Blended REOB Binder
Advanced Chemical & Physical Characterization

J-P. Planche, F. Turner, M. Farrar, R. Glaser,
W. Grimes, R. Boysen, T. Pauli

Asphalt Binder ETG

Fall River, MA, April 9, 2015

Western Research INSTITUTE

Western Research INSTITUTE

Acknowledgements

- FHWA funding and direction
  - FPIII and FPIII validation contracts
  - ARC agreement
  - Jack Youtcheff
  - Eric Weaver
  - Katherine Petros

Western Research INSTITUTE

Outline

- Background
- Chemical characterization of REOB Blends
- Structure characterization
- Physical characterization
- Aging Study
- Some Field Performance of Mixtures Containing REOB
- Summary
- Perspectives – Research needs

Western Research Institute

Background - Context

- **Increase in REOB availability & usage**
  - Since the 1980's: Re-Refined Engine Oil Bottoms (REOB) used to improve low temperature performance for asphalt binders / adjust low PG temperature
  - Economically attractive alternative vs. soft asphalt
  - Context of waste recycling and environmental stewardship making more used engine oil re-refined into new engine oil
- **However: Questions still pending**
  - What is the real effect of REOB on asphalt binder composition, structure and properties?
  - What is the long term effect of REOB on asphalt pavement performance?
  - Correlations between lab and field experience to predict field performance
  - Guidelines for the use of REOB (content/property limits?)

Background –WRI

- **FHWA Contracts on Fundamental Properties of asphalt binders III and validation outcomes**
  - **Development of new / unique analytical tools to characterize asphalt chemical and mechanical properties**
    - **Ex: SAR-AD and DSR 4mm spinoffs**
    - **Chemometrics software to link and predict properties**
  - **Application to various binders, including REOB blends**
- **FHWA Asphalt Research Consortium agreement**
  - **Design and survey of field test sections across US and Canada, some fortuitously including REOB**
- **REOB work in progress presented at TRB 2015-REOB WKS**
  - **Update today – Stay tuned!**

Western Research INSTITUTE

Experimental

- **Lab - Binder studies**
  - Composition - SAR-AD
  - Microstructure – AFM (tapping mode)
  - Rheology - DSR
  - Aging
    - Long term oven aging (70°C for 60 days / 100 micron film) to simulate 8 years / field aging in DC conditions
    - USAT to mimic RTFOT+PAV
    - PDSC
- **Field study - MN**
  - Pavement distress survey
    - REOB identification in MN1-4 by FHWA-TF
  - Comparison binder properties vs. field performance
- ***Note: Work in progress***

Western Research INSTITUTE

Experimental

Binders	REOB (%)	PG	Asphaltenes (%)	Wax Intevep (%) (1)	Crystal. Fraction DSC (%) (2)	Tg DSC (°C) (2)
AAG-1	0	58-10	5 (1) – 3 (2)	1.1	0.2	-11
	25					
AAF-1	0	64-10	13.3 (1) – 9.3 (2)	4.2	3.7	-26
	10					
MN1-4 (3)	~ 8	58-28	15.5 (3)	?	?	?

1) Jones et al, SHRP-A-645 report
2) Claudy et al: ACS 1992
3) ARC report

Western Research INSTITUTE

REOB and asphalt composition

Info on REOB composition from: *TRB 2015 Workshop #831*

- ***Arnold and Gibson***
- ***Krieck***

TURNER-FAIRBANK HIGHWAY RESEARCH CENTER

Variation and Complications
between and within REOB Suppliers

- **Phosphorous 1.5 - 1.9%**
- **Sulfur 1.5 - 1.9%**
- **Calcium 7,204 - 10,901ppm**
- **Iron 372 - 1,838 ppm**
- **Copper 704 - 1,563 ppm**
- **Zinc 4,554 - 7,213 ppm**
- **Molybdenum 288 - 669 ppm**

What is REOB?

Innovation – Quality - Service

- REOB is the highest boiling paraffinic lubricants
  - ~ 15% of the used oil
  - Contains about 4% Styrene Butadiene Polymer
- Engine oil additives (zinc and molybdenum) represent about 5% of the REOB.
  - These metal compounds are soluble.

Innovation – Quality - Service

Streiter Analysis

	Asphaltenes%	Resins%	Oils%	Oil Fraction Viscosity cP @ 50 C	Oil Fraction Pour Point, C
REOB	10.0	31.4	58.6	81	-20
PG 58-28 (9% REOB)	24.4	38.4	37.2	95	0
PG 58-28 (neat)	27.7	33.6	38.7	122	+9
PG 64-22 (neat)	28.6	33.1	38.3	197	+12

REOB and asphalt composition

- How does REOB composition compare to regular asphalt? How does it impact asphalt composition?
  - Study using SAR-AD™ separation

✓ SAR-AD: New way to analyze the generic composition of asphalts and heavy oils

✓ Fully automated, combined, and advanced separation of Saturates, Aromatics, Resins and Asphaltenes (SAR-AD)

✓ Small scale & fast: 2 mg every 4 hrs

✓ Developed at WRI under FPIII contract – FHWA funding

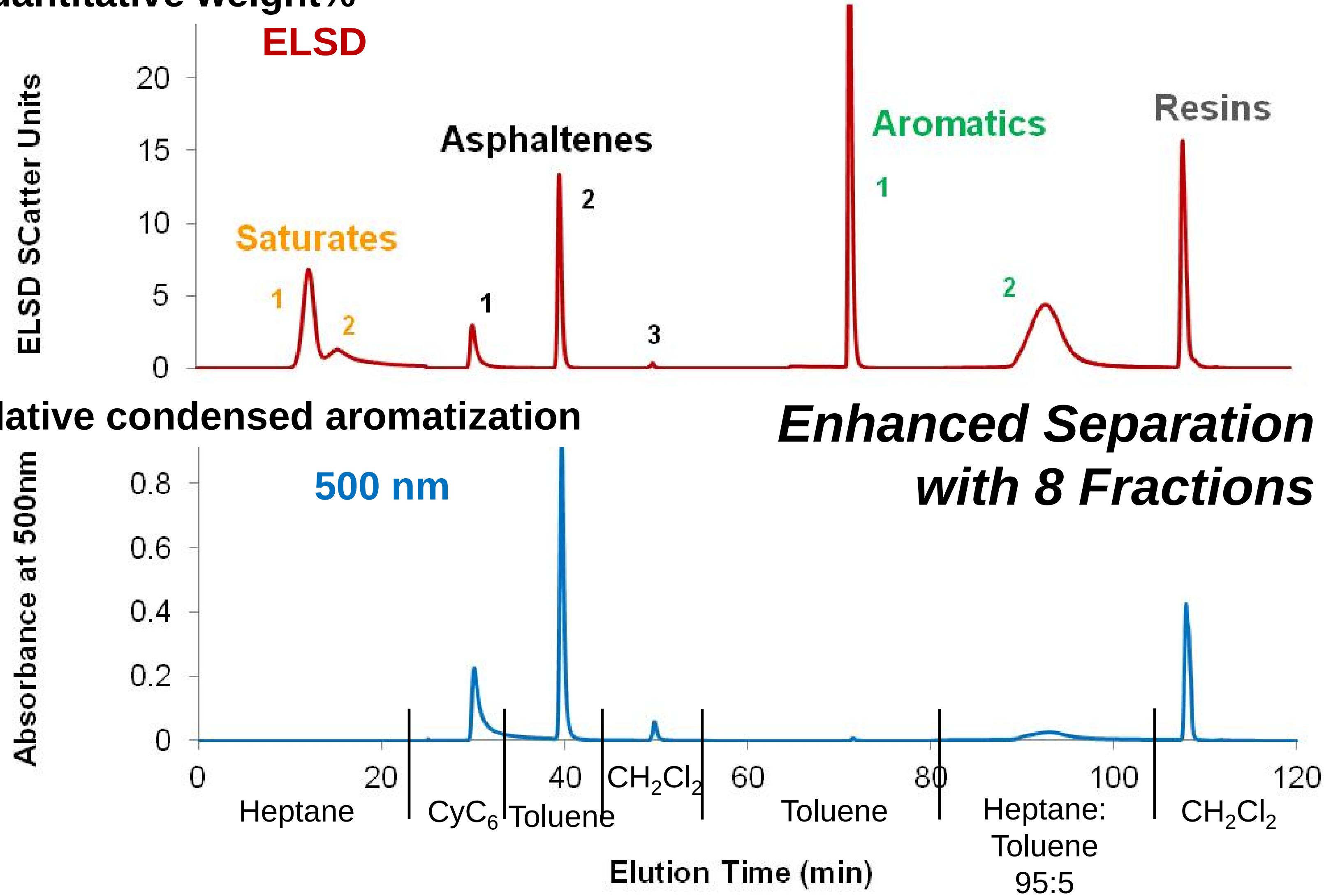
✓ Patents issued and pending

Western Research Institute

SAR-AD Separation Profile

✓**Quantitative weight%**

✓**Relative condensed aromatization**



Enhanced Separation with 8 Fractions

REOB and asphalt composition

- SAR-AD results – Unaged binders – AAG-1 blends

Sample	Detector	Maltenes				Asphaltenes			
		Saturates 1	Saturates 2	Total Aromatics	Resins	CyC_6	Toluene	CH_2Cl_2: MeOH	Total ELSD Asphaltenes
Llyomindster	ELS	13.8	7.6	51.6	13.8	4.4	8.8	0.1	13.2
PreRun QC	500nm			12.8	19.6	28.1	37.6	2.0	
AAG-1	ELS	12.6	5.6	55.1	23.5	0.4	2.8	0.0	3.2
	500nm			19.7	41.8	10.6	25.5	2.4	
REOB	ELS	66.8	2.9	6.9	22.9	0.1	0.4	0.1	0.6
	500nm			9.9	74.3	4.7	8.7	2.5	
AAG-1 25%REOB	ELS	24.1	5.4	49.3	19.5	0.3	1.4	0.1	1.8
	500nm			22.4	47.4	9.6	18.8	1.7	
75%AAG-1 +25%REOB calc	ELS	26.1	5.0	46.4	20.6	0.3	1.6	0.05	1.9
	500nm			18.6	51.2	8.6	19.0	2.6	

- AAG-1: very low asphaltenes, very compatible asphalt
- REOB: super low asphaltenes+high resins, high paraffinic saturates, low aromatics – Not a classic asphalt
- Blend: compatible additive – ***follow linear blending rules?***

REOB and asphalt composition

- SAR-AD results – Unaged binders – AAF-1 blends

Sample	Detector	Maltenes				Asphaltenes			
		Saturates 1	Saturates 2	Total Aromatics	Resins	CyC_6	Toluene	CH_2Cl_2: MeOH	Total ELSD Asphaltenes
AAF-1	**ELS**	**12.4**	**5.9**	**52.1**	**12.3**	1.4	5.0	0.1	**6.5**
	500nm			20.2	24.0	20.0	33.4	2.2	
REOB	**ELS**	**66.7**	**2.9**	**6.9**	**22.9**	0.1	0.4	0.1	**0.6**
	500nm			9.9	74.3	4.7	8.7	2.4	
AAF-1	**ELS**	**17.8**	**5.4**	**44.3**	**16.2**	2.1	5.3	0.05	**7.4**
10%REOB	**500nm**			17.4	26.2	22.6	31.9	1.8	
90%AAF-1 +10%REOB	**ELS**	**17.8**	**5.6**	**47.6**	**13.4**	1.3	4.6	0.1	**5.9**
Calc. blend	**500nm**			19.2	29.1	18.5	30.9	2.2	

- **AAF-1: fairly low asphaltenes, compatible asphalt**
- **REOB: same as previous - low asphaltenes, highly paraffinic**
- **Blend: not quite additive, showing more asphaltenes –** ***Compatibility & linear blending rules not as additive for AAF-1?***

REOB and asphalt composition

- SAR-AD results / AAG-1 blends - Long term aging (Oven)

Sample	Detector	Maltenes				Asphaltenes			
		Saturates 1	Saturates 2	Total Aromatics	Resins	CyC_6	Toluene	CH_2Cl_2: MeOH	Total ELSD Asphaltenes
AAG-1	ELS	**12.6**	**5.6**	**55.1**	**23.5**	0.4	2.8	0.0	**3.2**
	500nm			19.7	41.8	10.6	25.5	2.4	
REOB	ELS	66.8	2.9	6.9	22.9	0.1	0.4	0.1	0.6
	500nm			**9.9**	**74.3**	4.7	8.7	2.5	
AAG-1 25% REOB	ELS	**24.1**	**5.4**	**49.3**	**19.5**	0.3	1.4	0.1	**1.8**
	500nm			22.4	47.4	9.6	18.8	1.7	
AAG-1 + 25% REOB Aged 70C 12wks	ELS	**23.1**	**4.2**	**38.6**	**27.7**	1.4	4.9	0.1	**6.4**
	500nm			**15.0**	**38.5**	18.5	26.9	1.2	

