Innovative binder characterization methods

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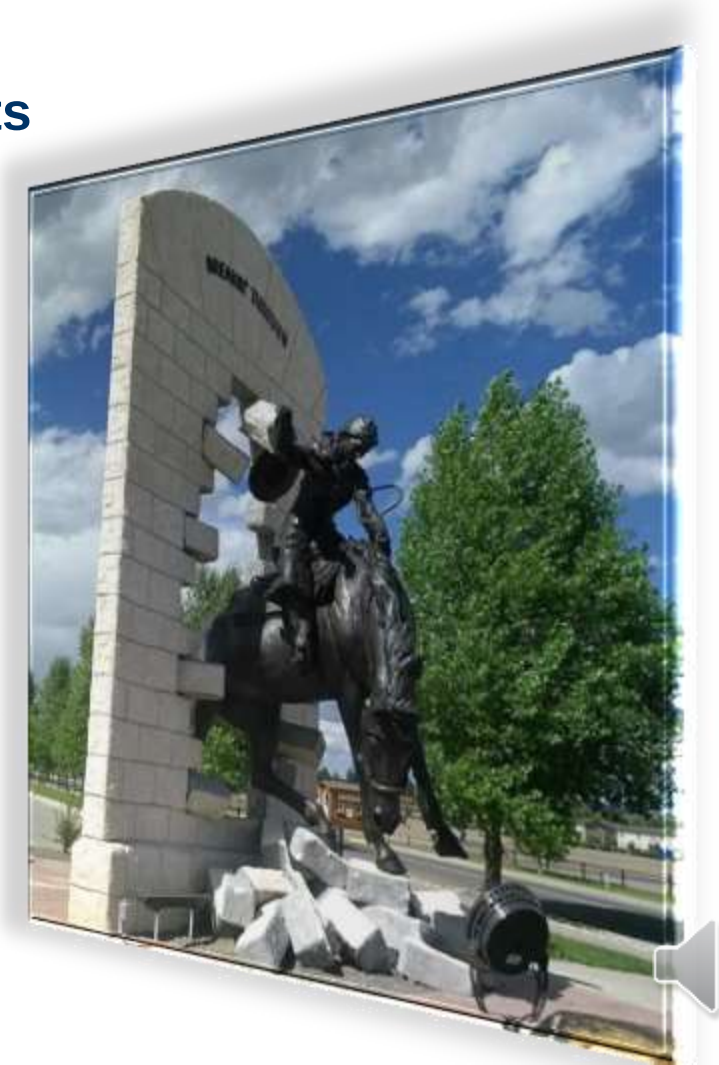
AMAP 2016 Annual Meeting

Seattle, WA, February 11, 2016

Acknowledgements

- **FHWA contract funding and direction**
  - **Fundamental Properties of asphalts and modified asphalts III (FPIII)**
  - **FPIII products validation**
  - **Jack Youtcheff**
- **Commercial clients**
- **WRI APT team**
  - ***"We want to break through!"***



Outline

- Presentation of WRI
- Focus on new innovative binder characterization methods
  - Status
  - Applications to particular asphalt binders
- Summary
- Perspectives

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Presentation of WRI

- **US non-profit 501(c)3**
  - **Affiliate of the Univ. of Wyoming**
- **Facilities in Laramie, WY**
  - **University of Wyoming Campus**
  - **Advanced Technology Center**
- **Fields of expertise**
  - **Energy (oil, coal, biomass)**
  - **Asphalt materials**
  - **Environment**

- **Annual sponsored events in July**
  - **Petersen Asphalt Research Conference:**
    - **53rd on July 18-21, 2016 combined with the ISAP 2016 symposium**
  - **Training day on "Asphalt Binder Chemistry and Advanced Testing" - 1st on July 16, 2015**

WRI-Asphalt and Petroleum Technologies

- **Main areas of R&D**
  - (Heavy) Crude oils – Petroleum products - Asphalt binders
  - Analysis, Characterization, Evaluation, Formulation, Forensics
  - Analytical method and instrument developments
  - Voluntary – National and International: Binder ETG, ASTM, ACS, TRB AFK20, ISAP, AI, NAPA, RILEM
- **WRI / APT Funding - non-profit 501(c)3**
  - ***No funding from the State / University***
  - Commercial contracts
    - Service, Research, Forensics, Consulting, Licensing
  - Contracts and agreements with DOT-FHWA
  - Heavy Oil Research Consortium with Oil companies
  - Asphalt Industry Research Consortium – **New!**

Deliverables

Project Finished: 06/30/2015

- ✓Models
- ✓Database
- ✓Test methods
- ✓Mix designs
- ✓Test sections

➢80+ Products on line

- **http://www.arc.unr.edu/**
- **Reports still under final review**

➢250 Researchers –scientists and engineers

New Technical Leaders of Today and Tomorrow…

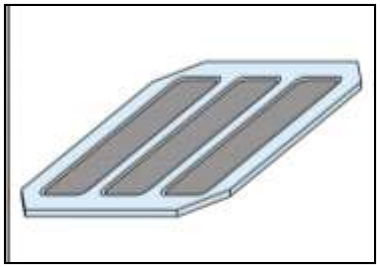
Fundamental Properties of Asphalt Binders III Deliverables

Project Finished: 05/31/2015

- **Technical white papers**
  - **23 papers**
  - **Reviewed and validated by FHWA**
  - **Online at: http://www.westernresearch.org/transportation.aspx?id=2662**
- **Final Reports**
  - **2 reports: Fundamental and Applied Research / Methodology**
  - **Still under review**
- **TechBriefs for selected products**
  - **6 Techbriefs**
  - **Still under review**
- **Communications: Various events & peer reviewed journals**

FPIII deliverables
Technical Research Briefs

- Asphalt Binder Oxidative Aging Chemo-Mechanical Model
- Automated HPLC SAR-AD Separation
- 4-mm DSR (Dynamic Shear Rheometry)
- The Universal Simple Aging Test (USAT)
- Asphalt Pavement – Micro-Sampling and Micro-Extraction Methods
- Analytical Method to Measure Water in Asphalt and its Application to Emulsion Residue Recovery



Validation and Refinement of WRI FPIII Products

- FHWA Contract #: DTFH61-13-C-00017
- Awarded Sept. 2013

FPIII Products

- 4 mm DSR
- Micro Sampling & Extraction
- SAR-AD
- Asphalt Aging Model
- Pressure DSC
- AFM

Binders and Mixtures samples

- **"Old" FHWA TF-ALF Fatigue Cores**
  - Taken just before reconstruction Earlier ones studied in FPIII
- **"New" ALF WMA/RAP Test Samples**
  - Newly constructed: for thin film aging and making predictions according to FPIII models
- **Field Site Samples – ARC / FHWA select.**
- **Others - FHWA Recommendation**
  - **Special cases like REOB blends**

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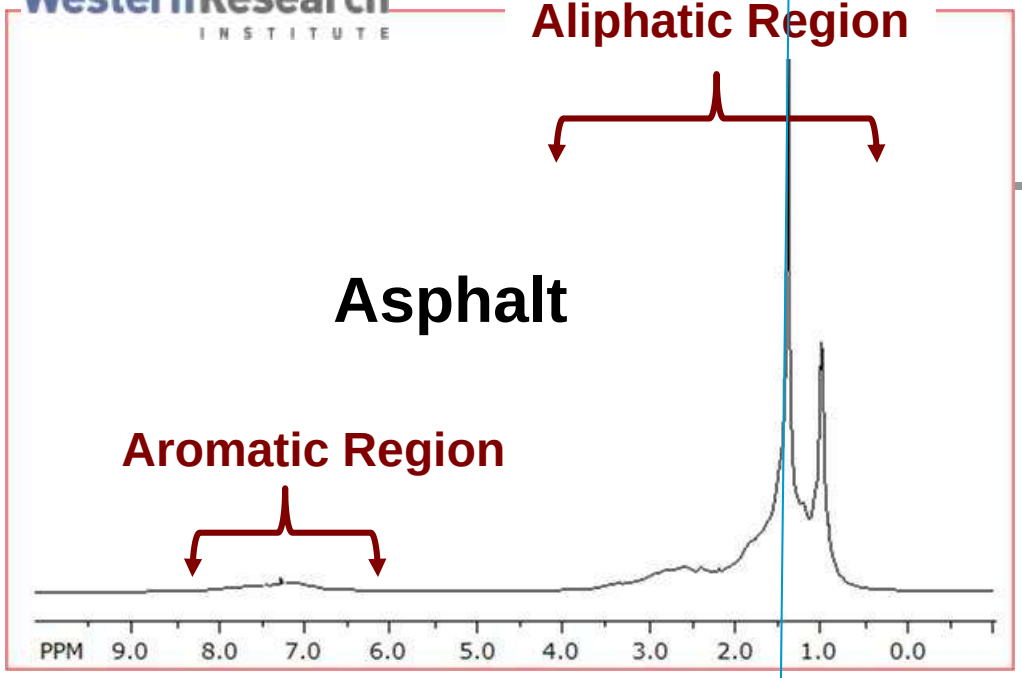
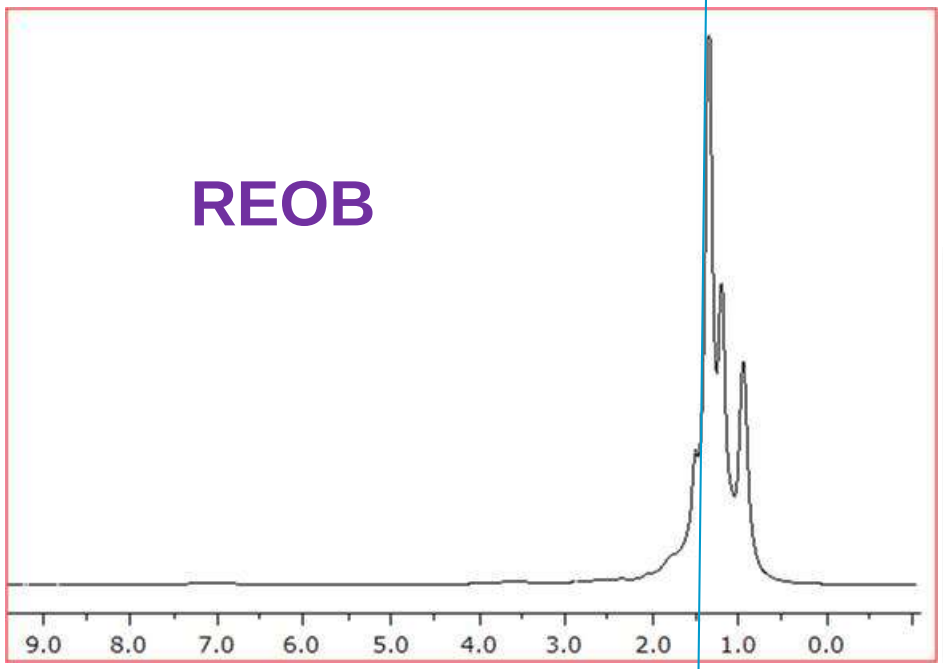
REOB Quantification in Asphalt by ^{1}H NMR



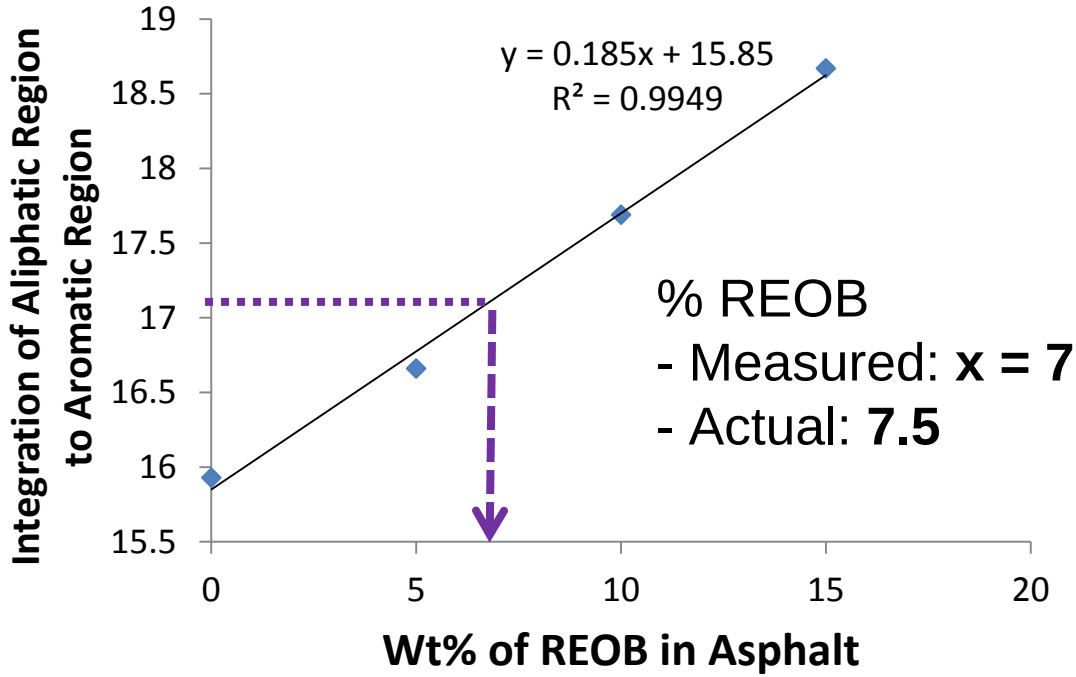


400 MHz, UW

- **Few aromatic protons in asphalt – many more aliphatics**
- **Even less aromatics in REOB mostly constituted of saturated alkanes (aliphatics) - different from asphalt saturates**

REOB Quantification in Asphalt by ^{1}H NMR

❑Calibration & Integration of unknown concentration



REOB specific resonances not present in asphalt

- ➢Calibration curve could be universal
- ➢NMR: more accurate and selective than XRF

WORK IN PROGRESS!

