Innovation in Modified Asphalt testing

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M. Farrar, T. Pauli, W. Grimes, R. Boysen

AMAP 14th Annual Meeting
San Antonio, TX
March 13th, 2013

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Outline

- **WRI - Transportation Technology**
- **(Modified Asphalt) Binder testing products from WRI**
  - **Fundamental – Binder aging model**
  - **Application of Binder testing miniaturization to field survey**
    - **FTIR-AFM**
    - **4mm-DSR**
    - **USAT**

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Presentation of WRI

- **Non-profit Research Institution affiliate of UW**
  - **85 scientists, engineers & support**
- **Facilities in Laramie, Wyoming**
  - **University of Wyoming Campus**
  - **Advanced Technology Center**
- **Fields of expertise**
  - **Energy and Environment**
  - **Transportation Technologies**

- **A long history**
  - **<u>1924</u>: Petroleum experiment station to study WY high-sulfur crude oil**
  - **<u>1983</u>: DOE Laramie Energy Tech Center de-Federalized to become WRI**
- **Annual sponsored events in July**
  - **Petersen Asphalt Research Conference: <u>50th</u> in 2013**
  - **Pavement Performance Prediction Symposium: 11th in 2013**

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WRI-TT
Areas of Activity

- **3 main areas:**
  - **Asphalt research and technology development (DOT-FHWA)**
  - **Analytical developments related to Oil, Asphalt and Environment (DOE – Oil companies Consortium for 10+ years)**
  - **Commercial contracts dealing with any of the above**

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WRI-TT/FHWA contracts

Fu ... ce

From the Molecules to the Asphalt pavement !…

Fundamental Properties of Asphalt Binders III

- Oxidative aging
- Embrittlement & moisture
- Emulsion residues
- WMA mechanisms
- RAP / RAS compatibility
- Influence of additives

ARC Asphalt Research Consortium

- Pavement performance prediction & modeling
  - Cracking, Moisture
  - Field validation
- Appli. temp. reduction guidance
  - Warm and Cold Mix Asphalt
- RAP mix Design
  - High % RAP & CIR

- Binders composition – properties Chemo-mechanical modeling
- Field survey: HMA, WMA, RAP & Chip Seals

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ARC Asphalt Research Consortium

Partners

- Western Research Institute
- Texas A&M University
- University of Wisconsin-Madison
- University of Nevada Reno
- National Center for Asphalt Technology
- Advanced Asphalt Technologies

- **Sub-contractors**
- University of Texas – Austin
- University of Illinois - UC
- Virginia Polytechnic and State University
- University of Rhode Island

200+ Researchers

60+ products – online @

Fundamental Properties III -
http://www.westernresearch.org/transportation.aspx?id=2308

ARC -
http://www.arc.unr.edu/Deliverables/ARC_Technology_Development_Product_Briefs_Mar2011.pdf