- Aged Blend: higher asphaltenes and resins, lower aromatics
- Fairly classical evolution upon aging
- Needs to be compared to AAG-1 aged

Western Research INSTITUTE

REOB and asphalt composition

- **SAR-AD results / AAF-1 Blends – Long term aging (USAT)**

Sample	Detector	Maltenes				Asphaltenes			
		Saturates 1	Saturates 2	Total Aromatics	Resins	CyC_6	Toluene	CH_2Cl_2: MeOH	Total ELSD Asphaltenes
AAF-1	ELS	12.4	5.9	52.1	12.3	1.4	5.0	0.1	6.5
	500nm			20.2	24.0	20.0	33.4	2.2	
AAF-1	ELS	17.8	5.4	44.3	16.2	2.1	5.3	0.05	7.4
10%REOB	500nm			17.4	26.2	22.6	31.9	1.8	
AAF-1		12.5	5.6	38.3	21.3	2.4	12.1	0.1	14.5
RTFOT / PAV				10.2	21.1	19.6	47.6	1.35	
AAF-1 / REOB	ELS	18.0	5.1	34.3	21.4	3.8	10.3	0.1	14.2
RTFOT / PAV	500nm			9.8	22.3	24.8	42.0	1.02	

✓ **Note: RTFOT+PAV simulated by USAT**

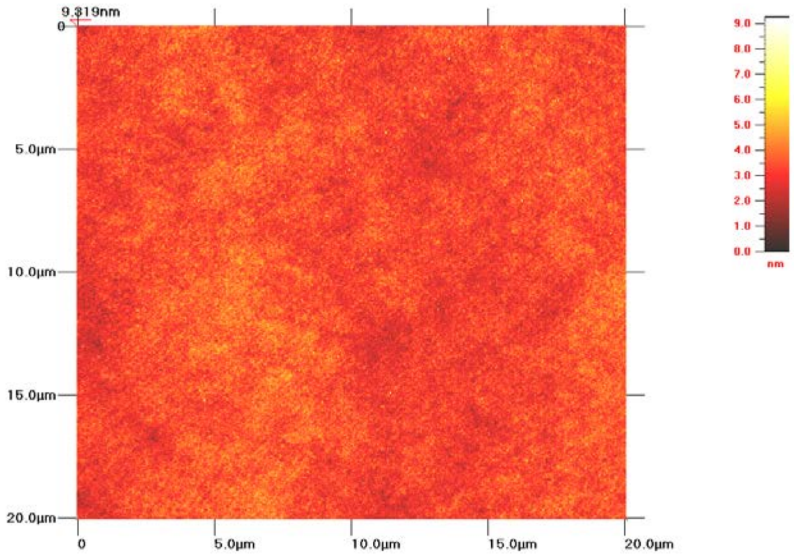
- **Aged Blend: higher asphaltenes and resins, lower aromatics**
- **10% REOB in AAF: no significant impact on aging**

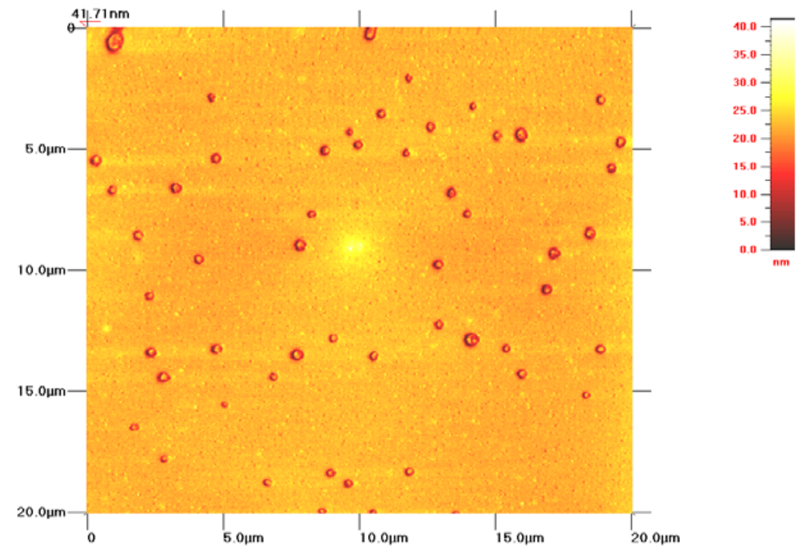
➢ **May indicate no catalytic effect in REOB causing accelerated aging, at least under PAV conditions**

Western Research INSTITUTE

REOB and asphalt microstructure

AFM topography images

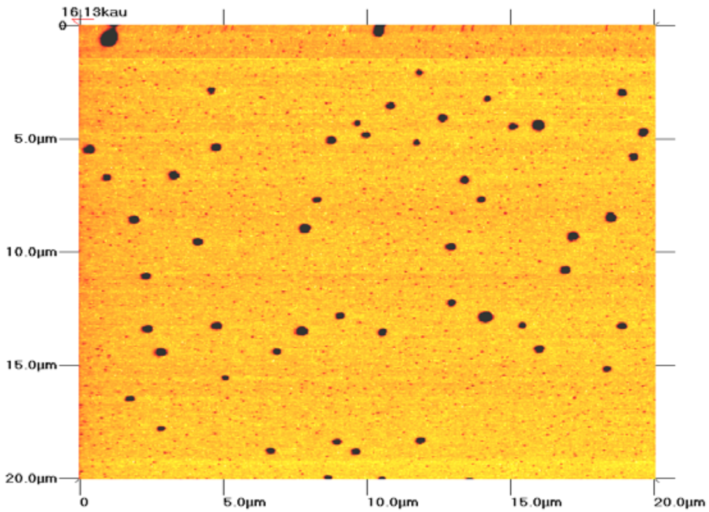


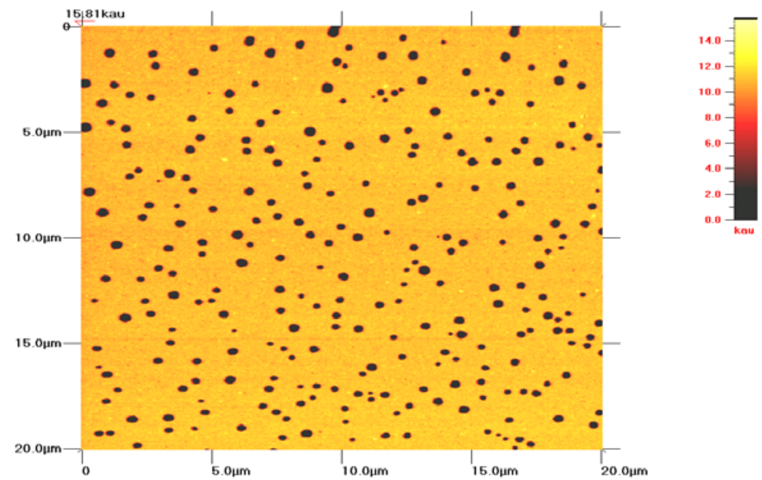


- **Neat AAG-1**
  - Nearly flat and featureless (only ~9-nm thick surface)
  - Very homogeneous: Typical of low asphaltene and low wax asphalt
- **AAG-1 + 25% REOB**
  - Relatively smooth flat surface (~40-nm)
  - Unusual small holes ~10-15-nm deep
  - Fairly homogenous

REOB and asphalt microstructure

❑ **AFM phase contrast images**



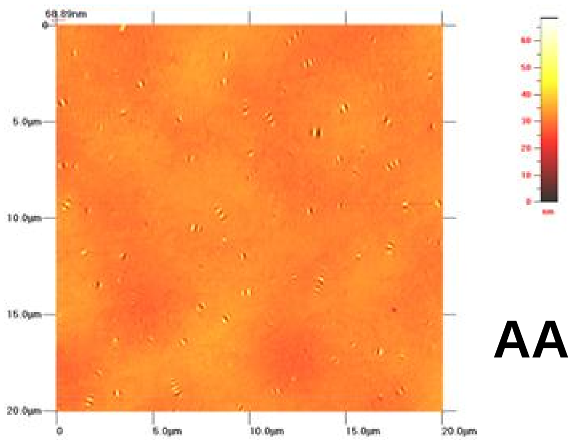


- **AAG-1+25%REOB**
  - **Two distinct material phases**
  - **Darker spots typical of either harder or less "sticky" phase**
    - ***Could be asphaltenes, polymers and wear metals?***

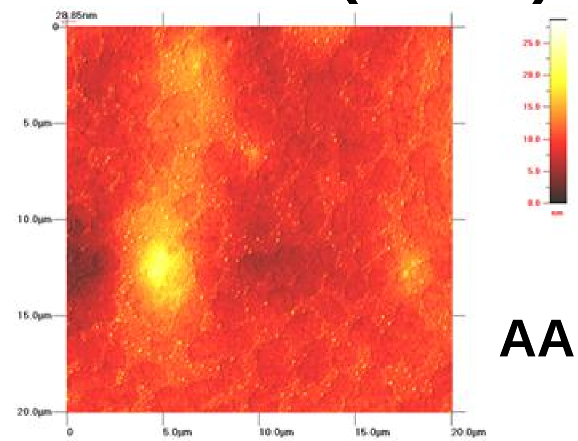
- **AAG-1 + 25% REOB aged 12-weeks at 70C**
  - **Increase in the number of dark spots**

REOB and asphalt microstructure

❑ AFM Topography of RTFOT+ PAV (USAT) aged blends



AAF-1

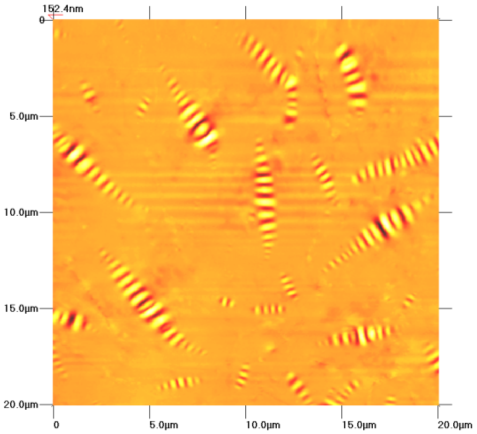


AAF-1 + 10% REOB

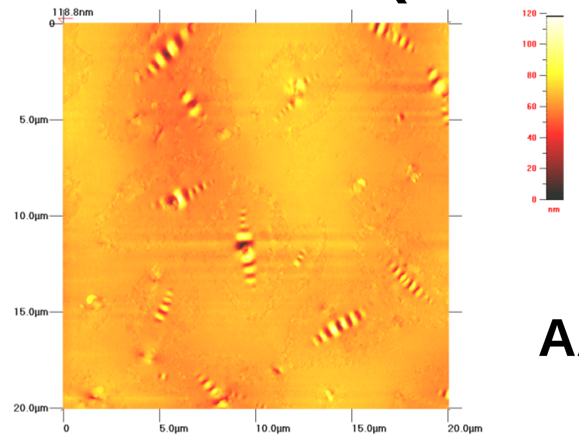
- **No thermal annealing**
  - **Topographic variation: 60-µm for neat AAF1 / 30-µm for AAF1+REOB**
  - **Neat asphalt: Numerous small “bee-structures”**
    - **Bees known to be related to wax crystalites**
    - **No distinct pattern aside from ‘’bees”**
  - **Asphalt + REOB: many tiny light-colored spots with no “bees”**
    - **In addition pattern of slightly depressed areas**

REOB and asphalt microstructure

AFM Topography of RTFOT+PAV (USAT) aged blends



AAF-1

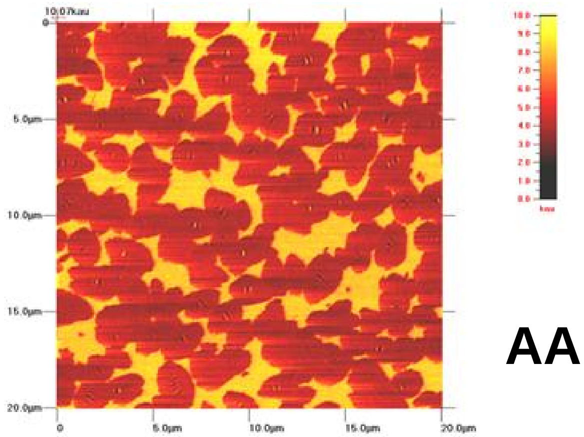


AAF-1 + 10% REOB

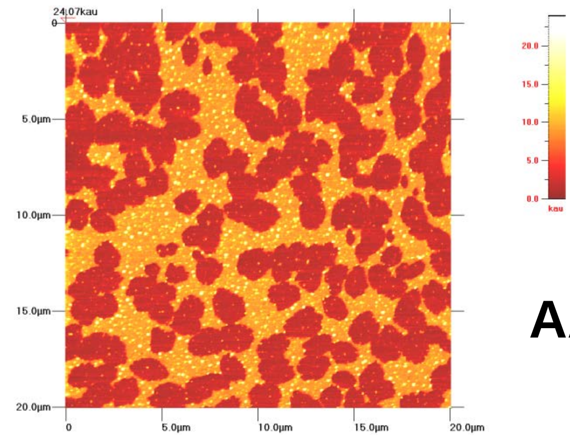
- Thermal annealing step at 120C
  - Neat asphalt: Large “bee-structures”
  - Asphalt + REOB : considerably smaller “bee-structures”
  - Otherwise, the two surfaces appear to be quite similar