Binder Chemical Characterization by SAR-AD™

- ✓ **SAR-AD:** separates asphalts and oils into distinct chromatographic and solubility subfractions
  - ✓ Saturates, Aromatics, Resins and Asphaltenes (SAR-AD)
- ✓ Advanced fully automated separation
  - ✓ Small scale - fast: 2 mg - 4 hrs
- ✓ Developed by WRI under FPIII contract (FHWA) and further optimized

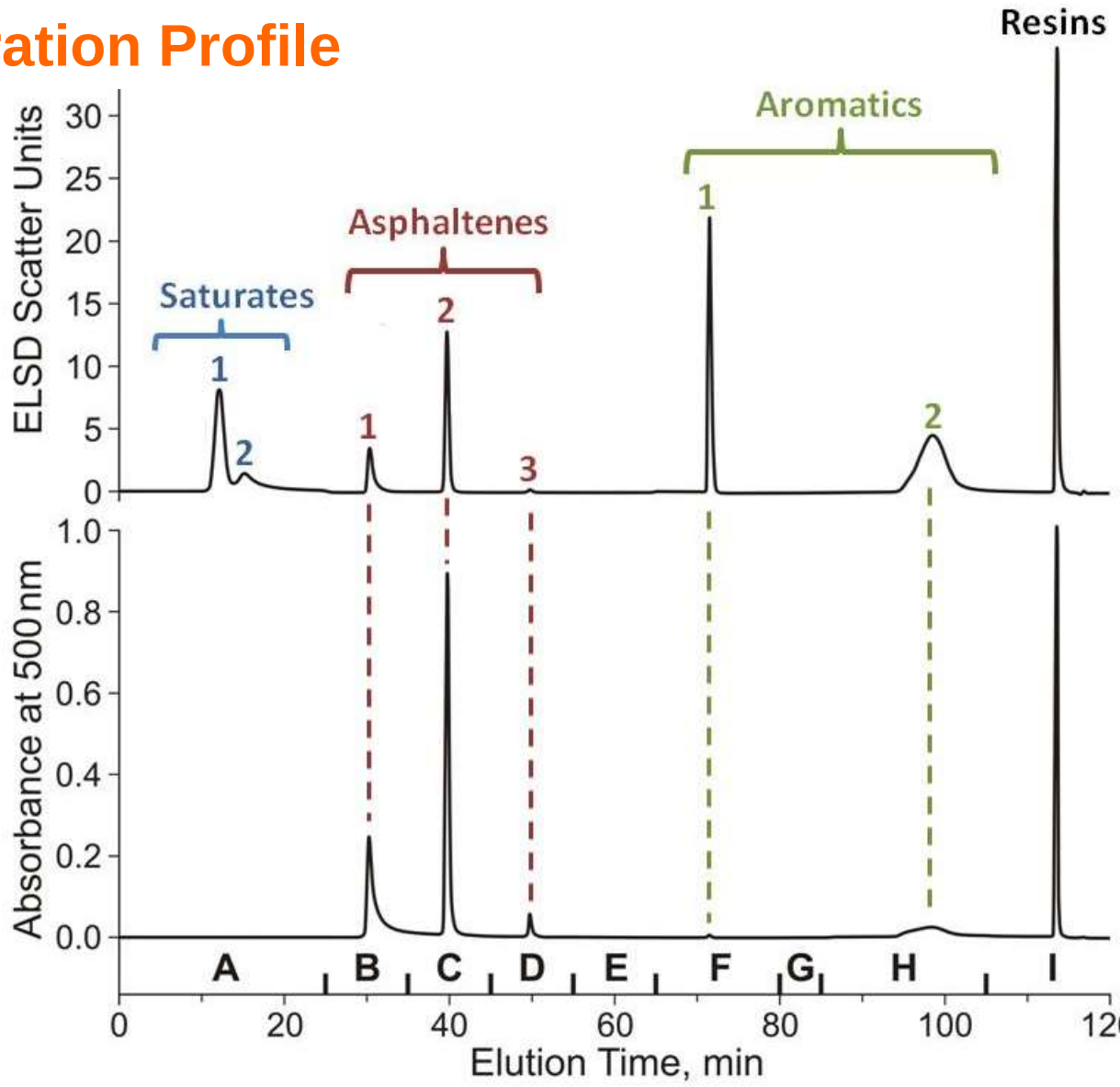
- **Application to REOB asphalt blends**
  - How does REOB composition compare to asphalt?
  - How does it impact asphalt composition?

Chemical Characterization by SAR-AD

SAR-AD Separation Profile

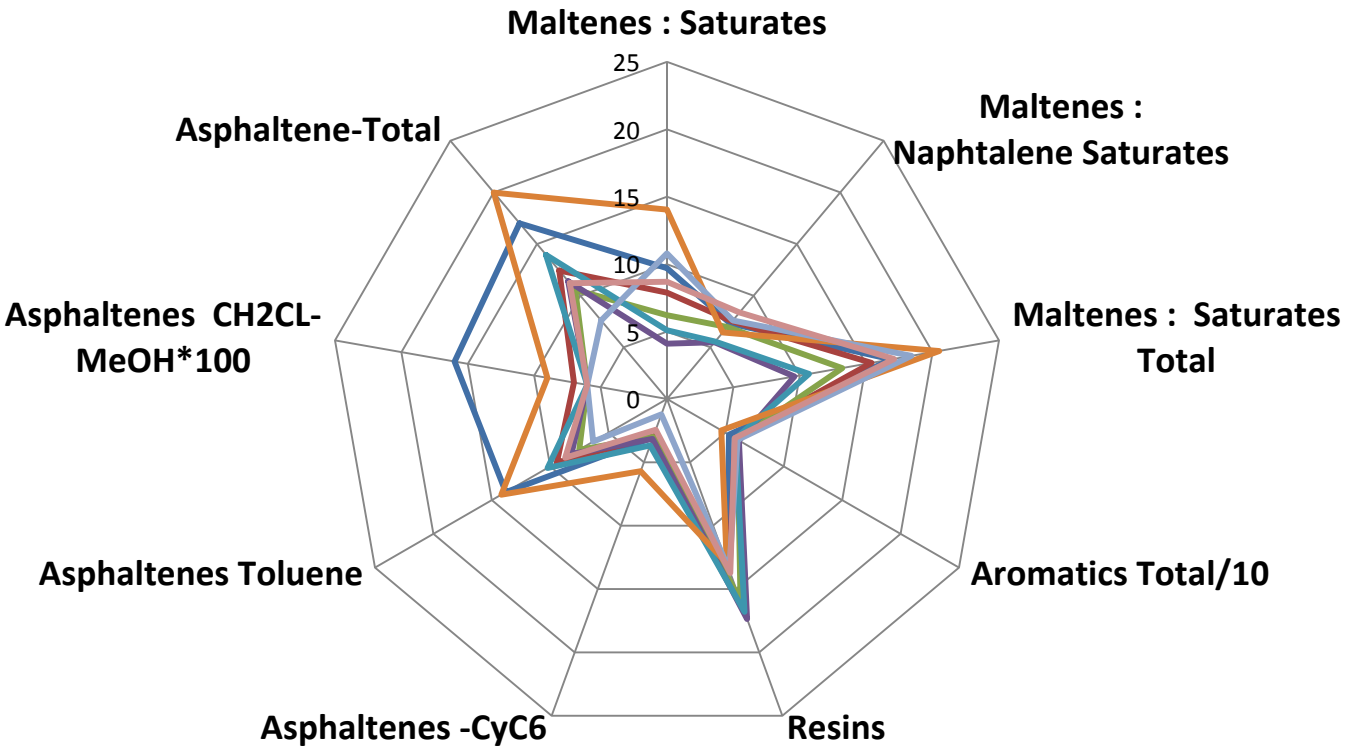
Quantitative weight%

Relative concentration of condensed aromatic material



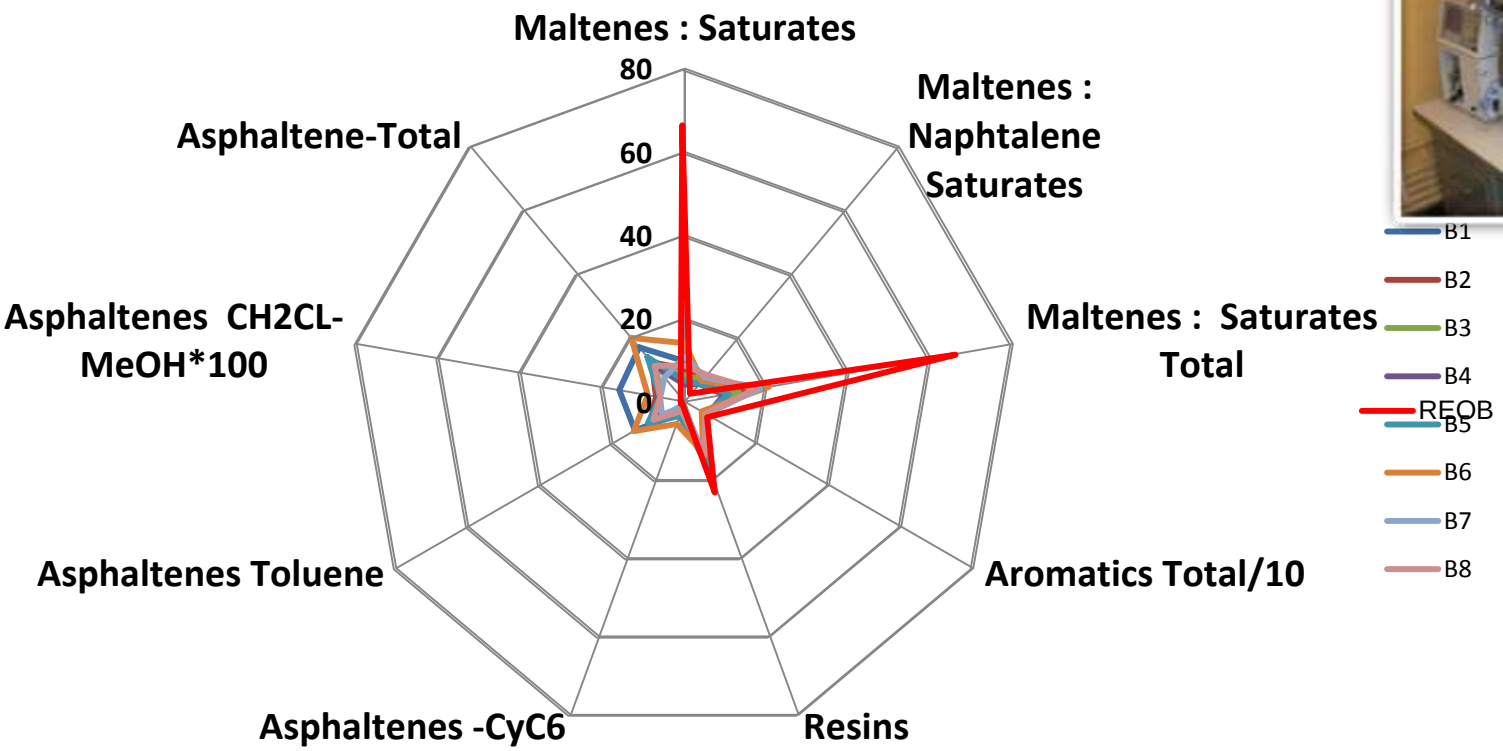
Chemical Characterization by SAR-AD

- **SAR-AD of Neat Asphalts**



Chemical Characterization by SAR-AD

- **SAR-AD of Neat Asphalts vs. REOB**



- **SAR-AD of REOB: Very different**
  - **Very low asphaltenes, aromatics, and naphthene saturates**
  - **Very high paraffinic saturates and high resins**
  - **Consistent with proton NMR**