Fundamental – Binder Aging

R. Glaser
J. Loveridge
F. Turner

Under

Fundamental Properties III
FHWA contract

Problem statement & Goals

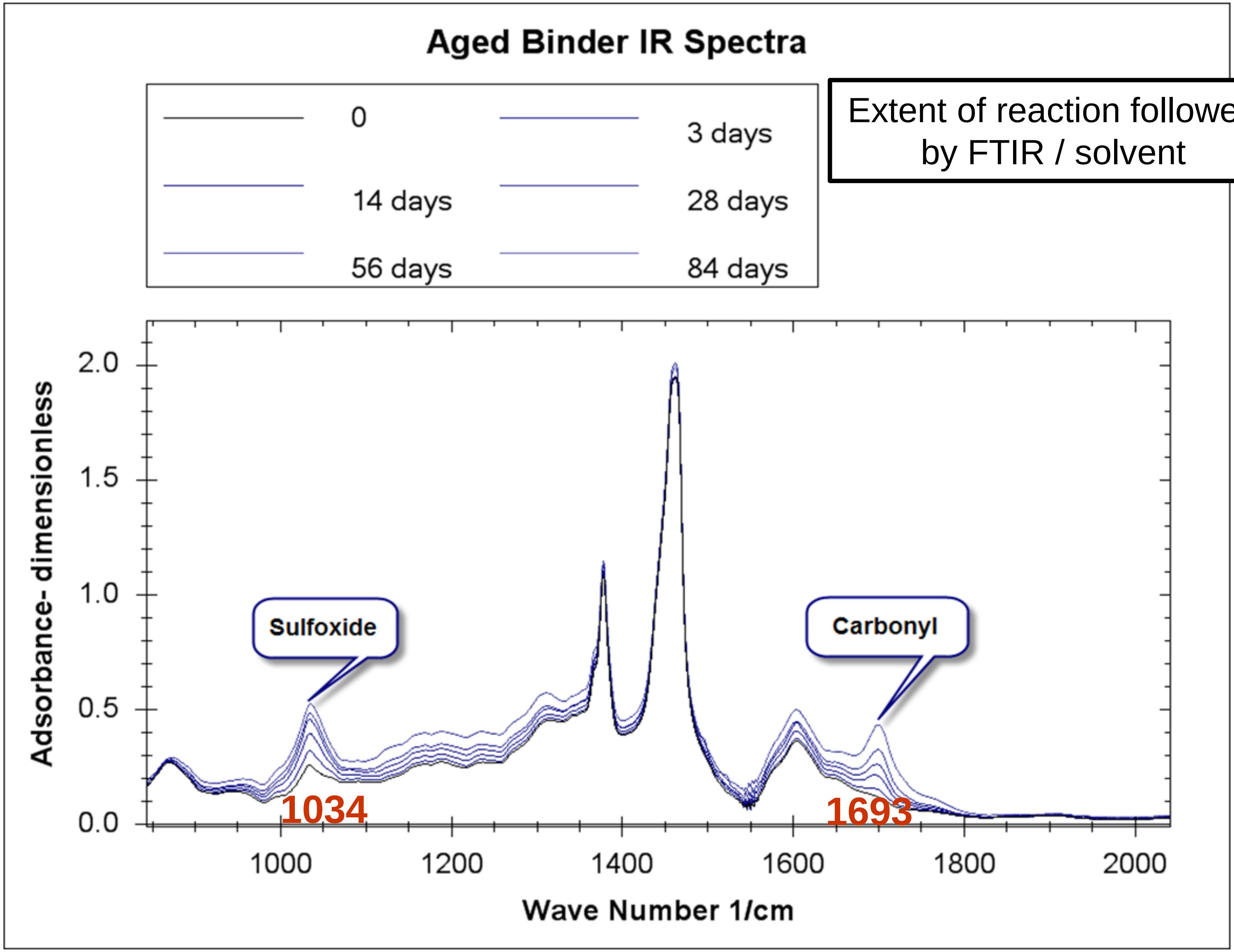
- **Statement**
  - Significant contribution of binder oxidative aging to pavement failure - cracking & raveling
  - Asphalt oxidation rate not accurately considered in current mix, pavement designs and performance prediction models
  - Binder selection not based upon aging properties due to cost and duration of oxidation kinetic studies
- **Goals**
  - Model describing binder oxidation (fundamentally derived mathematical or empirical fits)
  - Chemical components and properties affecting aging rate in the model
  - Analytical procedures to measure them
  - Oxidation impact on the change of asphalt physical properties

Experimental

- **Aging conditions**
  - Ambient pressure (0.74 atm) @ 4 temperatures (40 to 70ºC)
  - For 0 to 84 days (3 months total) aging time
  - Thin film (100 micron) in a ventilated oven
- **Binders**
  - 34 different binders = more than 150 aged samples!
  - SHRP core binders
  - ALF from FHWA-TF – base and modified
  - ARC test sites
  - MnRoad
- **Chemical and rheological characterization**
  - FTIR (34), elemental analysis (12)
  - DSR (20)

