics Parameters for use in Pavement Oxidation and Performance Modeling", Petroleum Science and Technology. 32:22,2691-2699 (2014)

Eberhardsteiner, L. Fussl, J., Hofko, B., Handle, F., Hospodka, M. Blab, R, and Grothe, H., "Influence of asphaltene content on mechanical bitumen behavior – experimental investigation and micromechanical modelling", materials and structures, 2014, DOI:10.1617/s11527-014-0383-7

Eberhardsteiner, L. Fussl, J., Hofko, B., Handle, F., Hospodka, M. Blab, R, and Grothe, H.,"Towards a microstructural model of bitumen aging behaviour", International Journal of Pavement Engineering, 2014

Eberhardsteiner, L. Fussl, J., Hofko, B., Blab, R, and Lacker, R. ,"Prediction of Hot Asphalt Stiffness – A Multiscale Approach", Transport Research Record, 2015 (submitted)

EN 12607-1, *Bitumen and bituminous binders — Determination of the resistance to hardening under the influence of heat and air — Part 1: RTFOT meth*od, CEN standard, November 2014

EN 12607-2*, Bitumen and bituminous binders — Determination of the resistance to hardening under the influence of heat and air — Part 2: TFOT method*, CEN standard, November 2014

EN12697-45, *"Bituminous mixtures – Test Methods for hot mix asphalt – Part 45: Saturation Ageing Tensile Stiffness (SATS) conditioning test"*, CEN standard, April 2012

EN 14769, *Bitumen and bituminous binders – Accelerated long-term ageing conditioning by a Pressure Ageing Vessel (PAV)*, CEN standard, April 2012

EN 15323, *Bitumen and bituminous binders – Accelerated long-term ageing conditioning by the Rotating Cylinder Method (RCAT)*, CEN standard, april 2007

Michael J. Farrar, P. Michael Harnsberger, Kenneth P. Thomas and William Wiser*, "Evaluation of oxidation in asphalt pavement test sections after four years in service",* International Conference on Perpetual Pavement, Ohio University, Columbus, Ohio, September 13–15, 2006

Glaser, R. R., J. F. Schabron, T. F. Turner, J-P. Planche, S. L. Salmans, and J. L. Loveridge, 2013, *Low-Temperature Oxidation Kinetics of Asphalt Binders*. Transportation Research Record, Journal of the Transportation Research Board, No. 2370, 63-68.

Glaser, R. R, and J. L. Loveridge, 2012, *Low Temperature Oxidation Kinetics of Asphalt Binders*. Preprints, Div. of Petroleum Chemistry, American Chemical Society, 57 (1): 9-11.

Glover, C. J., Prapaitrakul, N., Han, R. Jin, X., Cui, Y., Rose, A., Lawrence, J.J., Padigala, M., Park, E.S., Arambula, E., Martin, A.E., "Evaluation Of Binder Aging And Its Influence In Aging Of Hot Mix Asphalt Concrete: Technical Report," Texas Dept. of Transp. Research Report No. 0-6009-2, 522 pages, October, 2012

*Guide for Mechanical-Empirical Design of new and rehabilitated pavement structures, Final Report, Part 2 Design Inputs, Chapter 2 Material Characterization*, National Cooperative Highway Research Program, Transportation Research Board, National Research Council, March 2004

Han, Rongbin, Jin, Xin., and Glover, C. J., "Modeling Pavement Temperature for Use in Binder Oxidation Models and Pavement Performance Prediction," Journal of Materials in Civil Engineering, 23(4), 351-359 (2011).

Han, R., Jin, X., and Glover, C.J., "Oxygen Diffusivity in Asphalts and Mastics," Petroleum Sci. and Technol., 31(15), 1563–1573 (2013).