REOB and asphalt microstructure

❑ AFM Phase contrast of USAT aged blends



AAF-1

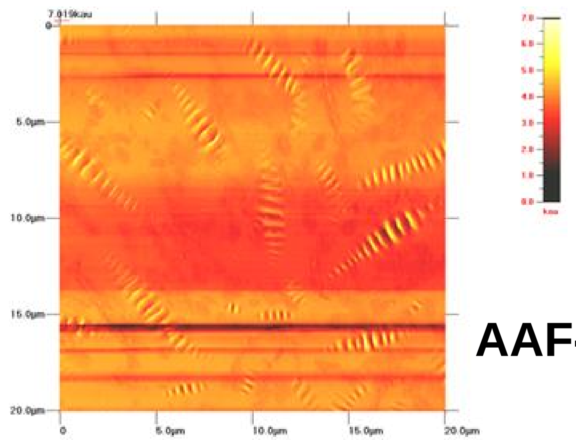


AAF-1 + 10% REOB

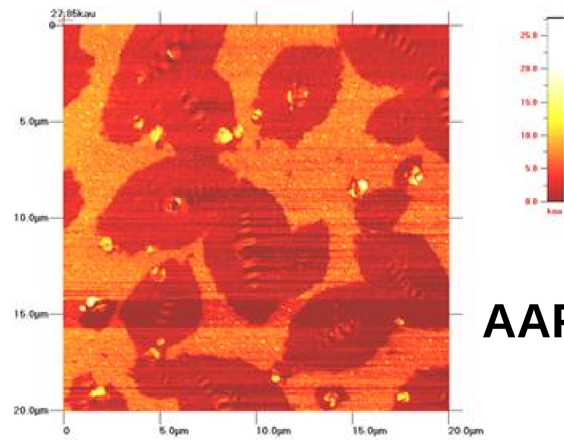
- No thermal annealing
  - Presence of a third material phase, indicated by the numerous small light-colored spots, on the surface of the sample with added REOB.
  - “Bee-structures” associated with the darker-colored phase in the neat asphalt, are absent in the sample with added REOB

REOB and asphalt microstructure

- **AFM Phase contrast of USAT aged blends**



AAF-1



AAF-1 + 10% REOB

- **Thermal annealing step at 120C**
  - **Distinct differences which were unclear in topographic mode**
  - **Neat asphalt: mainly a single phase with contrast associated with height features seen in the topographic image.**
  - **Asphalt + REOB: 3 distinct phases with small light spots, as well as the larger light-colored ‘nodules’ that are typically not seen in asphalt samples without REOB**

Western Research INSTITUTE

REOB and asphalt microstructure

- **Summary: What do the AFM images indicate?**
- **REOB components do not appear completely miscible with asphalt- presence of suspended fine particulate material**
- **REOB appears to suppress, but not eliminate, the formation of “bee-structures” i.e. wax crystals on the asphalt surface**
  - ➢ **Those changes indicate that REOB affects the relative compatibility of the various asphalt components – Temperature/time sensitive**
- **REOB affects the asphalt surface structure for fresh blends as well as aged**
  - ➢ **REOB appears to affect asphalt structure at all stages of its lifecycle**
- ***Additional thoughts…***
  - **More phase boundaries are often material stress risers. Consequently, the blending of REOB may make asphalt more prone to cracking**
  - **AFM may provide a simple and reliable method for detecting the presence of REOB in asphalt samples**

Aging study

- LONG TERM OVEN AGING
- PDSC

- OXIDATION KINETICS / EFFECT OF REOB ON
  - SHORT TERM REACTION
  - LONG TERM REACTION
  - EXTENT OF OXIDATION

- ASPHALT USED: AAG-1 AND AAG-1+25% REOB
- PRE-CONDITIONING: RTFOT

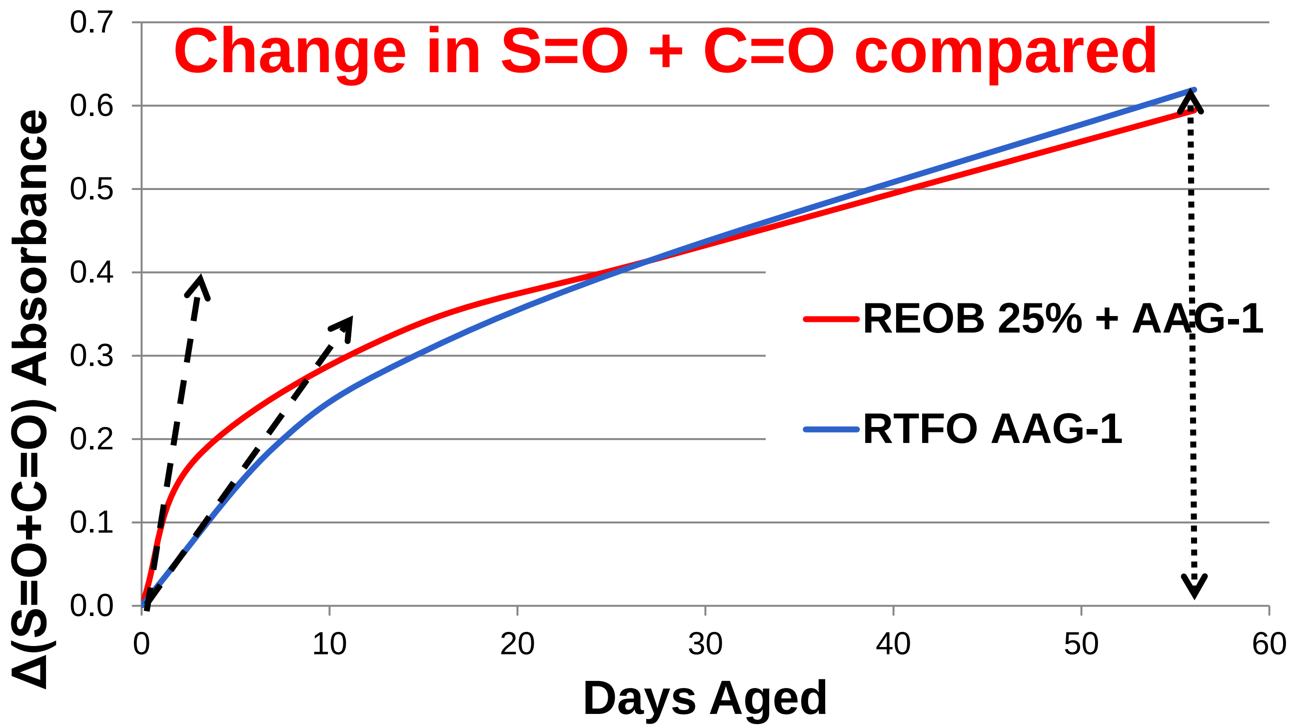
Western Research INSTITUTE

Aging study: Long term oven aging

Oxide change comparison suggest various mechanisms:

1. REOB effect is not a dilution effect – not inert
2. Faster first reaction: catalyst effect – metal?
3. REOB effect is not all in the fast reaction
4. Higher Reactive Material: Oxidation of REOB itself ?

➢ ***Overall aging amount not much different***



Aging study: High Pressure DSC

PDSC purpose and potential usage

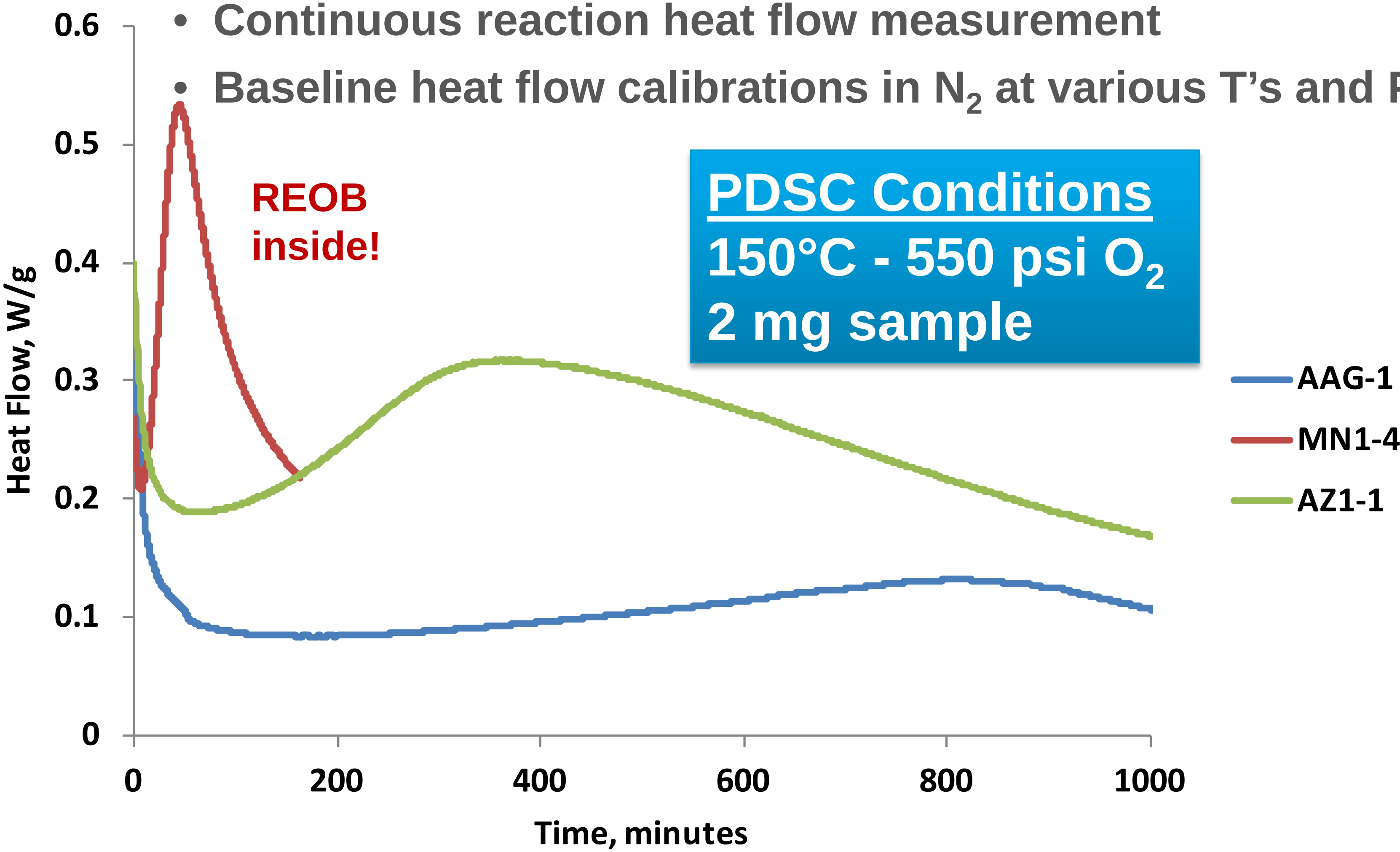
- **To accelerate oxidation for binder selection + prediction**
  - Thin film aging requires 8 weeks / PAV requires 20hrs
  - PDSC requires a few hours
- **Usage – Practical/Technical and Scientific**
  - Quick characterization of binder aging susceptibility
  - Formulation of asphalt binders against oxidation
  - Complete WRI oxidation model
    - Extension to higher Temp. & Pressure
    - Rapid determination of reactive material (RM)
    - Determination of oxygen partial pressure influence
- **Not NEW: ASTM Standard Test Methods (D5483/E2009)**
  - To evaluate oxidation induction time and onset temperature of Lubricating Greases