Results & Analysis
IR Spectra

Extent of reaction followed by FTIR / solvent



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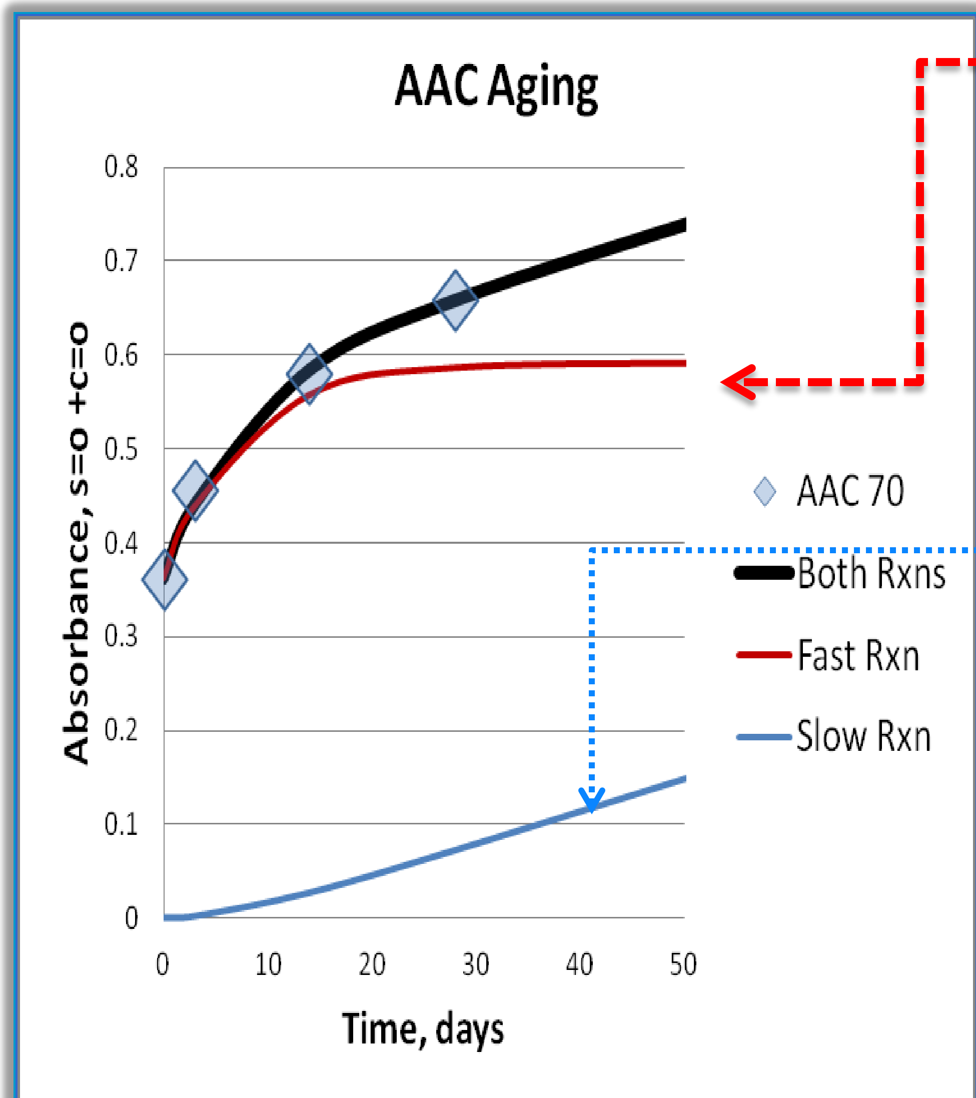
Dual Reaction Model



1. Fast Reaction:

RM+O_2→Products +FR*

2. Slow Reaction:

BC+FR*→BC*+O2→Products +FR*

- *RM: reactive material*
- *O_2 : molecular oxygen*
- *FR*: generic free radical*
- *BC: benzyl carbon*
- *BC*: benzyl carbon radical*

(after C. Petersen's oxidation model)

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Universal Rate Equation ?