Handle, F., Eberhardsteiner, L., Fussl, J. Hofko, B. Hospodka, M, Blab R. and Grothe, H.,"understanding the microstructure of bitumen: a CLSM and Fluorescence approach to model bitumen aging behaviour", 12th ISAP international conference on Asphalt Pavements, Raleigh, 2014

Handle, F., Eberhardsteiner, L., Fussl,J. Hofko, B. Hospodka, M, Blab, R. and Grothe, H. ," the bitumen mixture – a fluorescent approach" Materials and Structures, 2014 (submitted)

Hofko, B., Blab, R., Eberhardsteiner, L., Fussl, J. Grothe, H. Handle, F. and Hospodka, M., " *Impact Field Ageing on Low Temperature Performance of Binder and Hot Mix Asphalt*, ", 12th ISAP international conference on Asphalt Pavements, Raleigh, 2014

Hofko, B, Eberhardsteiner, L., Fussl, J., Grothe, H., Hospodka, M, Nahar, S., Schmets, A. and Scarpas, A., "*Microstructure and Theology of Bitumen – Friends or Foes?"*, Materials and Structures 2014 (submitted)

Hofko, B., Blab, R., Eberhardsteiner, L., Fussl, J. Grothe, H. Handle, F. and Hospodka, M.,"*Recent developments in the field of aging of bitumen and asphalt mixes*",Transport Research Record, 2015 (submitted)

Huang, S.C., R. Glaser, and F. Turner, 2012, *Impact of Water on Asphalt Aging*. Transportation Research Record 2293, 64-72.

Huh, J.-D. and Robertson, R. (1996). Modeling of Oxidative Aging Behavior of Asphalts from Short-Term, High-Temperature Data as a Step Toward Prediction of Pavement Aging. Transportation Research Record 1535:91-97

Jin, X., Cui, Y., and Glover, C.J., "Modeling Asphalt Oxidation in Pavement with Field Validation," Petroleum Sci. and Technol., 31(13), 1398-1405 (2013).

Jin, X., R. Han, Y. Cui, and C.J. Glover, "A Fast-rate – Constant-rate Oxidation Kinetics Model for Asphalt Binders," Industrial and Engineering Chemistry Research, 50(23), 13373-13379 (2011).

King, G., M. Anderson, D. Hanson, and P. Blankenship: "Using Black Space Diagrams to Predict Age-Induced Cracking," 7th Rilem Intl.Conf on Cracking in Pavements, vol 1, Scarpas, Kringos, Al-Qadi, Loizos (eds.), 2012.

Lu, X., Talon, Y., and Redelius, P. (Date?). Aging of Bituminous Binders – Laboratory Tests and Field Data. http://www.nynas.com/Global/Bitumen%20for%20paving%20applications/UK/25341.pdf

Mookhoek, S.D., Giezen, C. and Scarpas, A., "*Analyse stand van zaken rond veroudering asfalt (start notitie)*", InfraQuest-2013-55 NL-LAB Aging, 2013 (in Dutch)

Nichols, C. et al, "*BitVal - Analysis of Available Data for Validation of Bitumen Tests*", FEHRL report on phase 1 of the BitVAL project, download from http://bitval.fehrl.org/

Partl, Manfred N. ,Hussain U. Bahia, Francesco Canestrari, Chantal de la Roche, Herve' Di Benedetto, Herald Piber, Dariusz Sybilski Rilem State of the Art Advances in Interlaboratory Testing and Evaluation of Bituminous Materials, Chapter 7: Hot Recycling of Bituminous Mixtures, RILEM, Springer Dordrecht Heidelberg New York London, ISBN 978-94-007-5103-3, 2013

Petersen, J. C., and R. Glaser, 2011, Asphalt Oxidation Mechanisms and the Role of Oxidation Products on Age Hardening Revisited. Road Materials and Pavement Design, 12 (4): 795-819

L. Porot, L. Bobrisow, "Laboratory Mixture ageing protocol for RAP production", 4th Eurasphalt & Eurobitume Congress 2008

Prapaitrakul N., Jin X., Han R., and Glover, C. J. "A Transport Model of Asphalt Binder Oxidation in Pavements," Road Materials and Pavement Design, 10 (Special Issue), 95-113 (2009).

prEN 12697-52:2014, "*Bituminous mixtures – Test Methods- Part 52: Conditioning to address oxidative aging*", concept standard CEN TC227 WG1, may 2014

Ruan, Y., Davison, R.R., and Glover, C.J., "An Investigation of Asphalt Durability: Relationships between Ductility and Rheological Properties for Unmodified Asphalts," Petroleum Science and Technology, 21(1&2), 231-254 (2003)

Steiner, D., Hofko, B., Blab, R. Eberhardsteiner, L. Fussl, J. Grothe, H. Handle, F. and Hospodka, M., "*Towards an efficient laboratory aging protocol fo long-term ageing of compacted asphalt mix specimens*", Transport Research Record, 2015 (submitted)