Aging study: High Pressure DSC

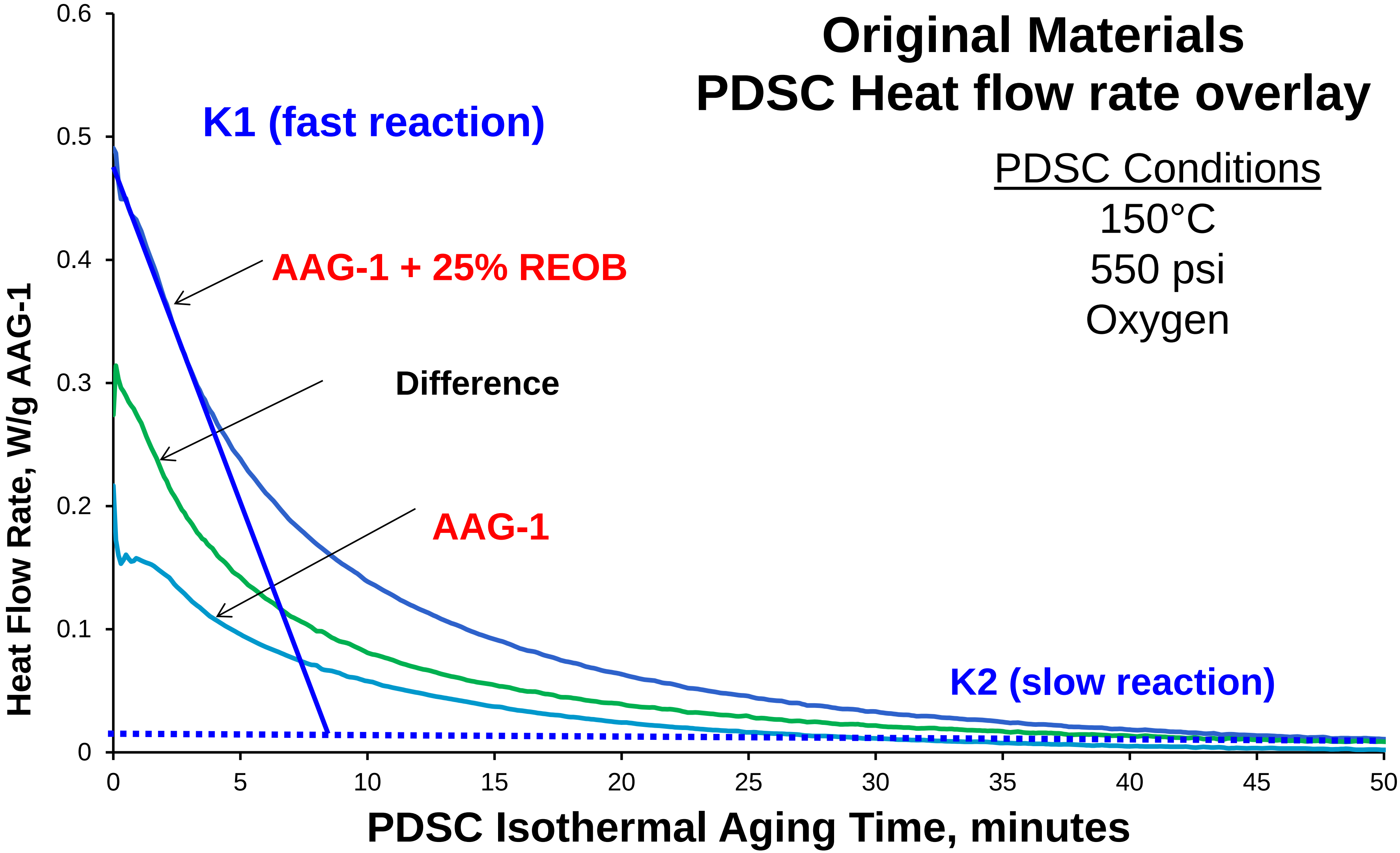
❑ Typical PDSC results - Heat flow rate overlay

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

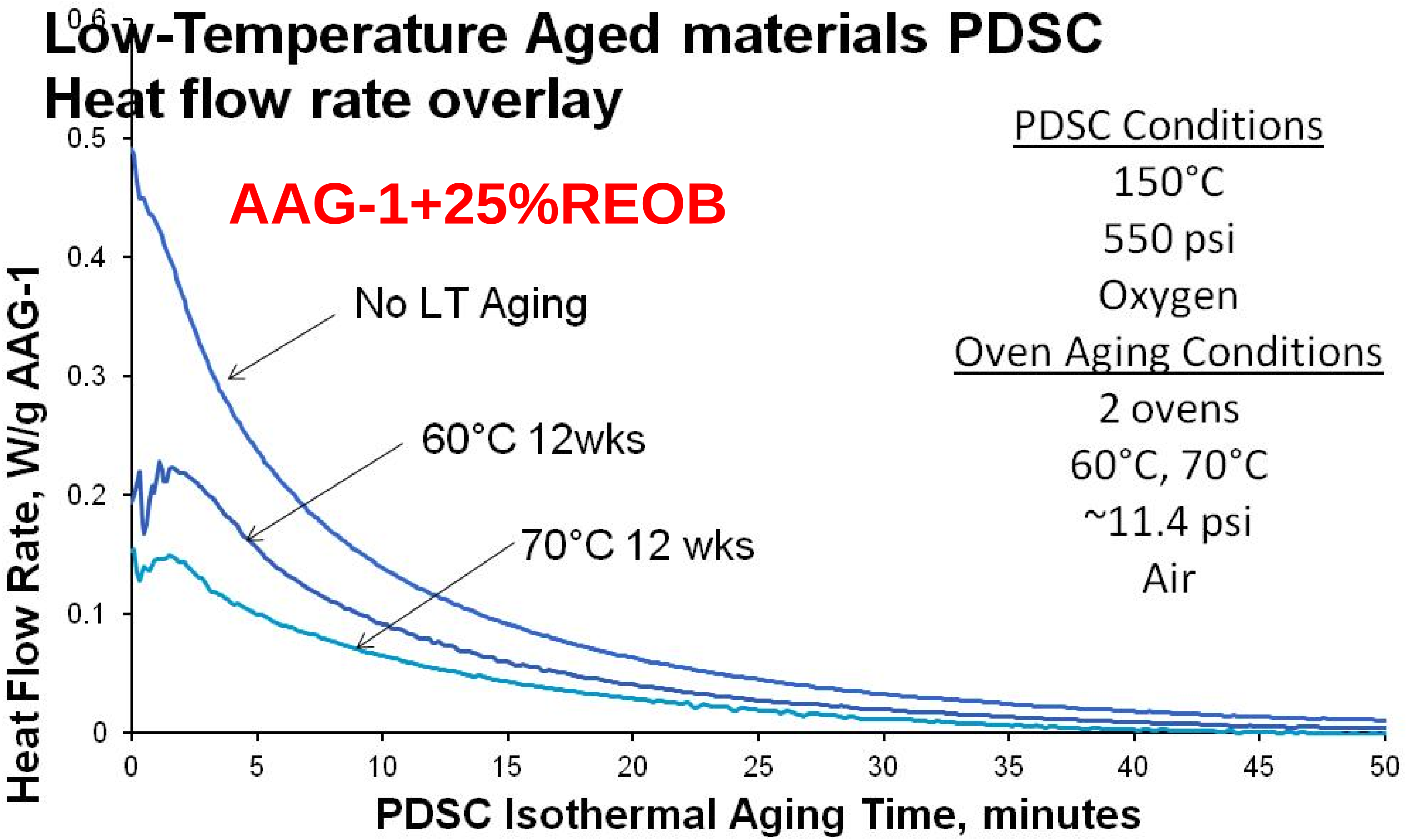
PDSC Conditions
150°C - 550 psi O_2
2 mg sample



Aging study: High Pressure DSC



Aging study: High Pressure DSC



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

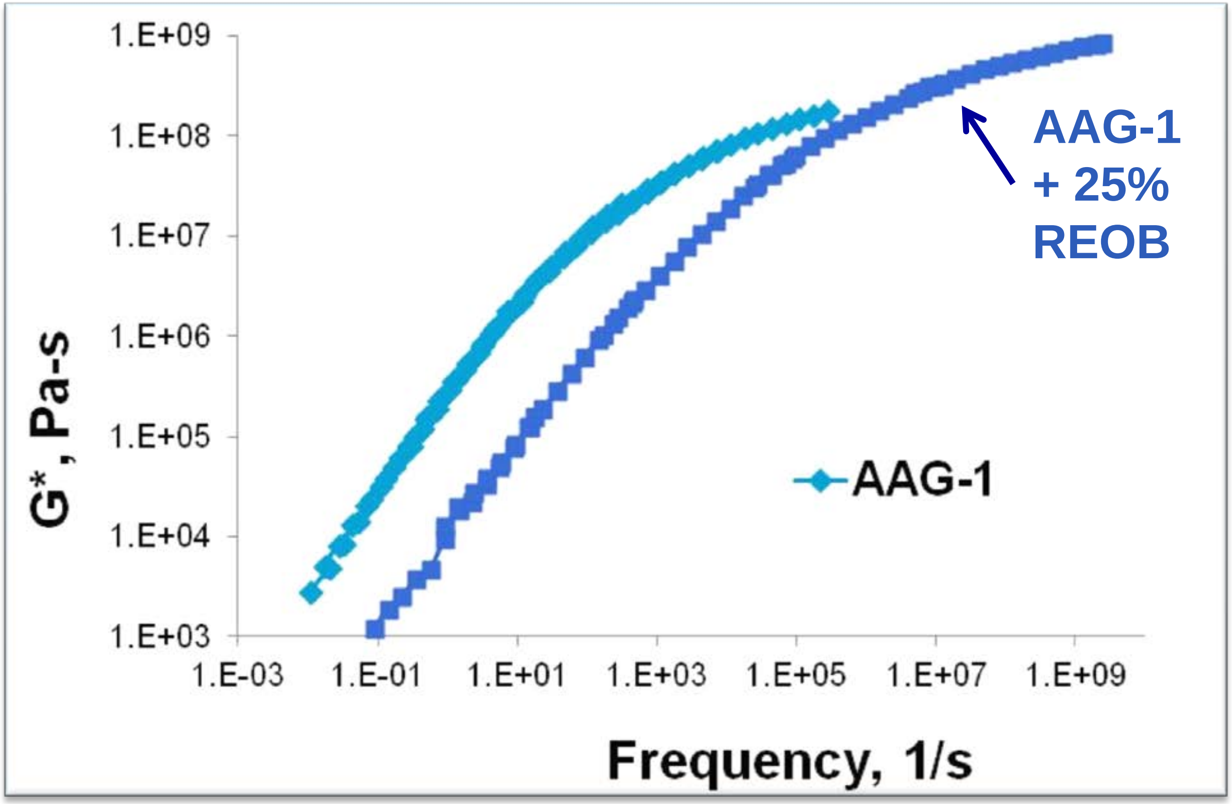
Rheology study

- DSR – classical
  - Master curve
  - Black space
- DSR Physical Hardening after RTFOT+PAV (USAT)
  - Comparison with published results, obtained using the BBR
- Asphalts:
  - AAG-1 and AAG-1+25% REOB
  - AAF-1 and AAF-1+10% REOB

Western Research INSTITUTE

Rheology study

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

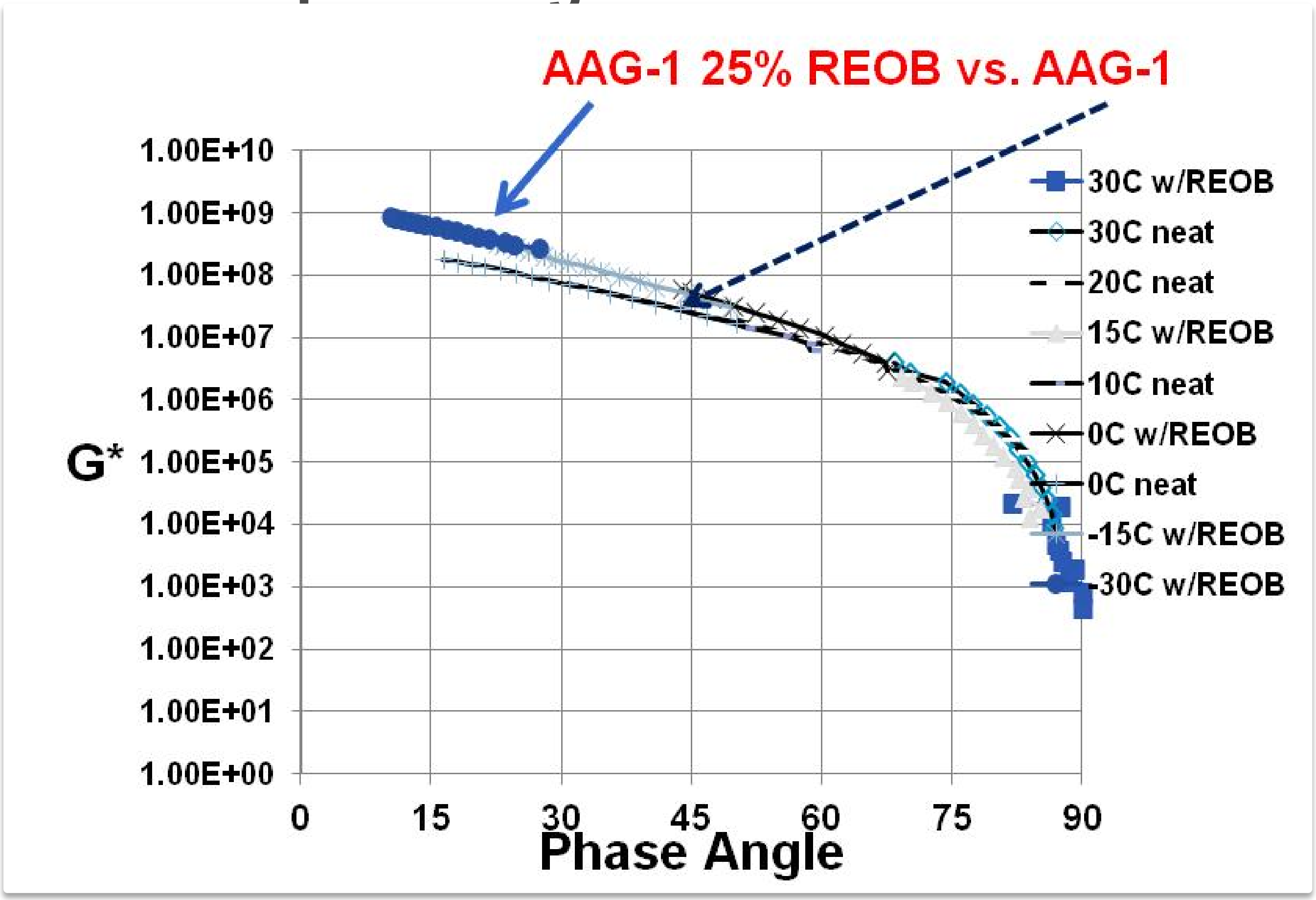


- Asphalt AAG-1 and AAG-1+25% REOB – both unaged
  - ➢ Clear REOB softening effect