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

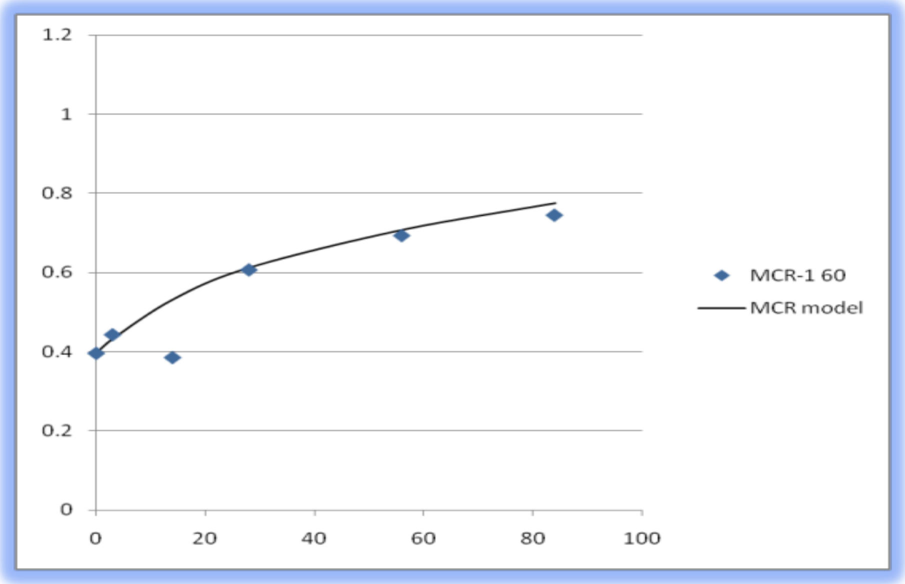
$$[sulfoxide + carbonyl] =$$

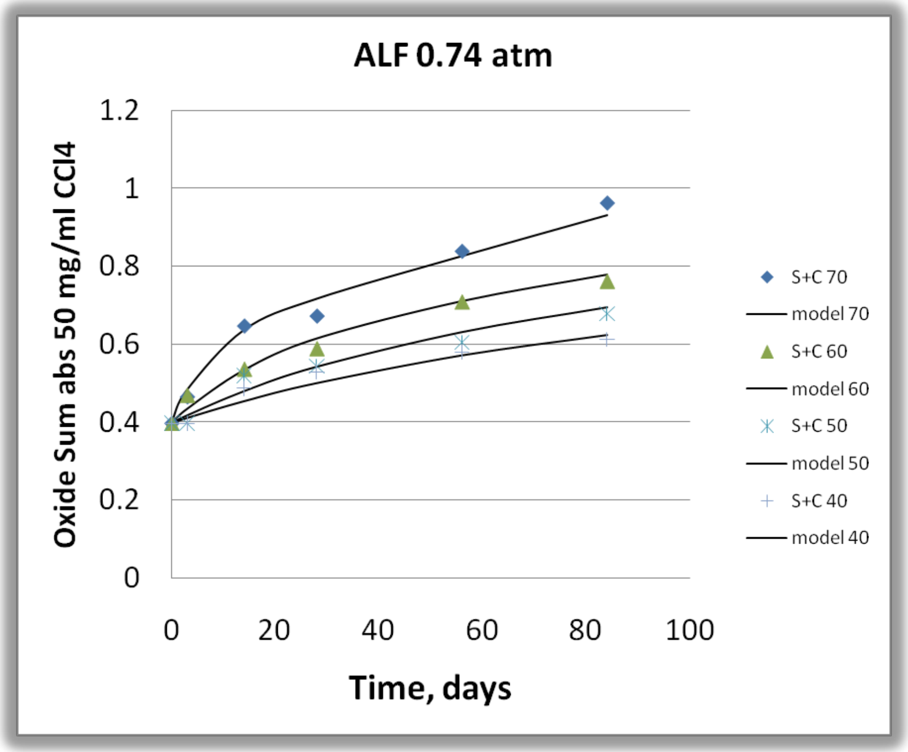
$$M\left(1-\frac{k_2}{k_1}\right)(1-e^{-k_1 {P_{O_2}}^{n} t}) + k_2 {P_{O_2}}^{m} M t$$