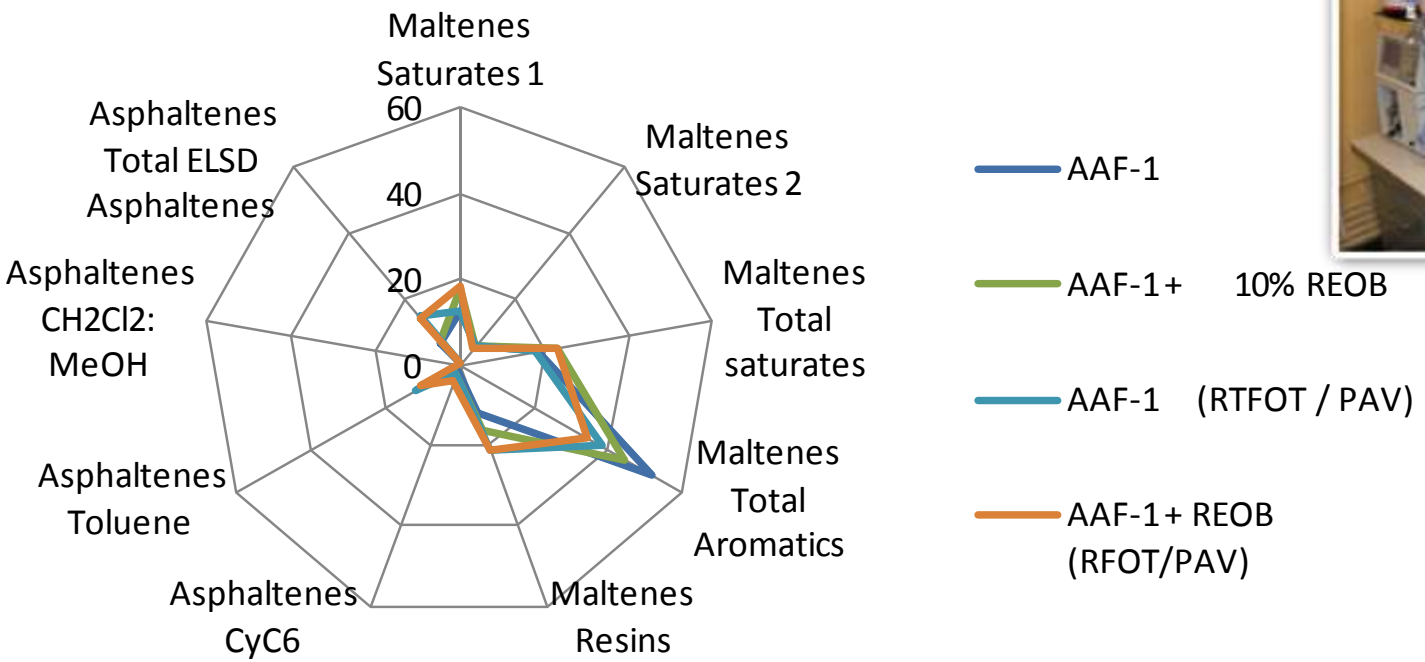
Chemical Characterization by SAR-AD

- **SAR-AD of Asphalt REOB blends**

- **Blends:** linear additive for low asphaltene asphalts – less linear for high asphaltene asphalts
- ***Potential compatibility issue between REOB and asphaltenes (polars – polycondensed aromatics) for some blends***

Chemical Characterization by SAR-AD

- **SAR-AD of Aged Asphalt REOB blends**



- **Blend Aging Trend: "classical"**
  - **Higher asphaltenes and resins**
  - **Lower aromatics**
  - **Stable saturates**
- **No significant impact of REOB under 1xPAV condition (USAT)**

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Consequences on Aging Study by High Pressure DSC

- **P-DSC (Differential Scanning Calorimetry) purpose and potential usage**

➢ **To accelerate oxidation for binder selection / prediction**

- Thin film aging - 8 weeks / PAV - 20hrs (possibly more)
- P-DSC: a few hours

➢ **Usage – Practical/Technical and Scientific**

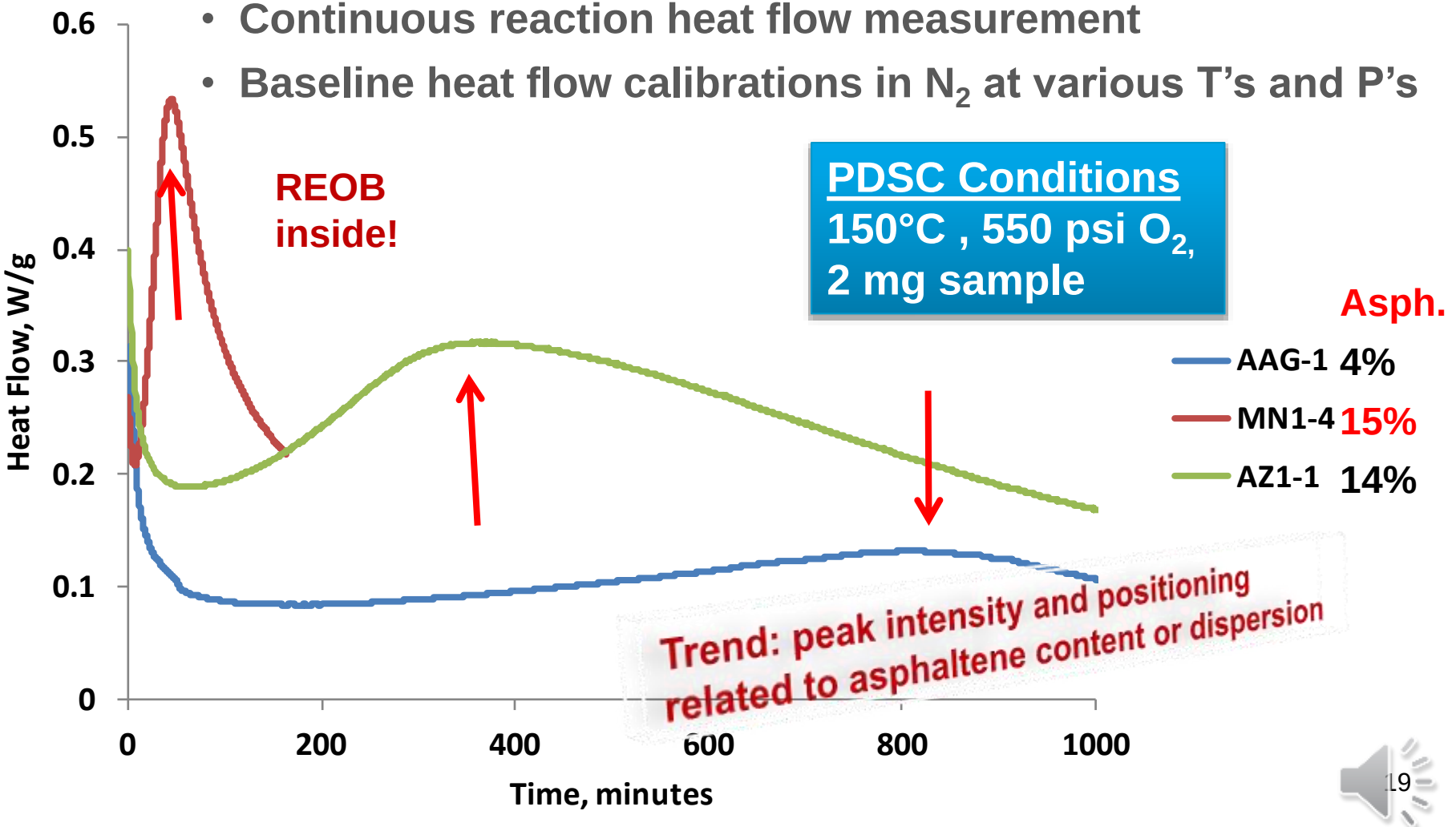
- Quick characterization of binder aging susceptibility
- Formulation of asphalt binders against oxidation
- Development of WRI oxidation model
  - Higher Temp. & Pressure
  - Determination of oxygen partial pressure influence
  - Rapid determination of reactive material (RM)

- **Not NEW: ASTM Standard Test Methods (D5483/E2009)**
  - Oxidation induction time and onset temperature of lube greases

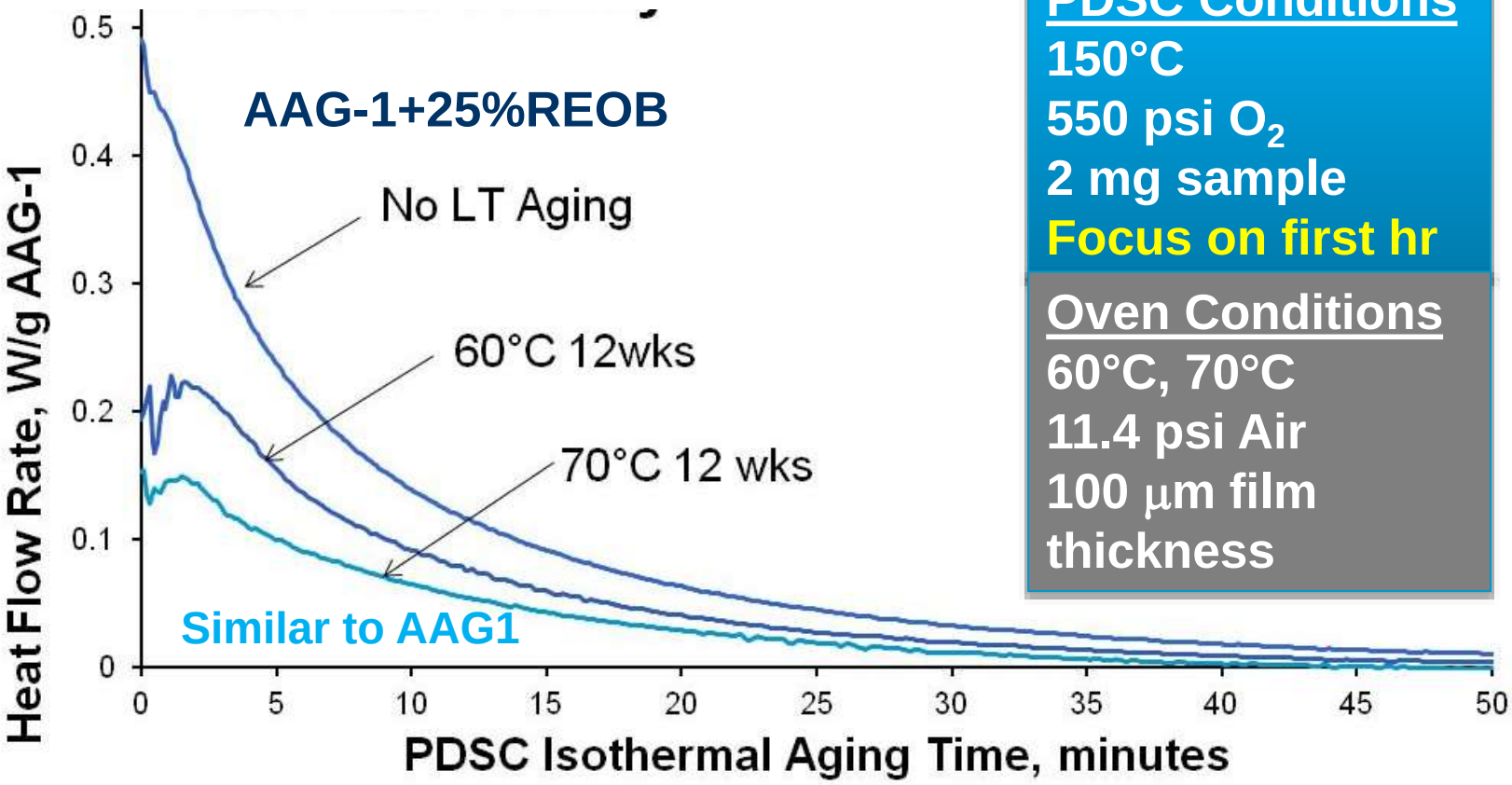
Consequences on Aging Study by High Pressure DSC

❑ Typical PDSC results - Heat flow rate overlay

- Continuous reaction heat flow measurement
- Baseline heat flow calibrations in N_2 at various T's and P's



Consequences on Aging Study by High Pressure DSC



PDSC Conditions
150°C
550 psi O_2
2 mg sample
Focus on first hr

Oven Conditions
60°C, 70°C
11.4 psi Air
100 μm film thickness

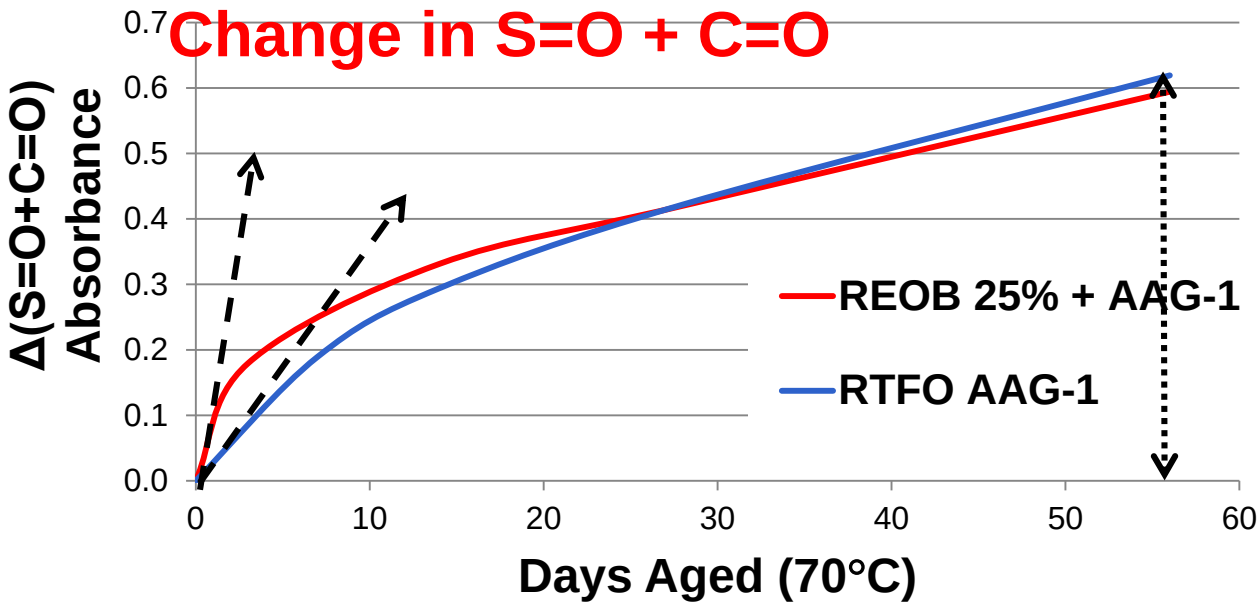
- AAG-1+ REOB appears more reactive (faster 1st reaction)
- But looks like original AAG-1 after long term oven aging