WesternResearch INSTITUTE

Rheology study

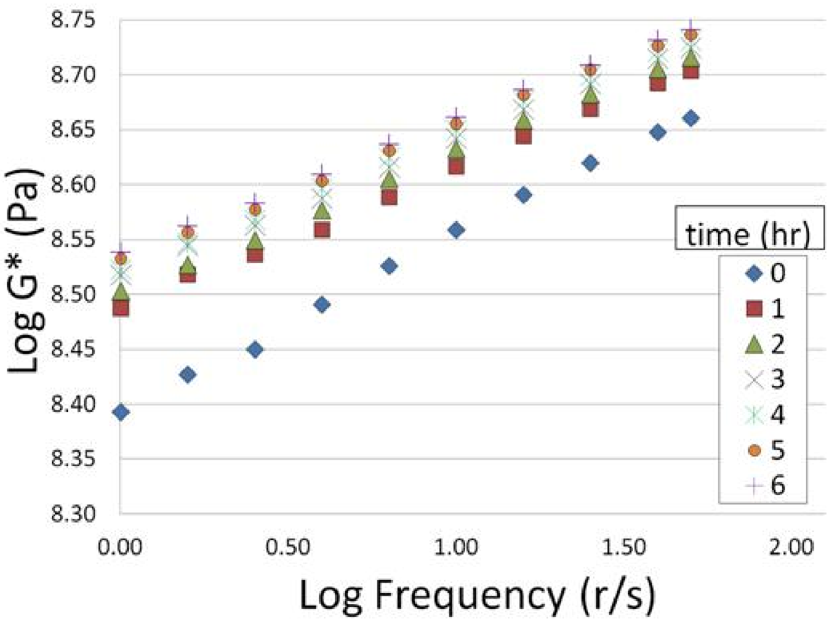
DSR Black space diagram



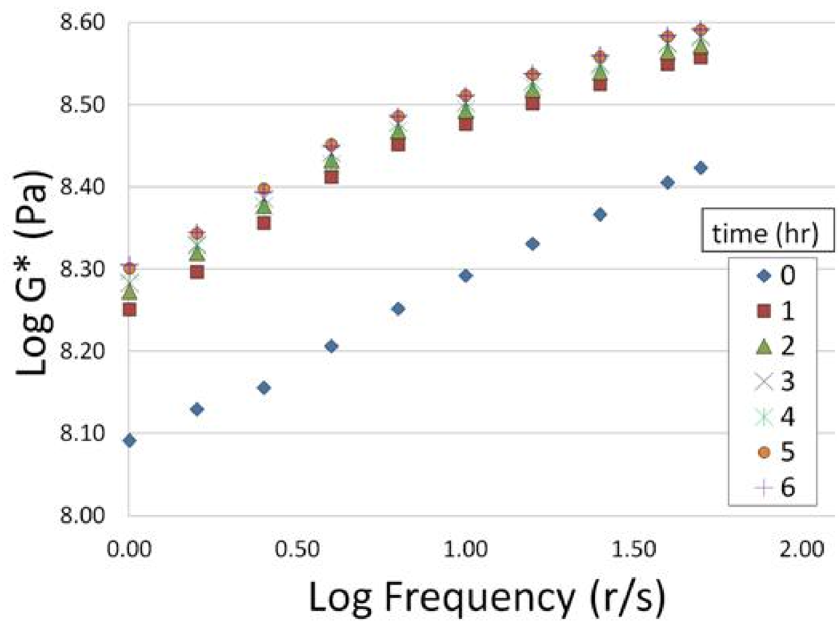
- Rheologically simple materials – before aging

Rheology study
DSR Physical Hardening

0% REOB AAF-1 RTFO/PAV



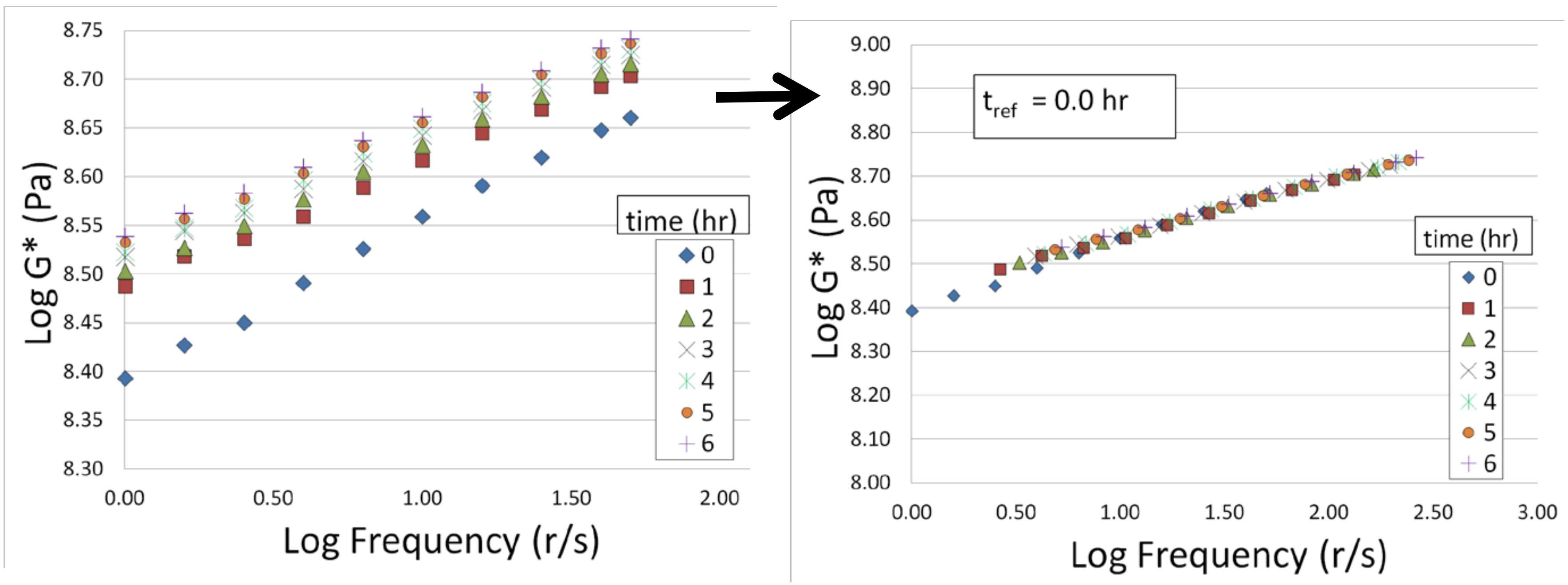
10% REOB AAF-1 RTFO/PAV



- **Isothermal conditioning at -15°C**
  - Frequency sweeps every hour for 6 hours
- **Outcome**
  - ➢Both binders physically harden over low temperature conditioning
  - ➢REOB/AAF-1 blend hardens a little more

Rheology study
DSR Physical Hardening

0% REOB AAF-1 RTFO/PAV



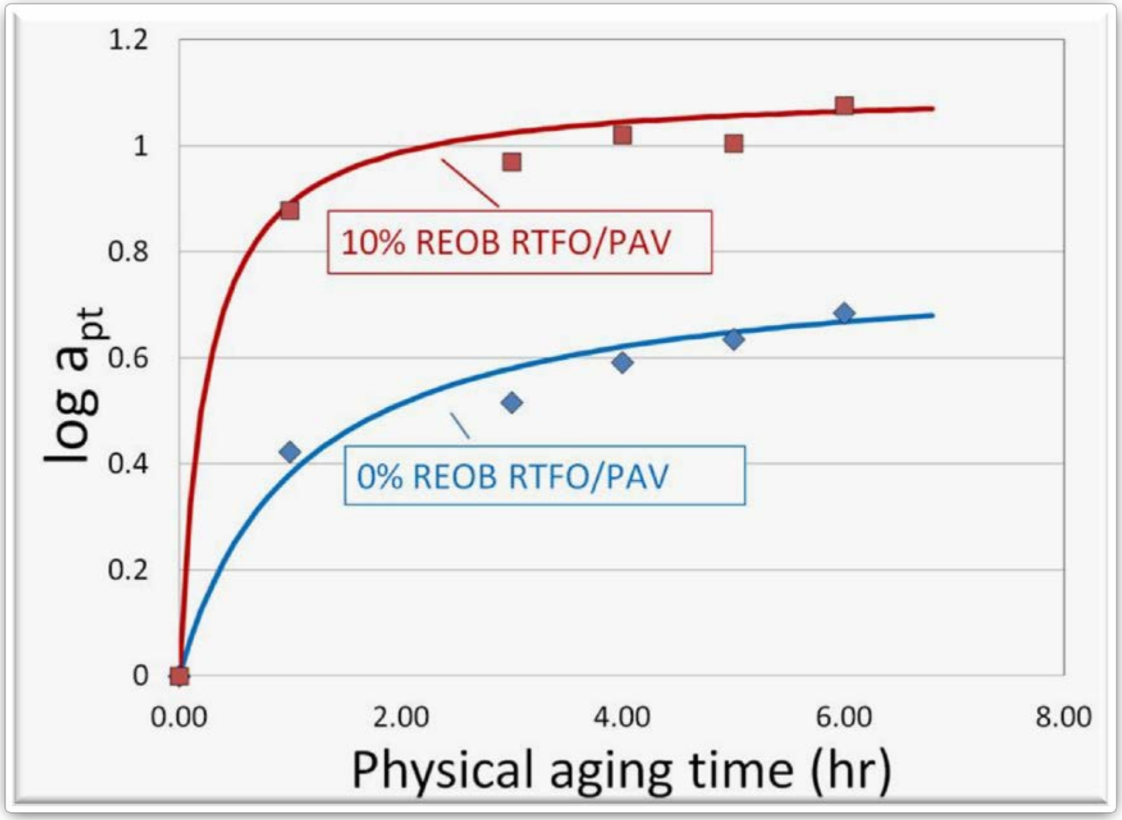
- **Isothermal conditioning at -15°C**
  - Frequency sweeps every hour for 6 hours

- **Time – physical hardening time superposition**
  - Reference time = 0 hours
  - Shift factors
- ***After Bahia, Anderson… AAPT 1991-92***