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

Reaction Kinetics Data Fits

Worst Fit : r^2 =0.86 for McA-R @60C

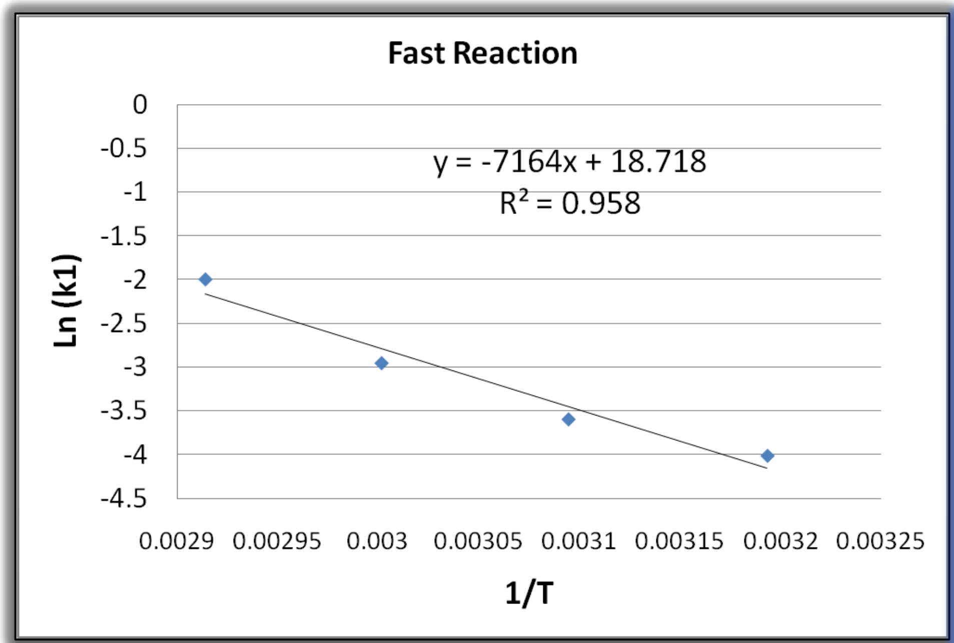


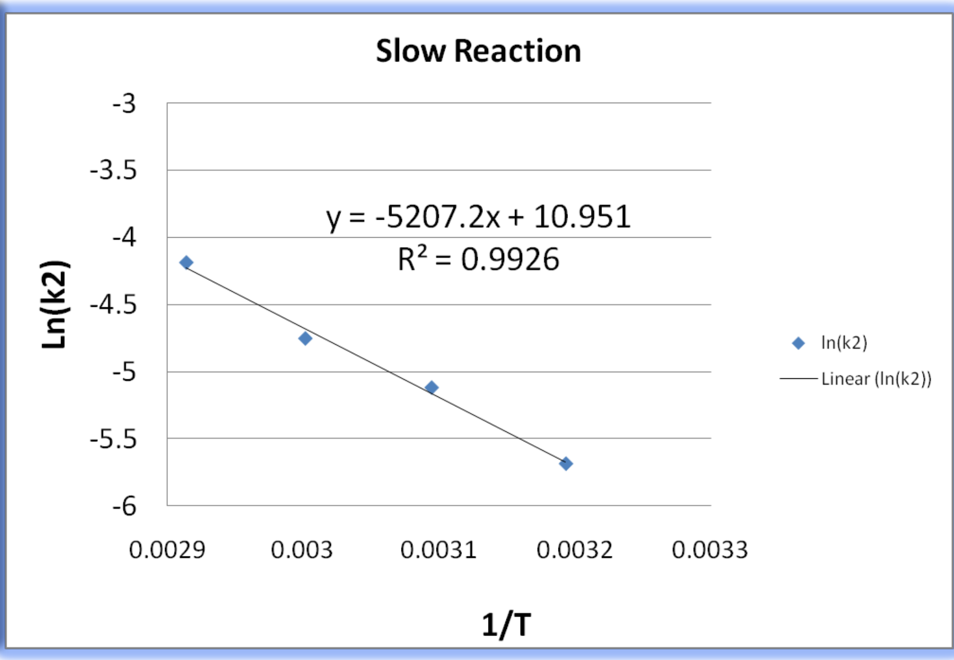


R^2 Fits from 0.860 to 0.995 for 12 binders @ 4 Temp.