Consequences on Long Term Oven Aging Study by IR

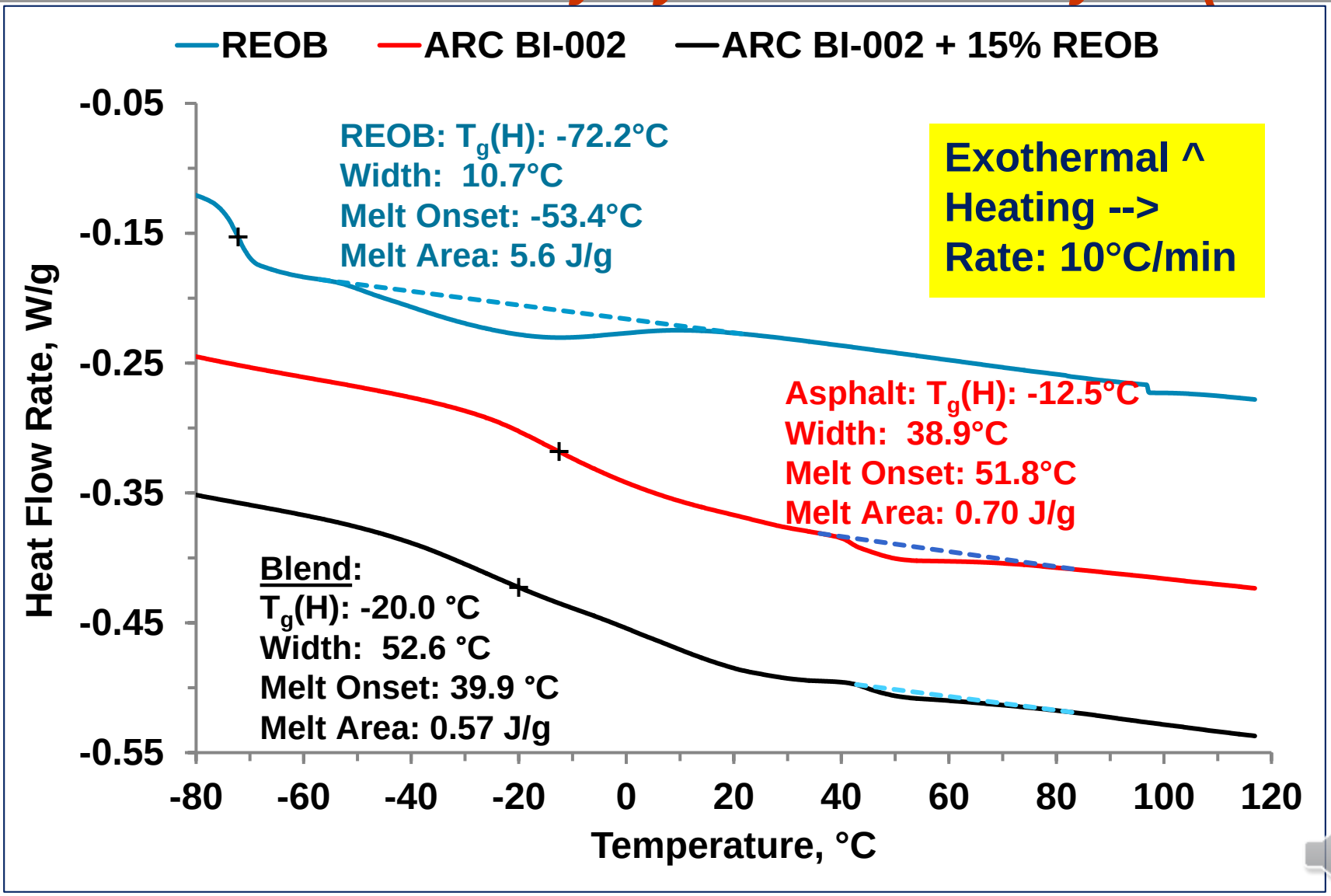
Oxide change comparison suggest various mechanisms:

1. REOB effect: not a simple dilution effect
2. Faster first reaction: catalyst effect from metal or from reactive material concentration (asphaltene separation)?
3. Not all in the fast reaction
4. Higher Reactive Material (RM): oxidation of REOB itself or RM concentration (separation)?

➢ ***However, long term aging amount not significantly different***

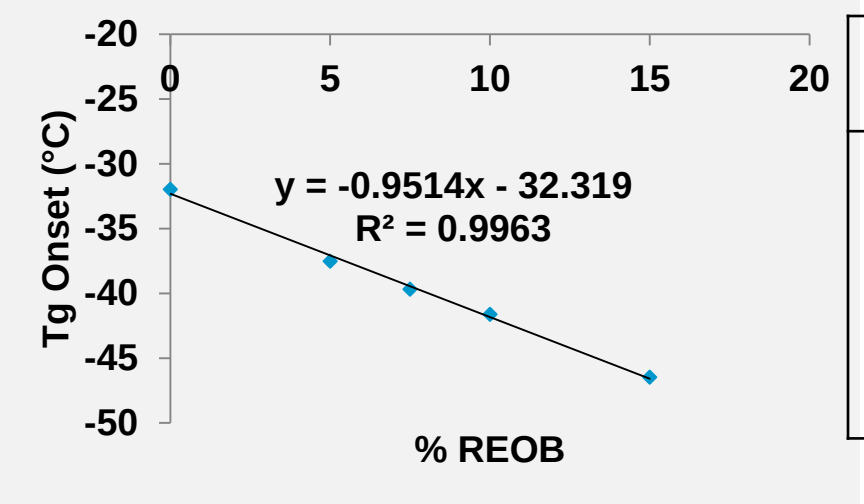


Consequences on Structure Study by Thermal Analysis (DSC)



Consequences on Structure Study by Thermal Analysis (DSC)

- **REOB effect on high vs. low asphaltene asphalt**
  - **High asphaltene: 18% in ARC BI-002 - PG 67-22**
    - **Linear blending vs. Tg but non linear vs. Tg width & end**
    - **Assumption that REOB destabilizes asphaltenes**



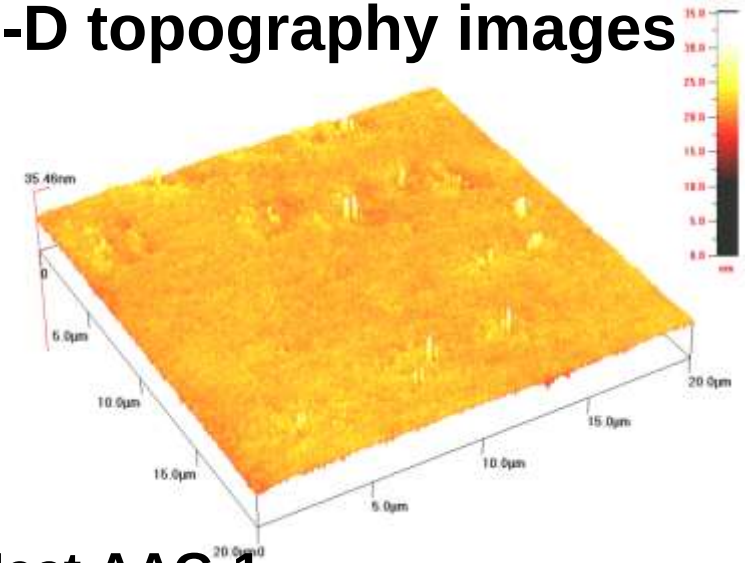
Sample	T_g onset °C	T_g end °C	T_g Width °C	T_g (I) °C
REOB	-77.3	-66.6	10.7	-74.3
ARC BI 0002	-32.0	6.9	38.9	-17.4
+ 5% REOB	-37.5	6.1	43.6	-20.7
+ 7.5%	-39.7	8.6	48.3	-21.7
+ 10%	-41.6	4.0	45.6	-23.9
+ 15%	-46.5	6.1	52.6	-32.3

  - **Low asphaltene: 3% in AAG-1**
    - **Linear blending: Tg parameters all decrease as expected**
    - **No asphaltene destabilization**

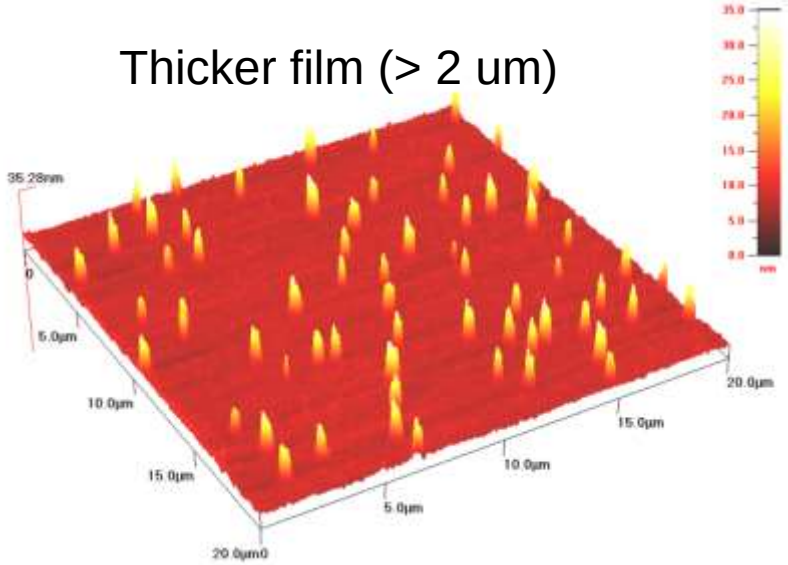
Sample	T_g onset °C	T_g end pt °C	Width °C	T_g (I) °C
AAG-1	-25.9	21.2	47.1	-5.3
+ 25% REOB	-47.1	-5.8	41.3	-32.9

Consequences on Structure Study by AFM

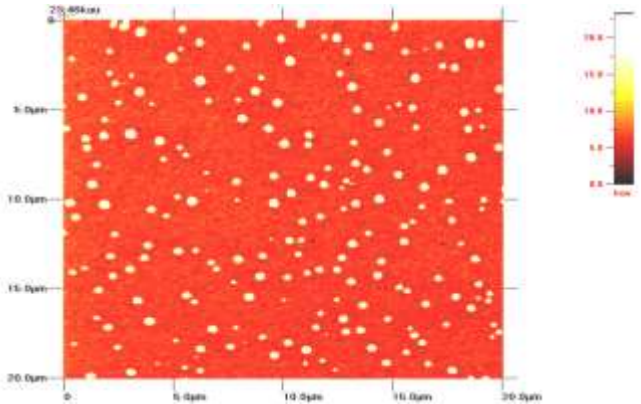
- **3-D topography images**



Thicker film (> 2 um)



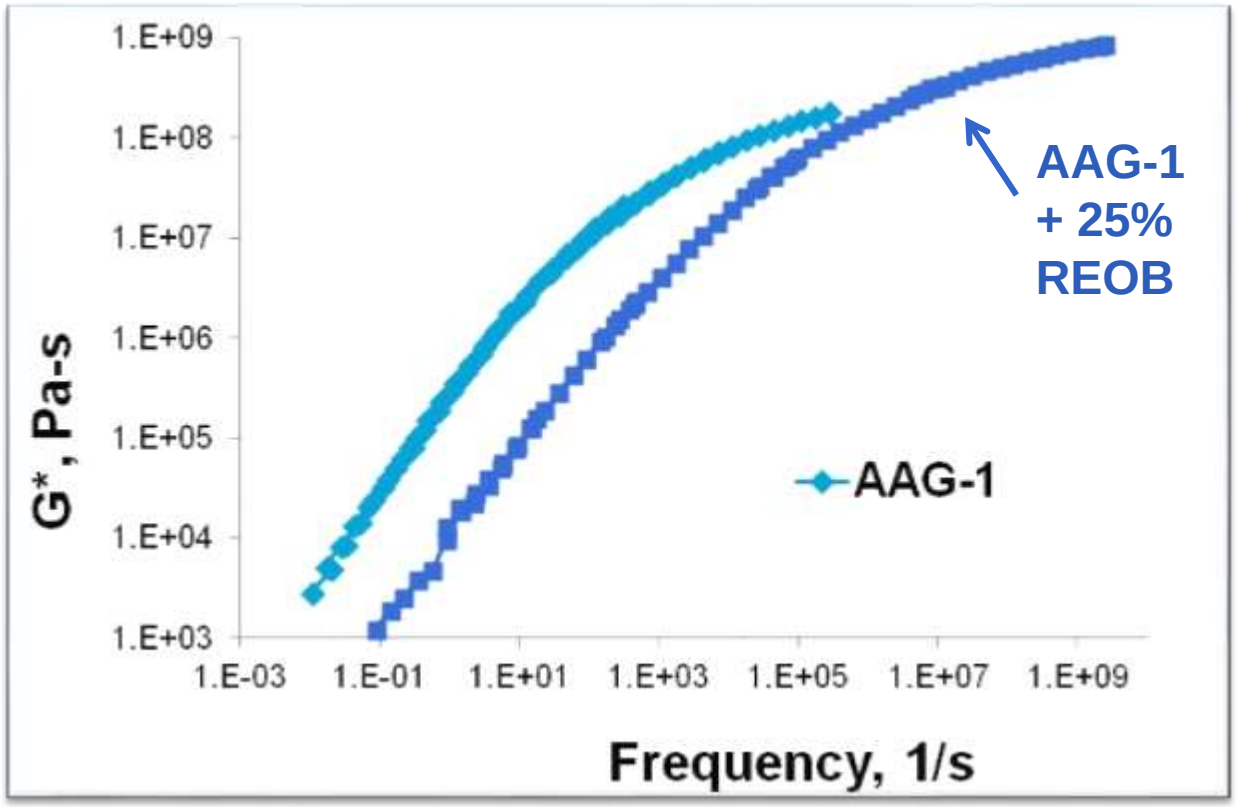
- **Neat AAG-1**
  - **Few bee structures (known to relate to wax crystallites)**
- **+ 25% REOB**
  - **Bees are gone and spikes appear**