Western Research INSTITUTE

Rheology study
DSR Physical Hardening

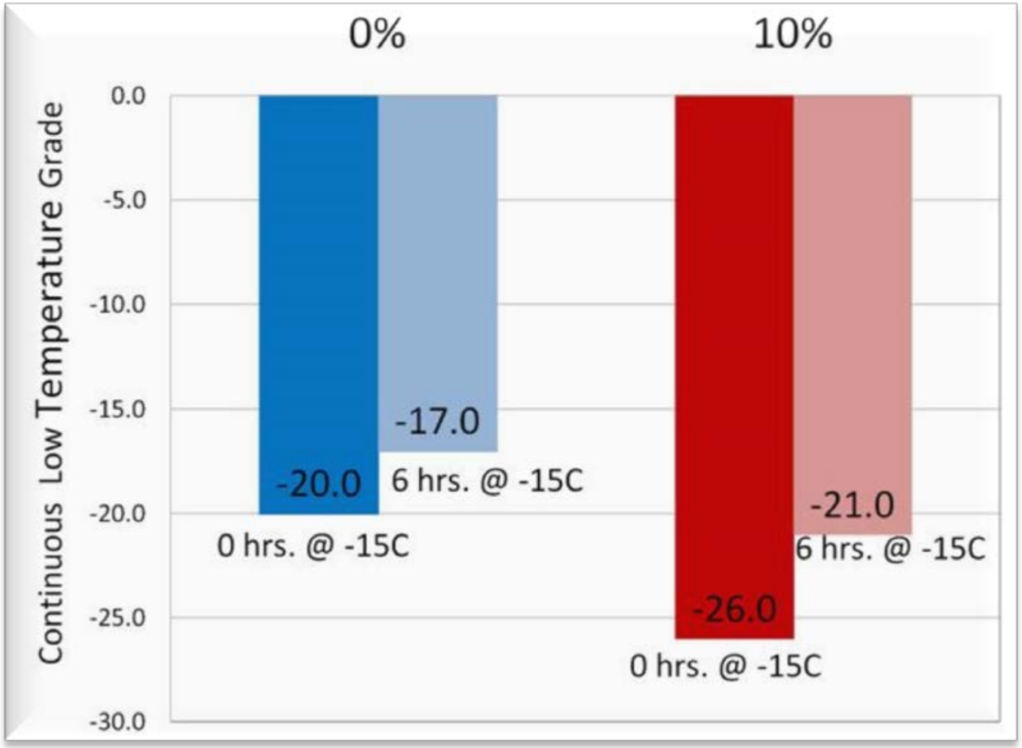
•Time – Physical Hardening Time Superposition Shift Factor



- ➢Similar hardening behavior
- ➢Higher extent with REOB

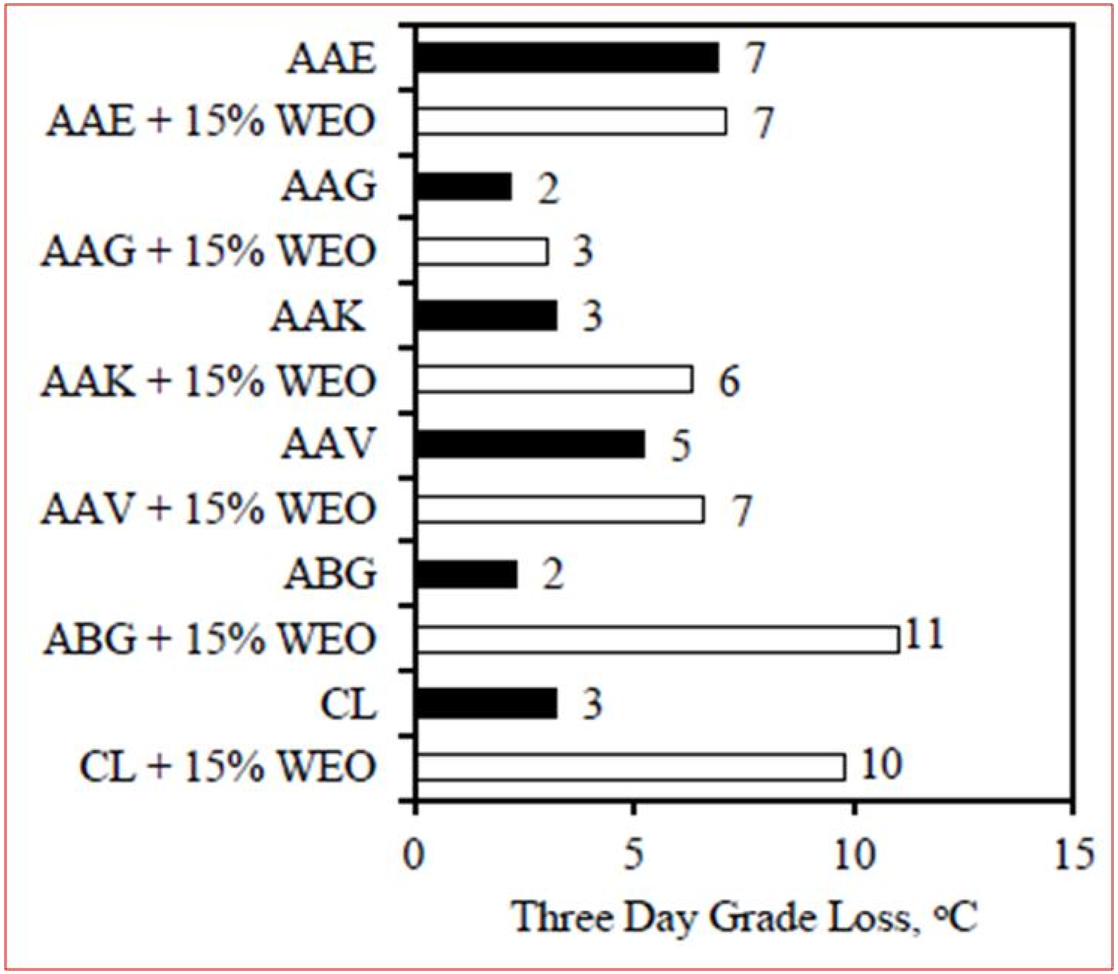
Rheology study
DSR Physical Hardening

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



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

BBR - Physical Hardening (with and without REOB)



- **Physical hardening effects** on SHRP core asphalt binders
  - •Unmodified and modified with 15% REOB (WEO)
  - •RTFO/PAV aging
  - •W and w/o conditioning for 3 days at -14°C
- **Grade loss**
  - •Equal or greater for all REOB modified binders
  - •Between 7 and 11°C abs. or 0 and 9°C difference
  - •AAG blends minimal, consistent with other data

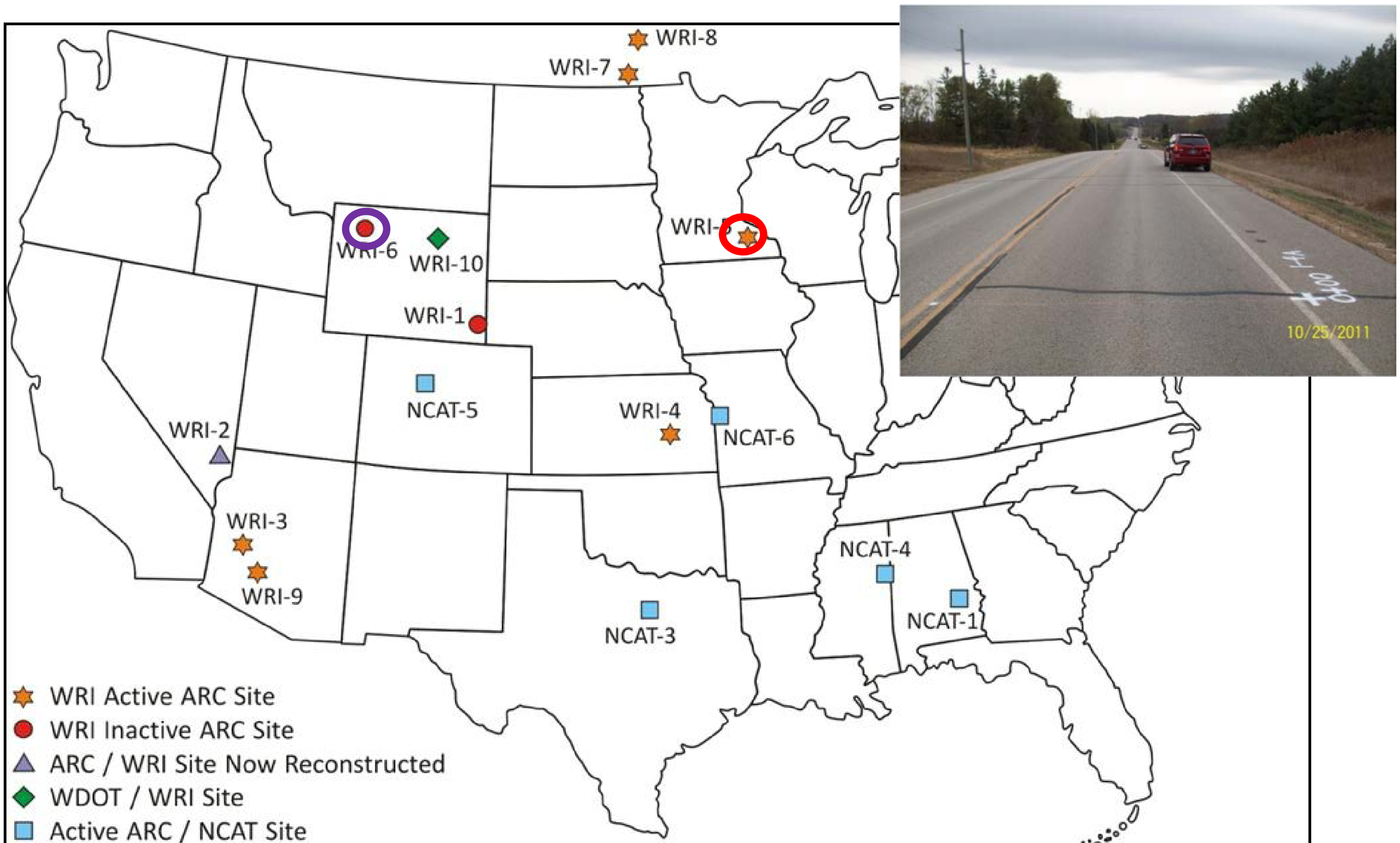
[1]Johnson et al TRB (2014)

Western Research INSTITUTE

Field study

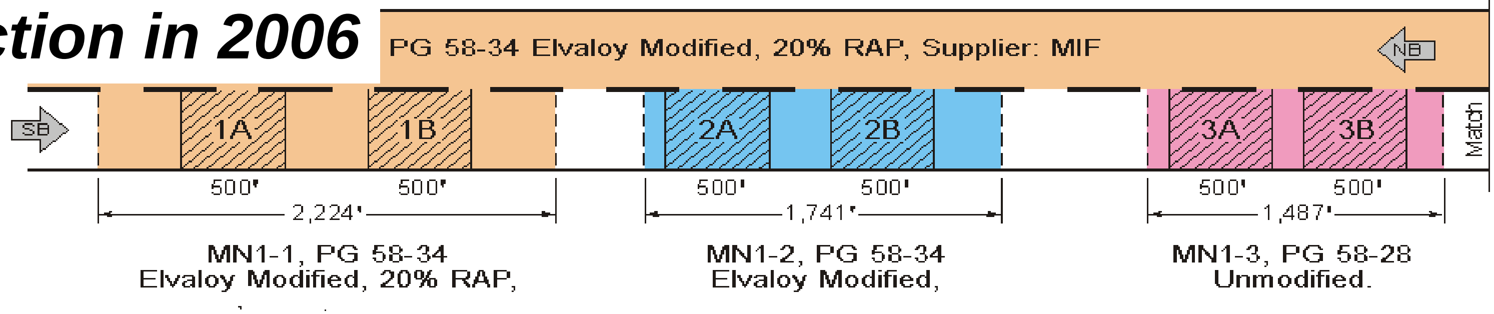
- **FHWA/ARC/WRI and FHWA/ARC/NCAT Validation sites in the US and Canada -> MN site**

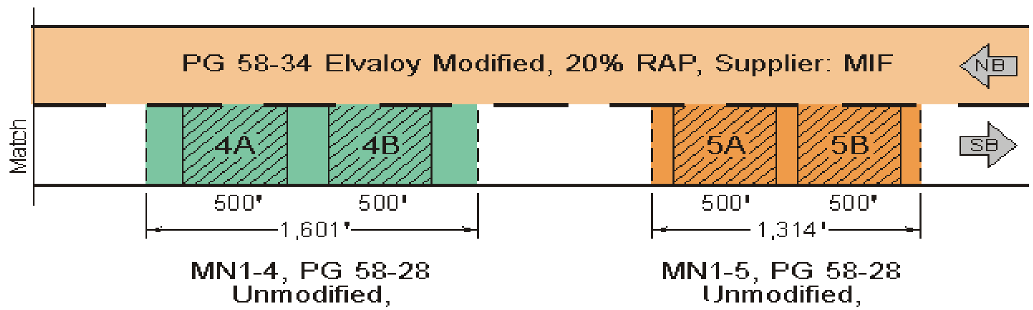
YNP
✓No issue after 3 years
✓Chip seal covered

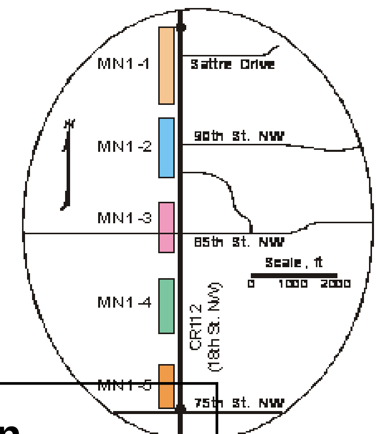


Field Study - Rochester, MN
Comparative Test sites

❑Construction in 2006







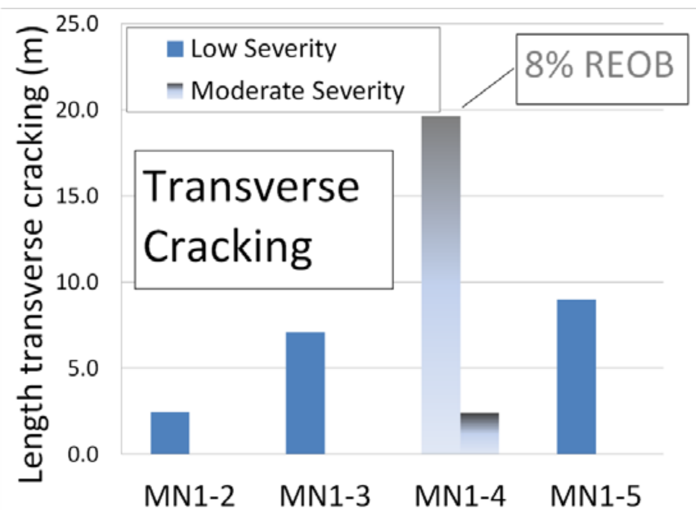
Sample Designation	Performance Grade Project specifications	Source Description
MN1-2	PG 58-34	Canadian blend, Elvaloy modified
MN1-3	PG 58-28	Canadian blend
MN1-4	PG 58-28	Middle East Blend
MN1-5	PG 58-28	Venezuelan blend

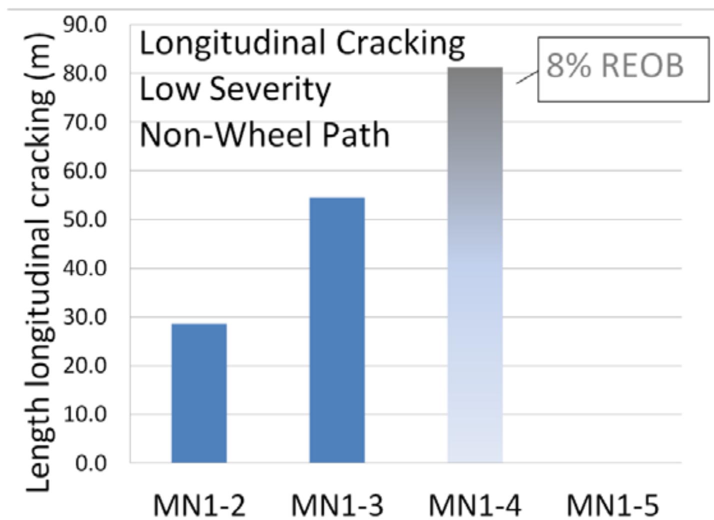
➢**REOB found in MN1-4, at about 8% content, by XRF (FHWA-TF)**

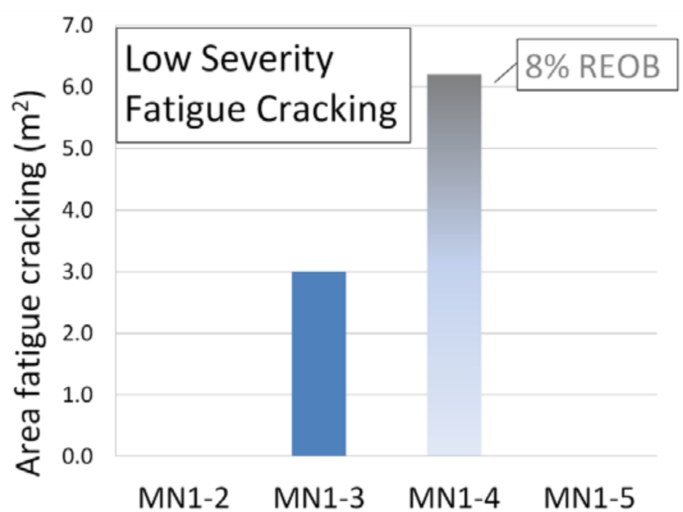
Western Research INSTITUTE

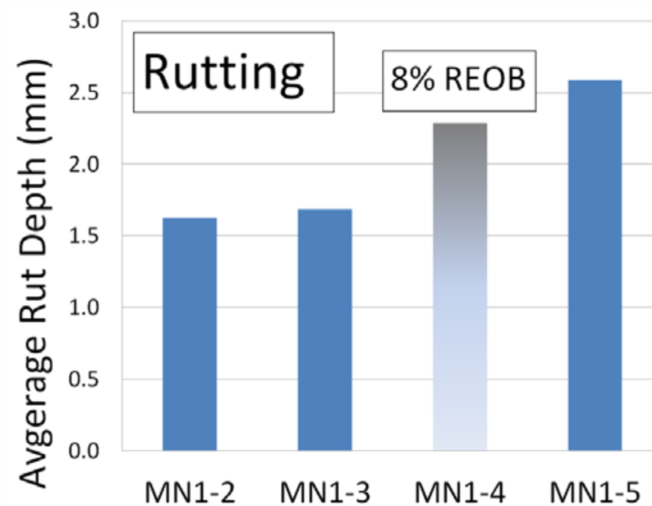
Field Study - Rochester, MN Comparative Test sites

❑2012 Distress Data (500 feet test sites)



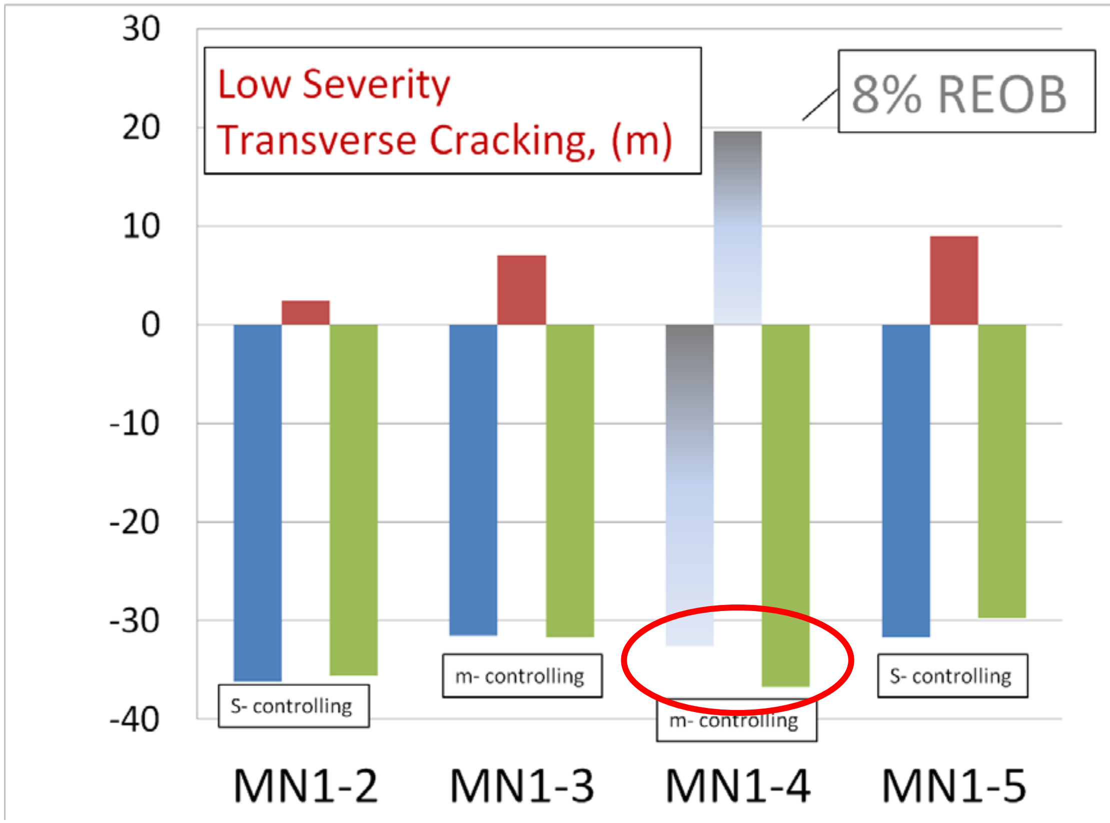






Field Study - Rochester, MN Comparative Test sites

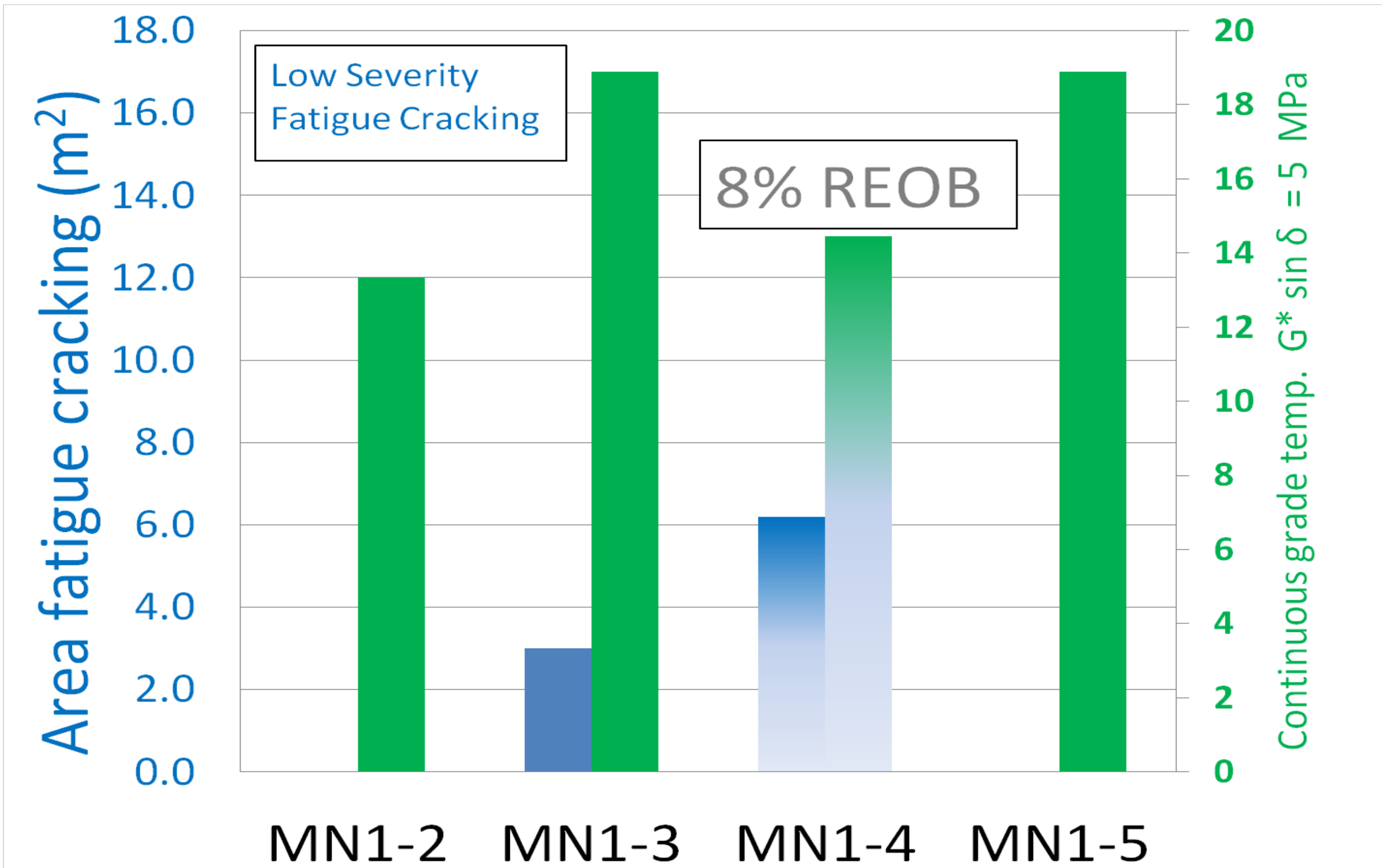
❑Transverse cracking vs. BBR (RTFOT+PAV)



- **BBR limited T grading did not predict** the transverse cracking issue on the MN1-4 test section
- **Neither did ABCD**
- **<u>But</u> the BBR Tc is significantly m-value (-5°C) control**
  - Ref and agreement with G. Reinke's presentation