- **AAG-1+25% REOB aged at 70 °C for 12 weeks**
  - **Aging increases number of spikes**
  - ***Asphaltenes?***

Consequences on Rheology

❑ DSR Mastercurve (using 4-mm DSR at low temperatures)

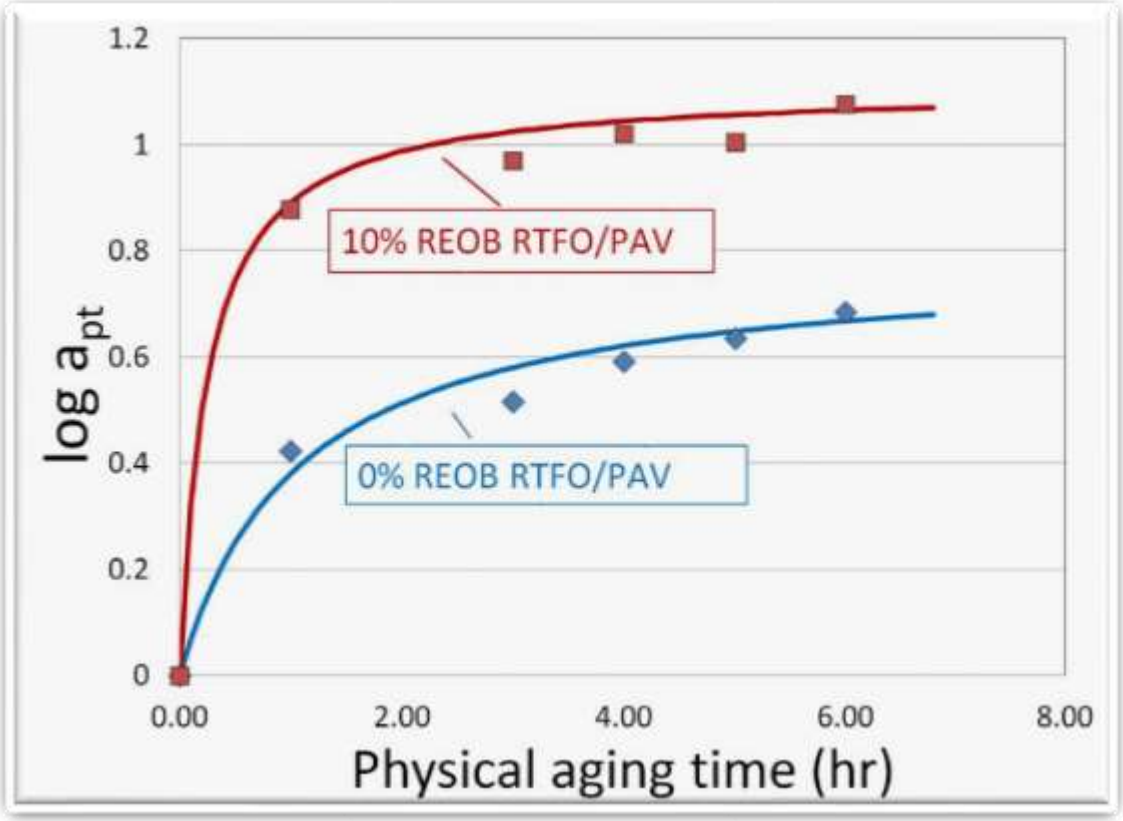


- Asphalt AAG-1 and AAG-1+25% REOB – both unaged
- Black space: REOB blend "rheologically simple"

➢ Clear REOB softening effect – consistent with low Tg

Consequences on Rheology

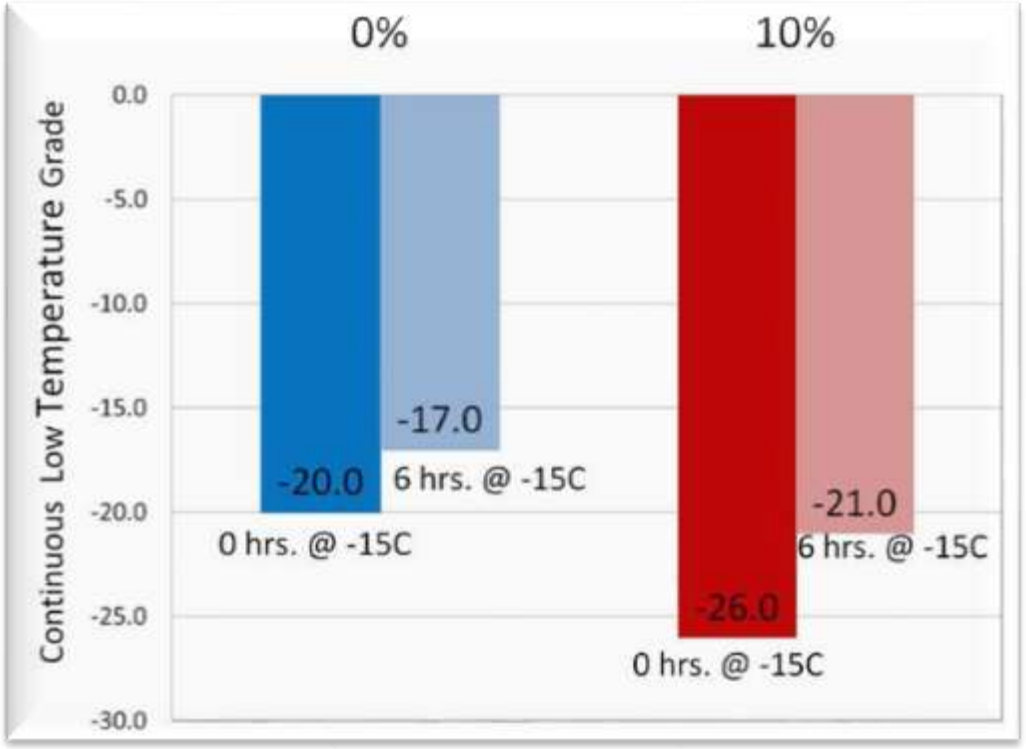
- **Physical Hardening of REOB blends AAF1-RTFO/PAV**
  - **Time Superposition Shift Factor at -15°C (DSR 4-mm)**



- **Similar hardening behavior**
- **Higher extent with REOB – time dep. structuring?**

Consequences on Rheology

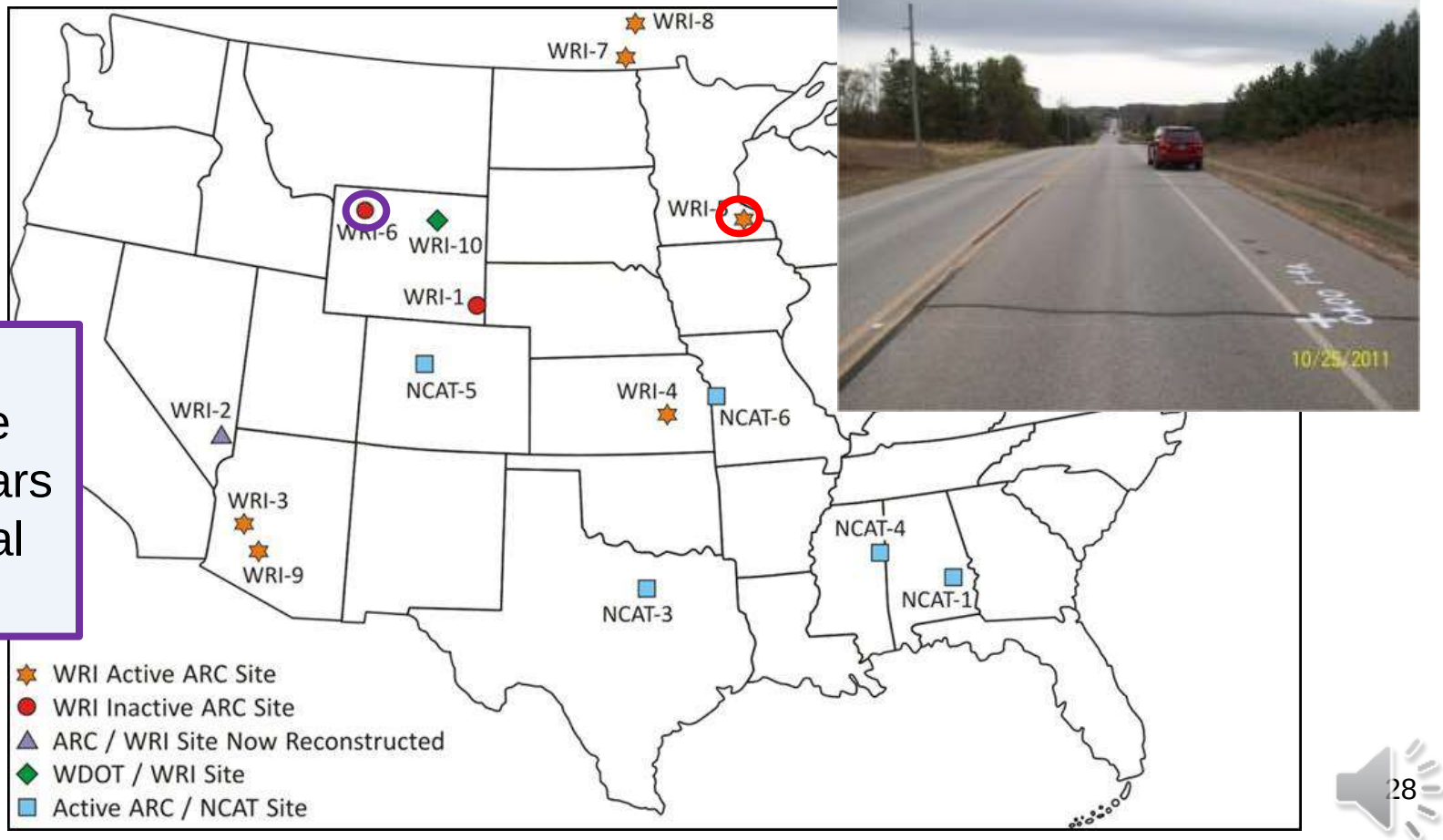
- **Change in Continuous Low Temperature Grade with isothermal conditioning (-15 °C)**



- **3°C for AAF-1 w/o REOB**
- **5°C for AAF-1 + 10% REOB**

REOB Blends Field Study

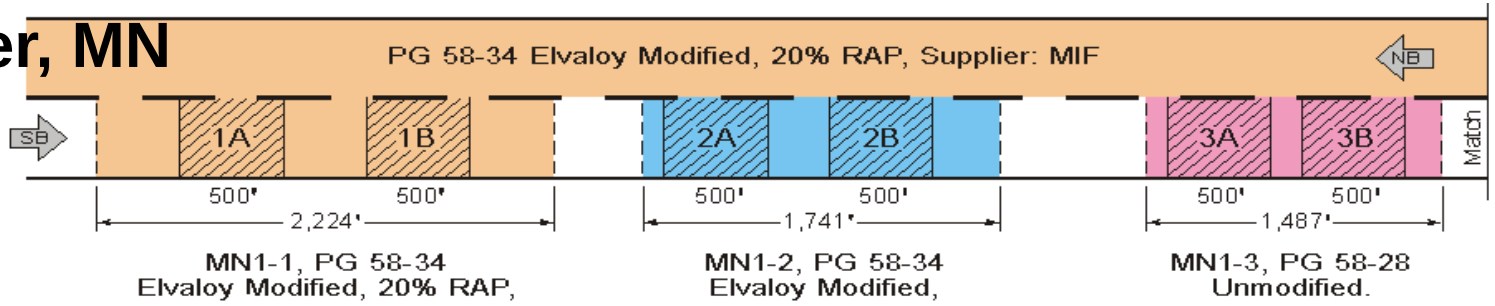
- **FHWA/ARC/WRI and FHWA/ARC/NCAT validation sites in the US and Canada → MN site**



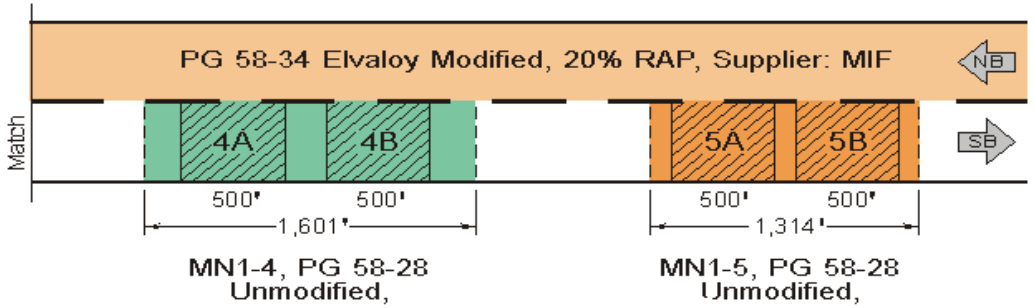
YNP
✓No issue after 3 years
✓Chip seal covered

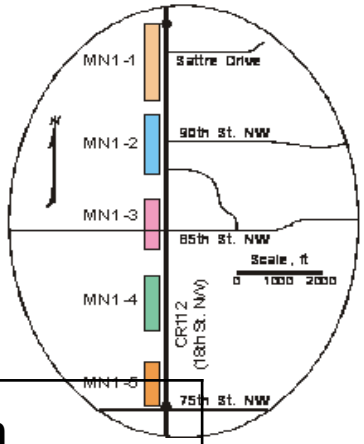
REOB Blends Field Study

- **Rochester, MN**



- ***Construction in 2006***



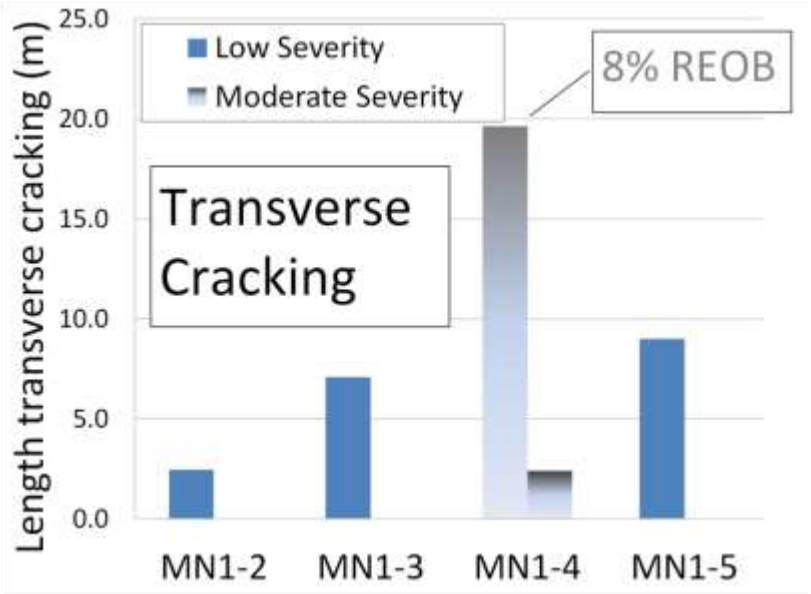


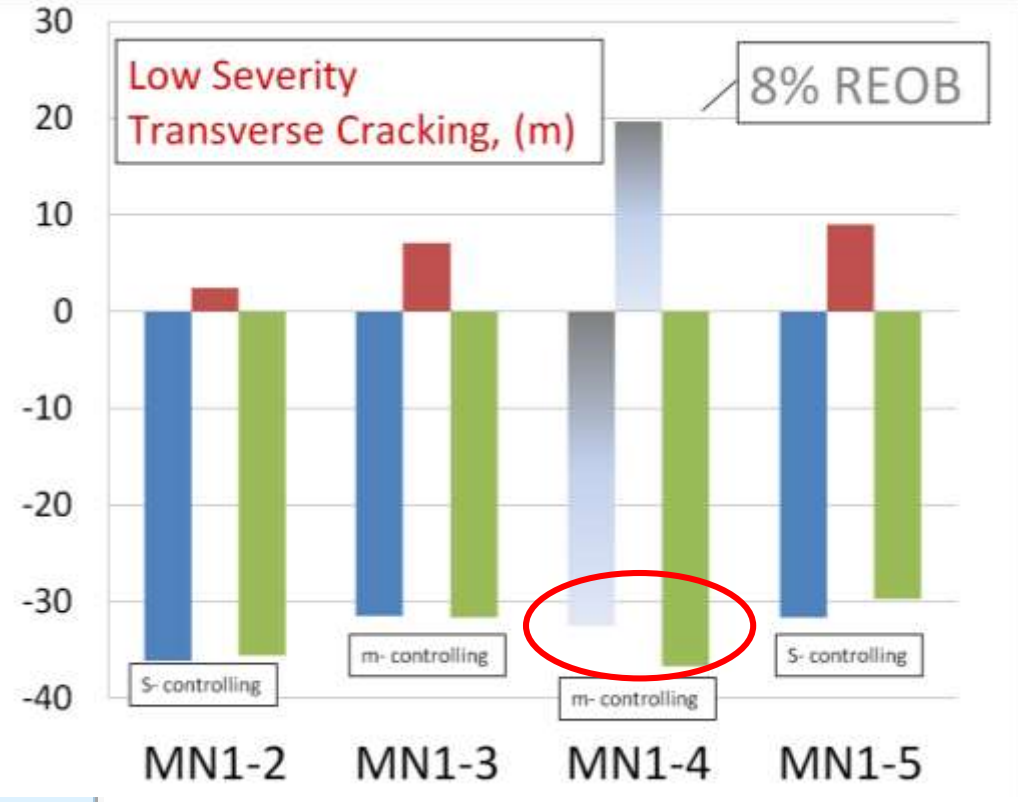
Sample Designation	Performance Grade Project specifications	Source Description
MN1-2	PG 58-34	Canadian blend, Elvaloy modified
MN1-3	PG 58-28	Canadian blend
MN1-4	PG 58-28	Middle East Blend
MN1-5	PG 58-28	Venezuelan blend

➢**REOB in MN1-4, at about 8% content, by XRF (FHWA-TF)**

REOB Blends Field Study

❑2012 (6 years) Transverse Cracking Data (500 feet)



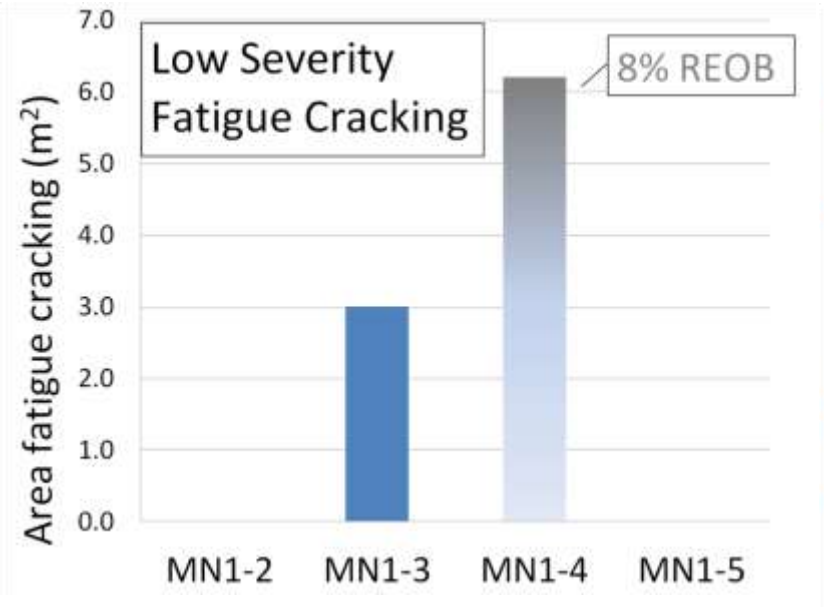


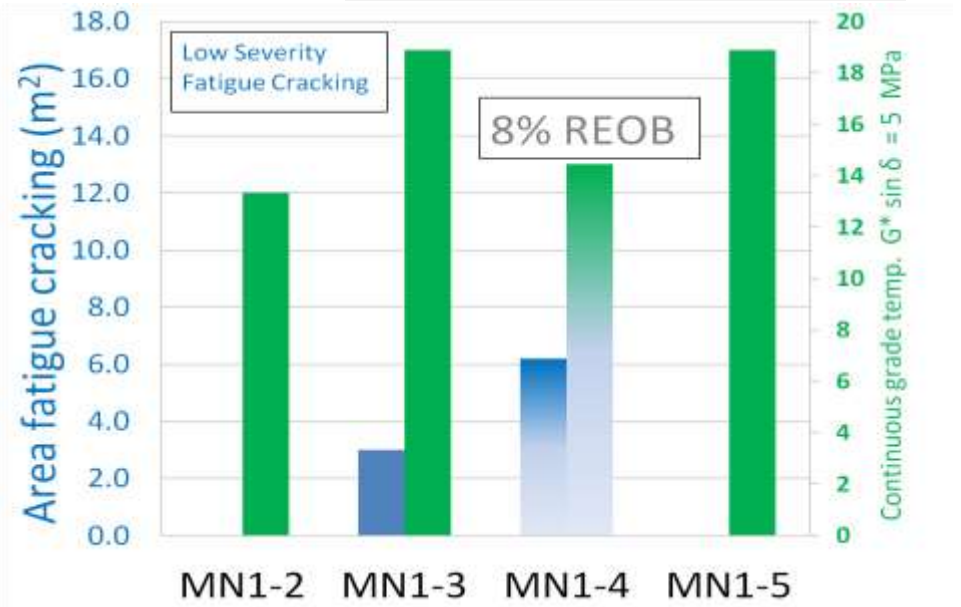
- **Transverse cracking in MN1-4 not predicted by BBR Tc**
  - **Neither by ABCD (classical conditions)**
- **But BBR Tc significantly m controlled: ΔTc = 5°C**
  - **Agreement with other studies**

REOB Blends Field Study

❑2012 (6 years) Fatigue Cracking Data (500 feet)

T @ G*x sin δ = 5 MPa

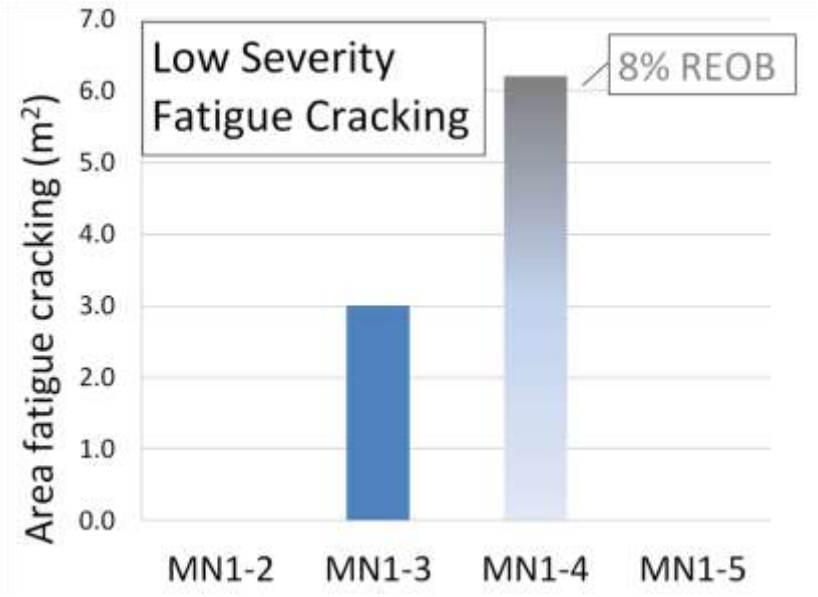




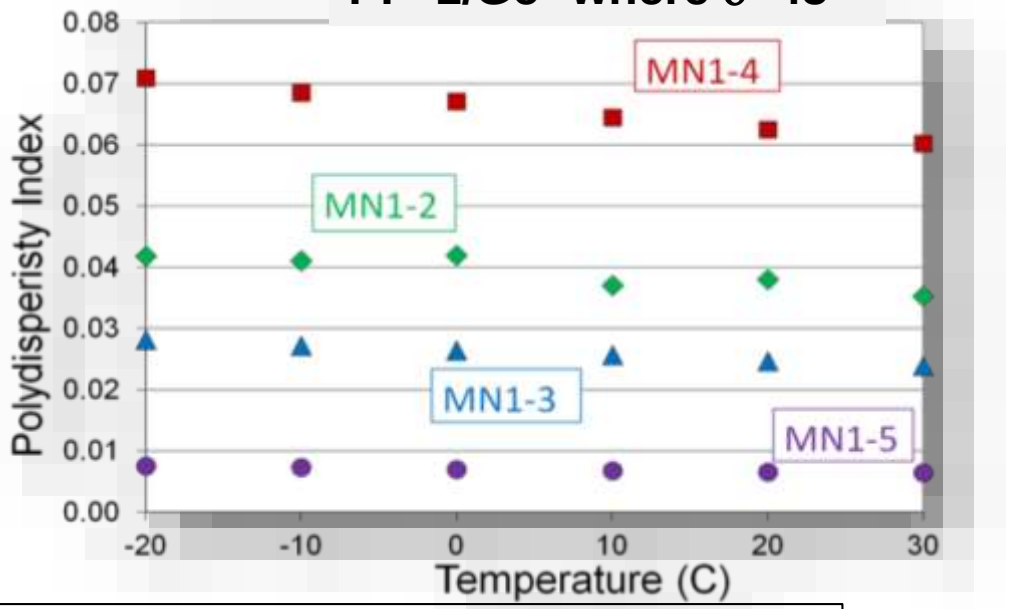
➢**Fatigue Cracking vs. DSR (RTFOT+PAV):**
Continuous grade intermediate temperature did not predict the fatigue cracking on the MN1-4 test section