Field Study - Rochester, MN
Comparative Test sites

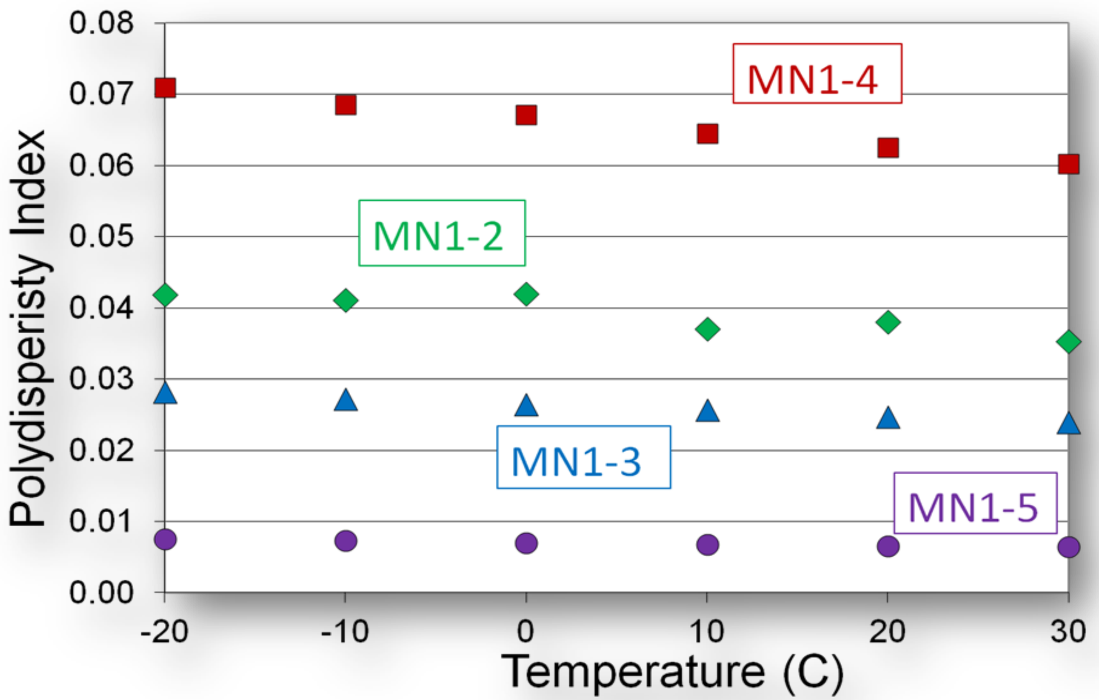
❑Fatigue Cracking vs. DSR (RTFOT+PAV)



Continuous grade temperature, G* sin δ = 5 MPa did not predict the fatigue cracking on the MN1-4 test section

Field Study - Rochester, MN Comparative Test sites

❑ **Crossover Modulus (Gc*)** {where δ=45° or G'(ω) = G"ω)}



- **The PI of MN1-4 stands out**
- Indicator of the extensive cracking in the section?

RTFOT+PAV aged materials

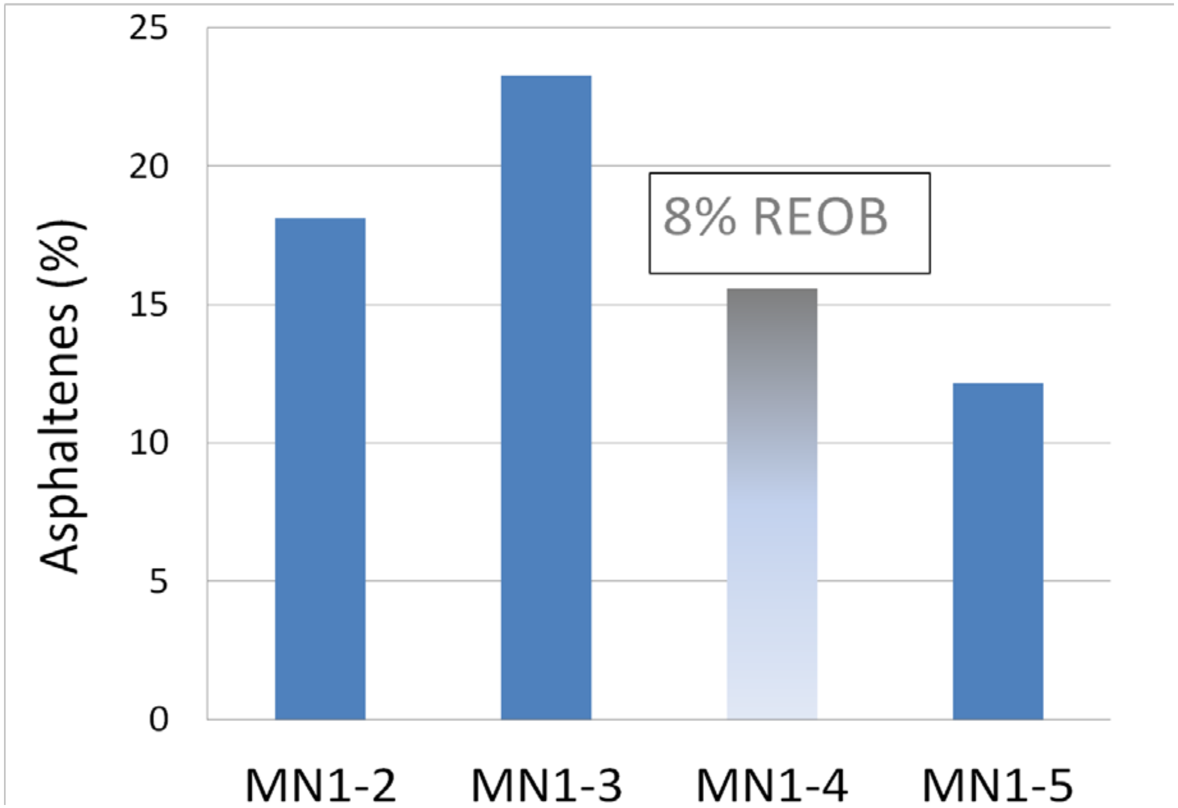
- In polymer science, inverse of G_c* used to estimate the Polydispersity Index or Molecular Weight distribution
- Consistent with the R value from CA model or the Glover-Rowe parameter

PI → molecular mobility → fracture and healing → cracking

Western Research INSTITUTE

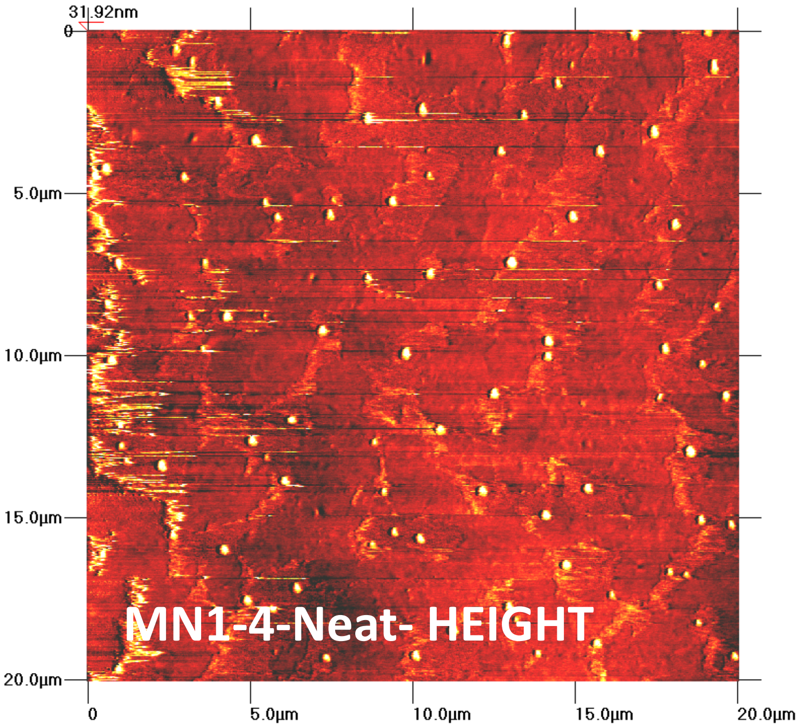
Field Study - Rochester, MN Comparative Test sites

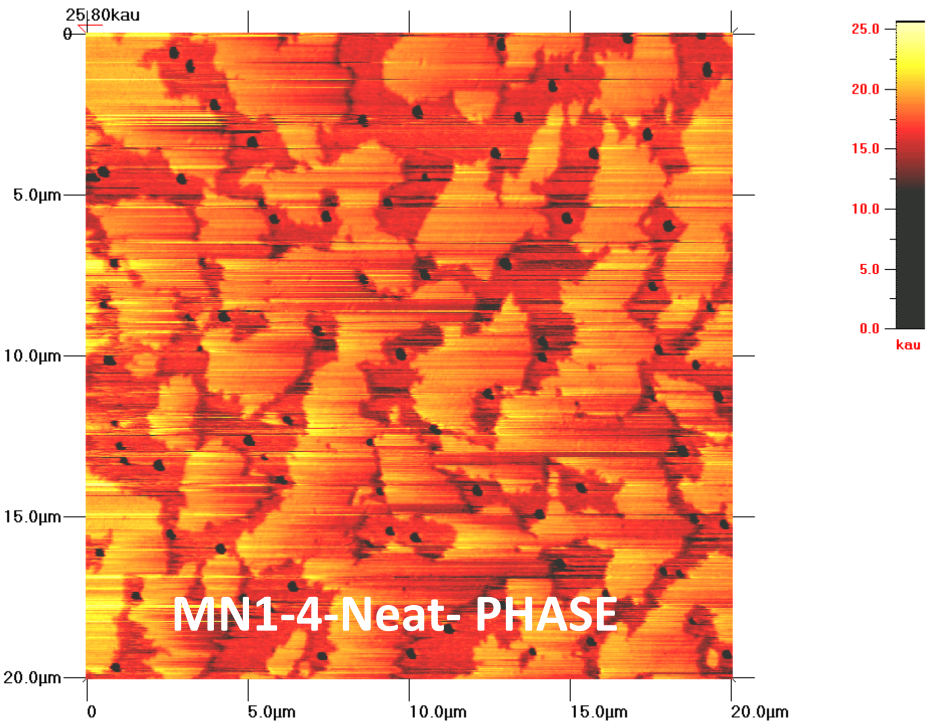
- ❑ **Asphaltene content**



- ❑ Apparently not directly related to the extensive cracking on MN1-4

Field Study - Rochester, MN Comparative Test sites





- **AFM topography & phase contrast image of MN1-4 asphalt – close-up (Unaged materials)**
  - **Multiphase structure**
  - **No bees but sink holes – in accordance with the other AFM studies**

Summary

- **Preliminary and ongoing study at WRI**
- **REOB impact noticeable on binder composition, structure and properties, beyond dilution effect**
  - **Composition: different from asphalt (low asphaltene, high paraffin), appearing compatible in compatible asphalt**
  - **Multiphase microstructure**
    - **Presence of “sink holes” expanding over aging – yet to identify**
    - **Effect on “bees” – wax formation disturbed – T sensitive**
  - **Oxidative Aging: multiple effects**
    - **Rate change: faster first reaction + REOB oxidation**
    - **Limited oxidization extent overall**
  - **Rheological behavior: fairly simple, but**
    - **Expected softening effect on original materials**
    - **Detrimental effect on the relaxation properties (m-value control) and crossover modulus upon aging**
    - **Tendency for physical hardening (by DSR), confirming others**

Western Research INSTITUTE

Summary

- **Field performance – limited data**
  - **Potential cracking issue in cold climate (MN), both thermal and fatigue, in comparison with other similar PG asphalt w/o REOB**
  - **Could be captured through DSR (BBR) evaluation after appropriate aging / conditioning**
  - **Extracted binder multiphase microstructure - confirmation**
  - **YNP (WY) pavement performed well for 3 years**
- **REOB identification techniques emerging, beside XRF**
  - **AFM**
  - **PDSC**
  - **DSR (BBR) – m-value control / physical hardening**

Perspectives – Research Needs

Western Research INSTITUTE

- **Asphalt – REOB blends**
  - Blending rules? Compatibility rules?
  - Asphalt and REOB origin dependency?
  - Effect of polymer and/or PPA?
  - Dosage effect on properties, particularly cracking potential? Threshold?
  - What are the criteria for appropriate blends?
- **Aging characteristics of REOB blends**
  - Metal catalysis effect?
  - Chemical aging rate and composition dependency
  - Rheological aging rate
  - **Aging characteristics of REOB blends with RAP, RAS, PPA, PMA…?**

Western Research INSTITUTE

Perspectives – Research needs

- **Field performance – wider survey needed**
  - **Well identified test sections, under various climatic and traffic conditions**
- **Selection of the techniques to best assess Asphalt / REOB blends in a relevant and cost effective manner, among currently available techniques**
  - **Rheological DSR tests and parameters**
  - **Microstructure by AFM**
  - **Physical-Chemical analysis: IR, AFT, SAR-AD, DSC, SEC**
  - **Physical/chemical Aging tests and models**

➢ **Need for a thorough well planned study with various REOB and asphalt sources, and various aging conditions**

THANK YOU!

July 13-15, 2015

52nd **Petersen Asphalt Research Conference**

Organized by Western Research Institute

Western Research INSTITUTE

www.petersenasphaltconference.org

International Society for Asphalt Pavement

2016 ISAP *Yellowstone & Jackson Hole Symposium* & 53rd Petersen Asphalt Research Conference

July 18 ~ 21, 2016

From Molecules to Innovative Pavements

Western Research
INSTITUTE

www.ISAP2016symposium.org