REOB Blends Field Study

❑2012 (6 years) Fatigue Cracking Data (500 feet)



PI= 1/Gc* where δ=45°

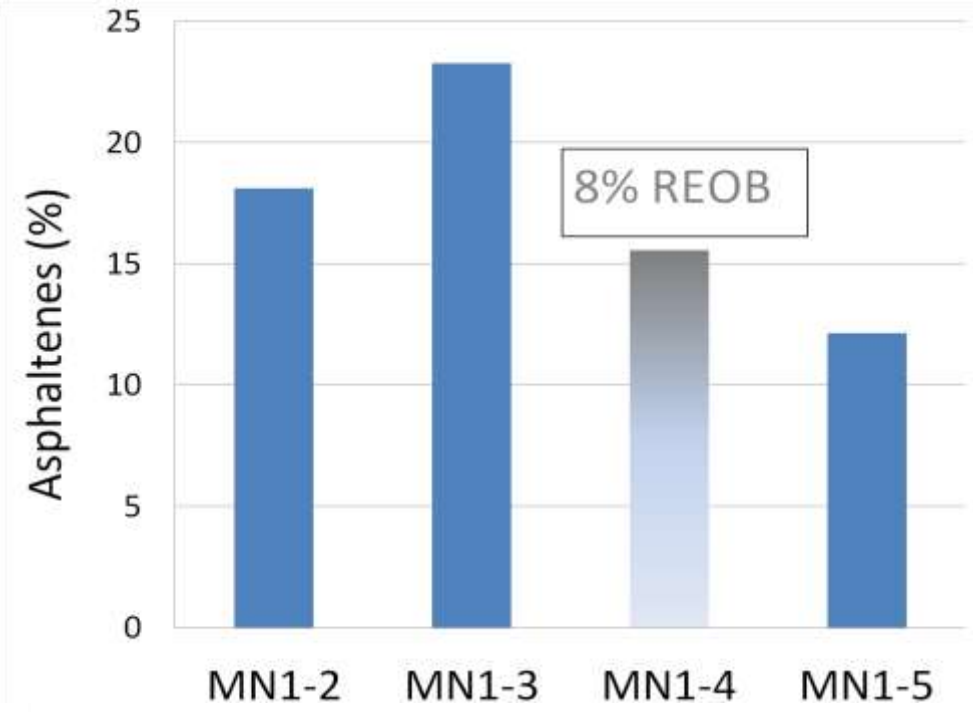


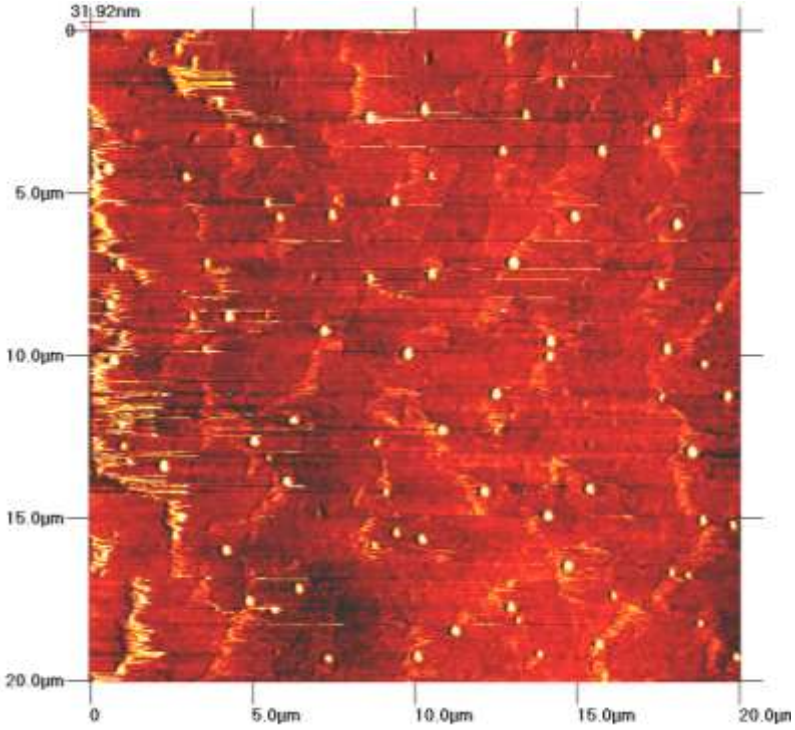
❑**Fatigue Cracking vs. DSR (RTFOT+PAV):**
Inverse of crossover modulus stands out for MN1-4

- **Seen for gel asphalt like aged or air-blown** - possibly related to asphaltene interaction – separation effect?
- **Fatigue cracking indicator - healing?** Consistent with R from CA model or the Glover-Rowe parameter.

REOB Blends Field Study

❑Asphaltene content vs. REOB





- ➢No direct link to the extensive cracking on MN1-4
- ➢But high asphaltene content (vs. AAG-1 and AAF-1)

❑AFM topography image of MN1-4 asphalt (unaged)

- ➢Multiphase structure: No bees but sink holes/spikes
- ➢Likely to become more incompatible during aging

REOB Study Summary

- ✓ **Identify and quantify: NMR an accurate/selective tool**
- ✓ **Assess differences between asphalts and REOB**
  - **Chemical composition (SAR-AD)**
  - **Microstructure (DSC, AFM)**
  - **Oxidative aging (IR, PDSC)**
  - **Rheology (DSR, 25 and 4 mm plates)**
- ✓ **Understand the effect of REOB**
  - ✓ **Asphalt chemistry and structure**
  - ✓ **Asphalt rheology**
  - ✓ **Asphalt aging (physical and chemical)**
- ✓ **Main driver: REOB compatibility with the asphalt matrix, interactions with asphaltenes and waxes**
- ✓ **A path forward to the right combination seems possible**

WORK in PROGRESS !

DSR 4mm spinoffs Applications

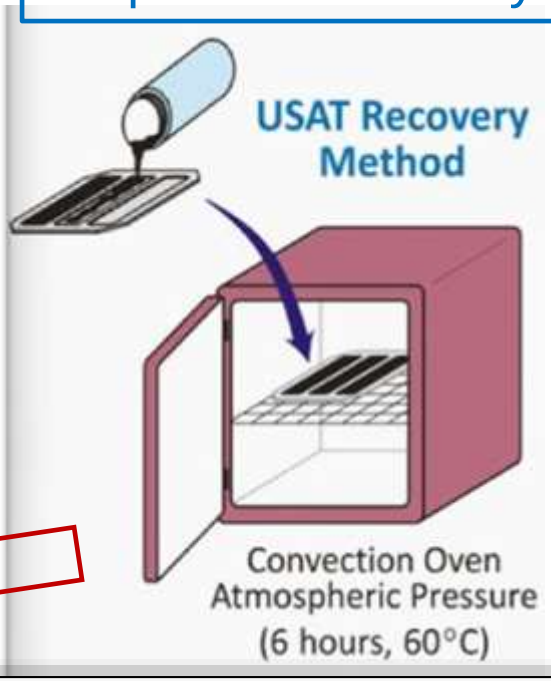
✓NCAT *Pavement Preservation Effectiveness* Study

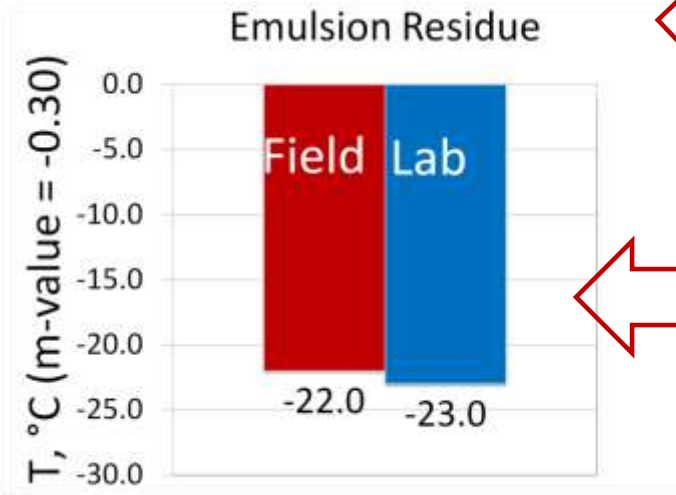
- **With NCAT and Ingevity (initiator)**
- **Proposal: Use Micro-Sampling and Micro-Tools on emulsion residue to *collect* from the pavement, *recover* the original emulsion residue from the lab and *evaluate* properties (DSR, IR)**

DSR 4mm spinoffs Applications

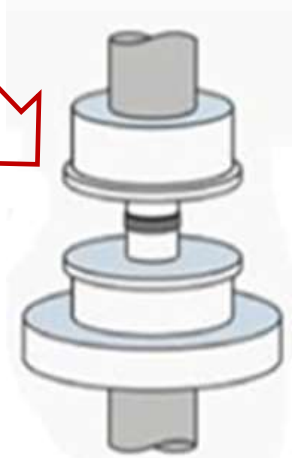
Sampling: Chip seal + Underlying pavement

Emulsion residue – low temperature evaporative recovery





m-value



4-mm DSR

- **Effect of oxidation on lab residue & field performance**
- **Positive effect of some preservation solutions on underlying pavement**

New Perspectives of Applications

WRI - Asphalt Industry Research Consortium

- **Focus: a few research needs, well identified, not currently addressed but of prime importance**
- ***Initial idea:*** **Asphalt Fingerprinting to help mitigate asphalt source variability issues, to help the industry better select / formulate asphalt binders with respect to:**
  - **Quality consistency**
  - **Long term performance**
  - **Cost-efficiency**

❑ ***Asphalt variability: growing issue in the industry***

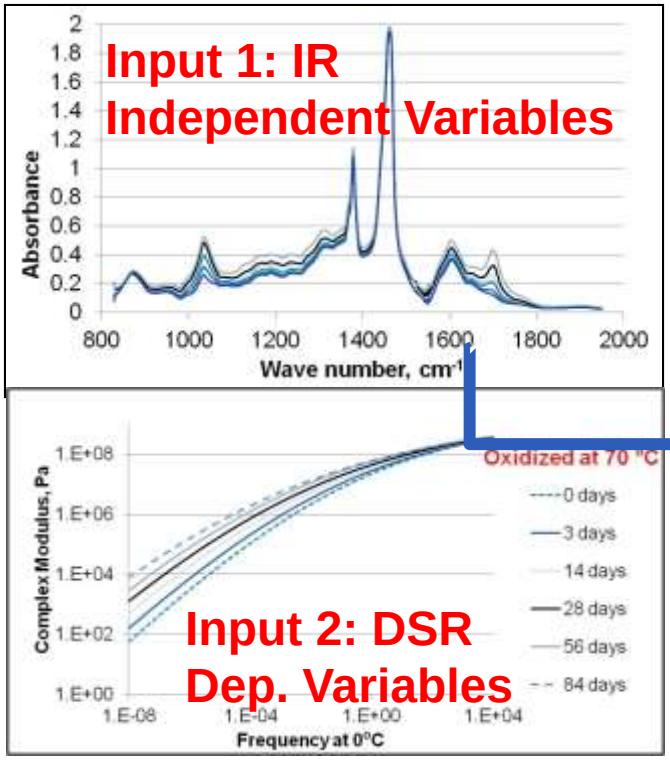
AIRC launched on June 1, 2015

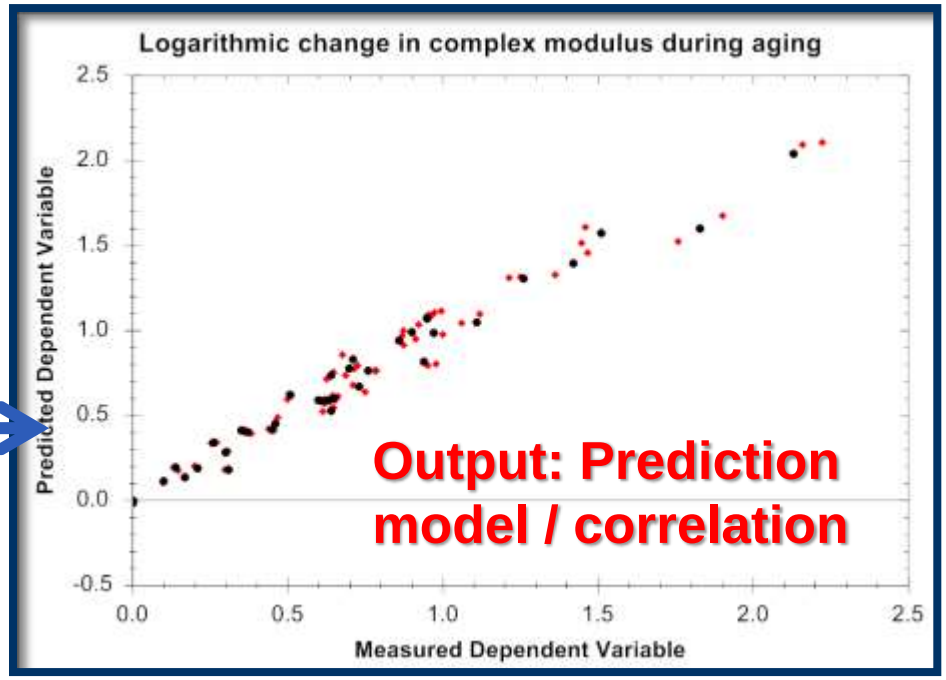
AIRC current and potential participants

- **Binder user / suppliers / producers**
- **US and International**

What for: Understanding, Correlation and Prediction

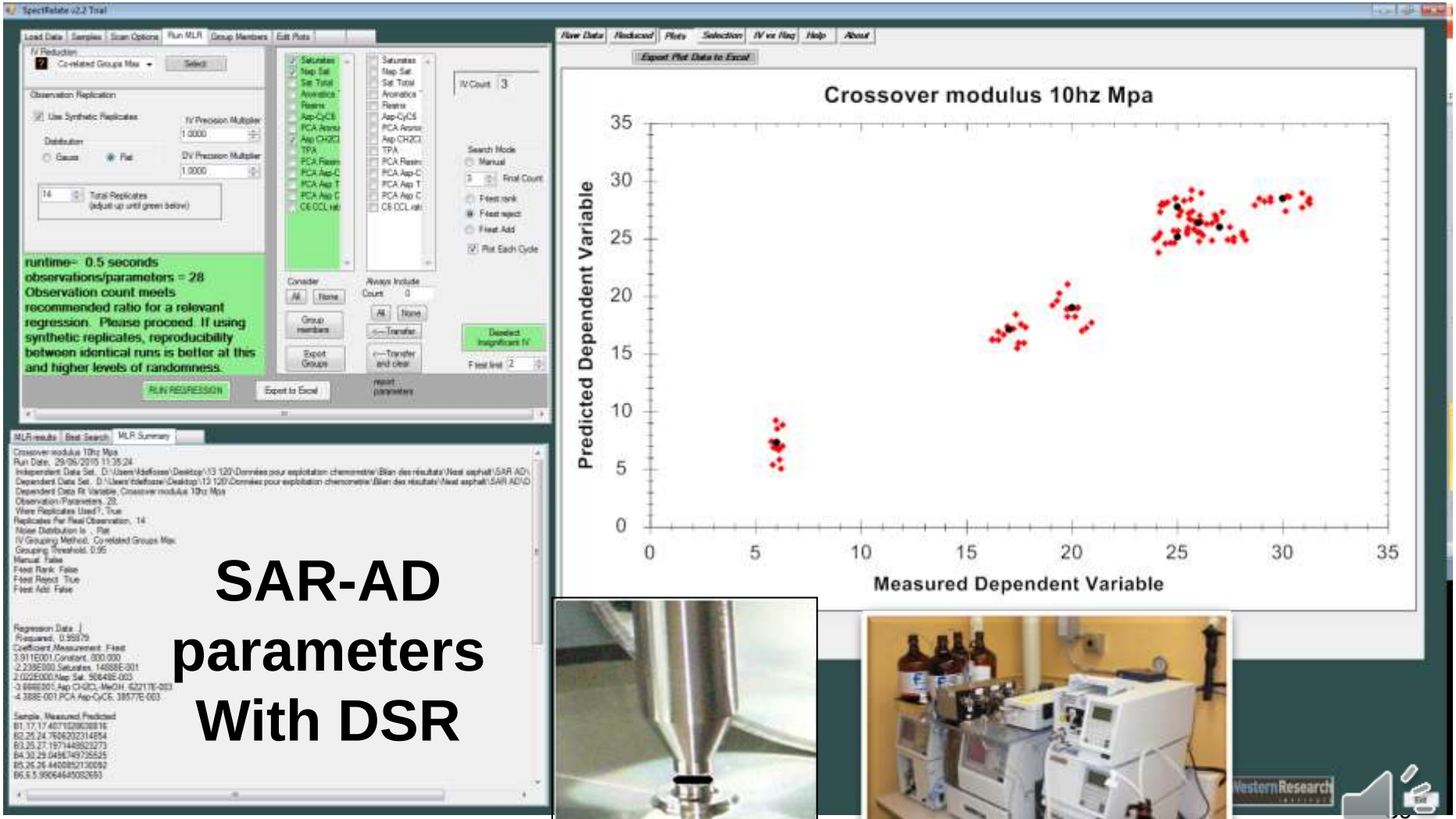
- **Example: Effect of air oxygen oxidation on asphalt rheology - Using FTIR, DSR and *ExpliFit™ software***





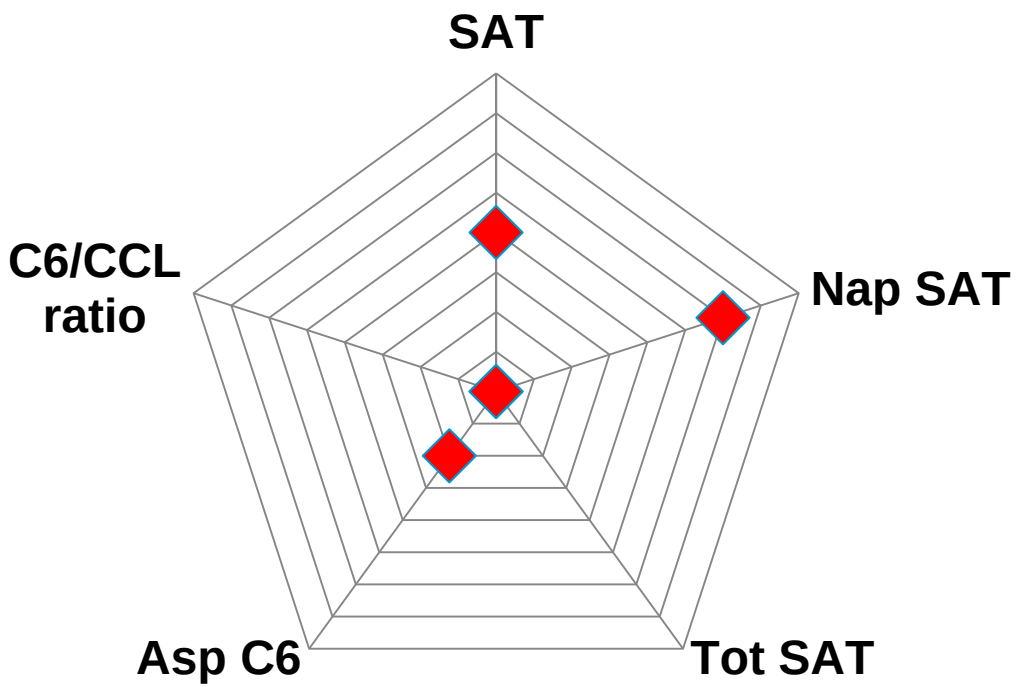
- Asphalt rheology changes with oxidation ***correlated*** to changes in asphalt chemistry - ***Predicted*** from a simple IR reading

What for: Understanding, Correlation and Prediction



What influences the Storage Modulus?

G' at 10°C 1 Hz (RTFOT)

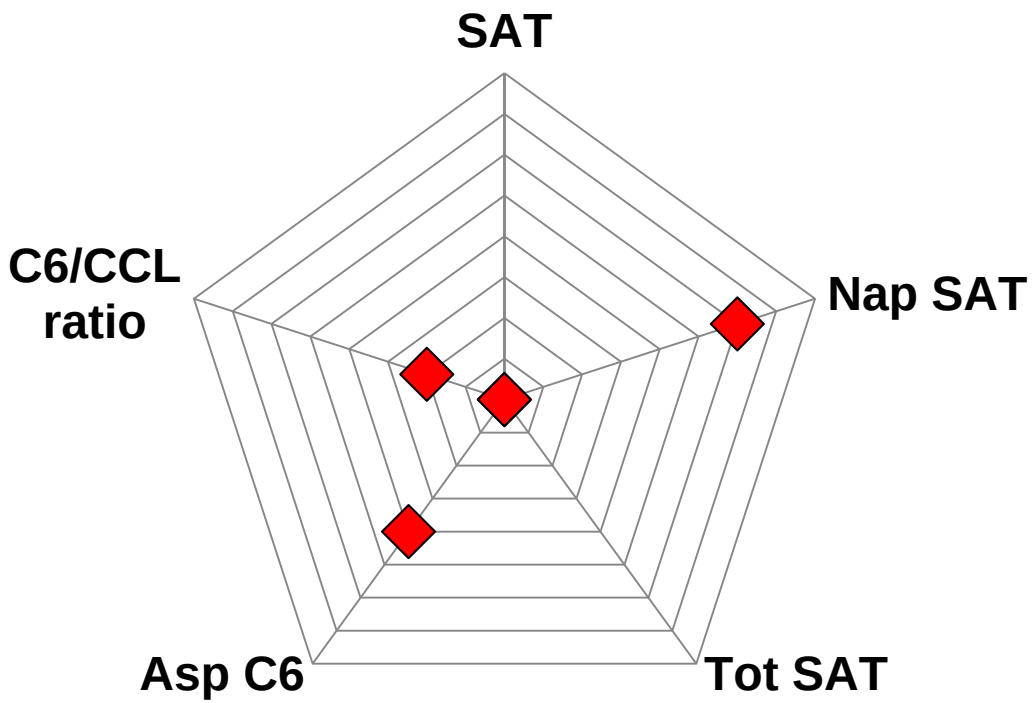


Significance
3- most
2- moderate
1- least

From saturates…

What influences the Storage Modulus?

G' at 30°C 1Hz (RTFOT)

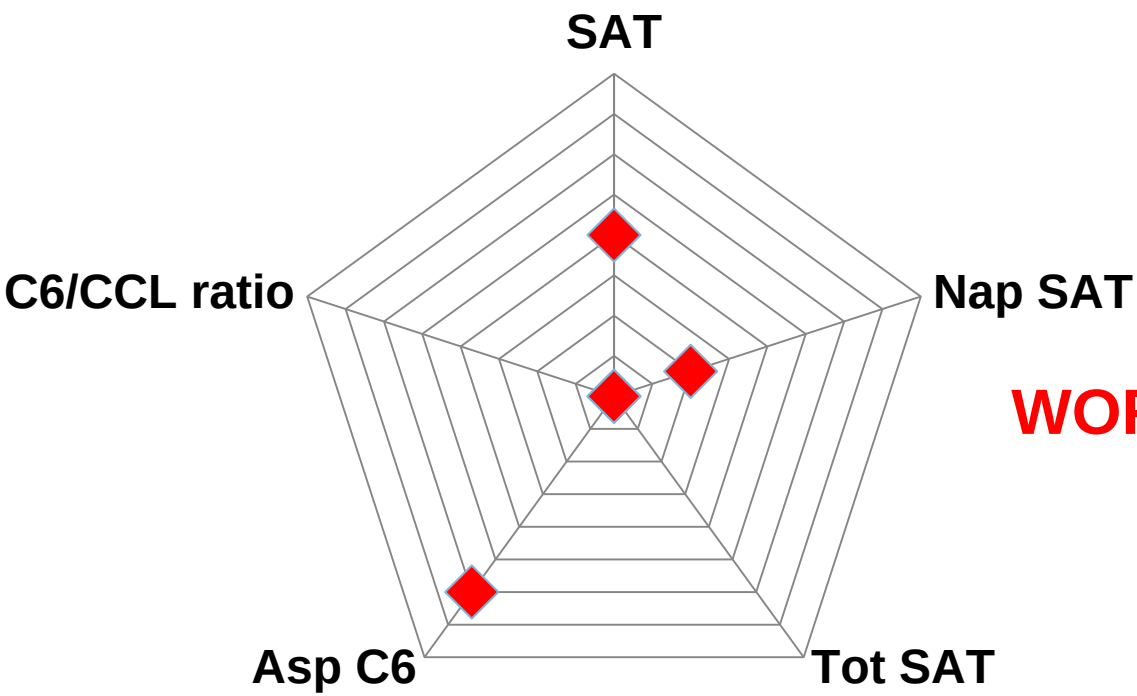


Significance
3- most
2- moderate
1- least

To saturates and asphaltenes…

What influences the Storage Modulus?

G' at 60 °C 1 Hz (RTFOT)



Significance
3- most
2- moderate
1- least

WORK in PROGRESS !

To asphaltenes + saturates +…

•Other factors include MW, …

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AIRC Anticipated Deliverables

- ✓ **Understanding / establishing some key relationships (year 1)**

  Crude oil composition ←→ Asphalt binder composition ←→ Asphalt binder properties ←→ Asphalt mix properties ←→ Asphalt pavement performance

- ✓ **Quantification of these relationships**
  - ✓ **Analysis - Mapping**
  - ✓ **Correlations - Equations**
  - ✓ **Prediction models**

- ❑ ***Further thoughts: possible links with NCHRP 9-60?***

Closing remarks - Innovative binder characterization methods

- **WRI Asphalt and Petroleum technology R&D**
  - Benefit from a solid Fundamental basis, thanks to Federal funding
    - Synergies / cross-fertilization with petroleum products
  - ***Now applied to industry oriented research***,
  - Development of innovative, fast, and predictive models, test methods and analytical tools, using small samples
    - Applied to understanding / quantification of modifiers effect at binder level, and correlation with mix / pavement
  - Seeking to solve problems of the Industry, Users and Owners, looking for more Partnerships
    - FHWA, FERHL, Industry, Academia
    - Consortiums: AR-C, HOR-C, AIR-C and **InfraVation**

Call for abstracts:	April 15, 2015
Abstracts submissions:	**Aug 15, 2015**
Invitations for full paper submissions:	**About 90 papers from 20 countries**
Full paper submissions:	**Feb 01, 2016**
Notification of paper acceptance/rejection:	**April 01, 2016**

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