Good Fit : r^2 >0.95 for ALF @40-70C

Activation Energy Data Fits

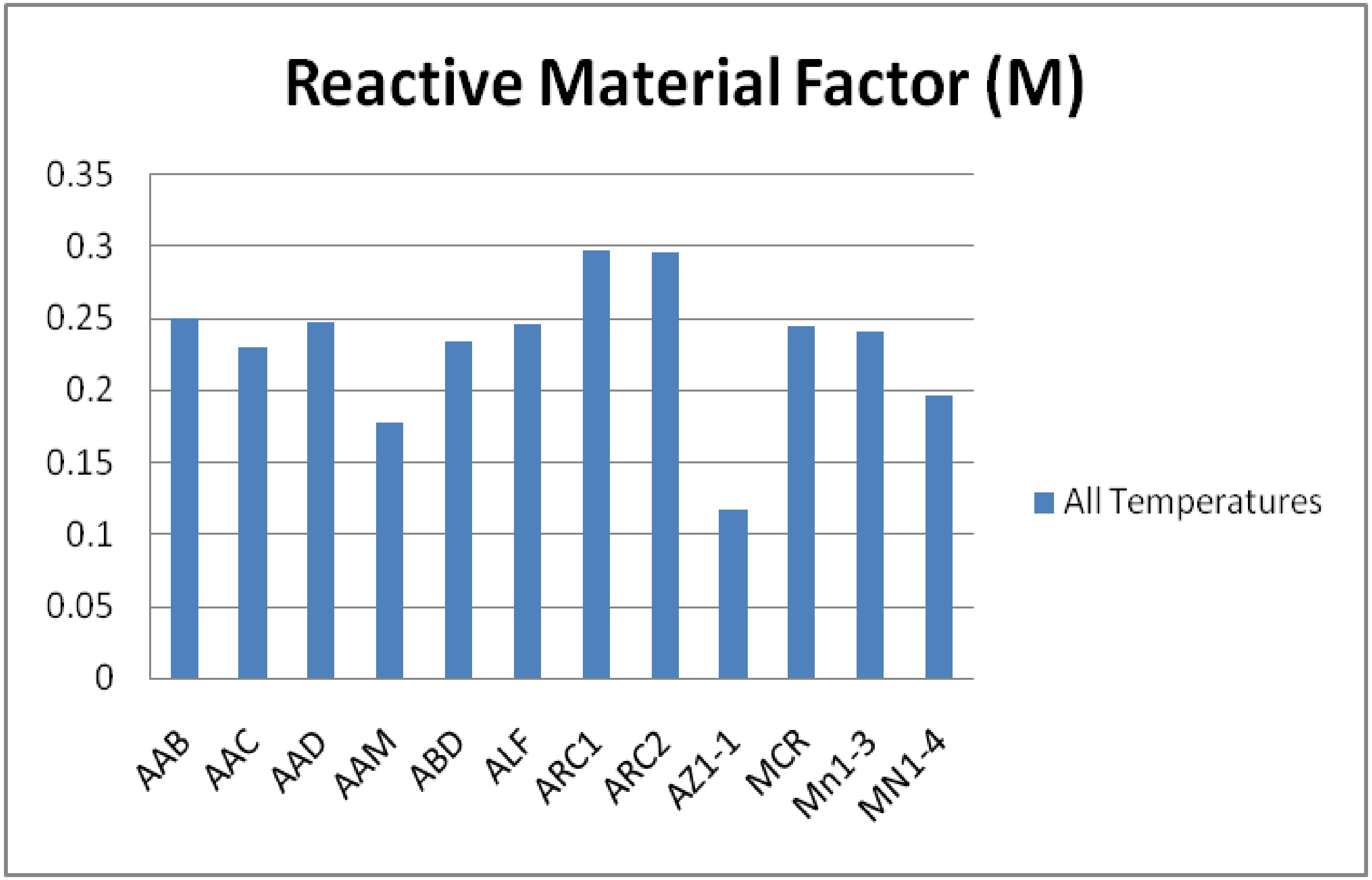




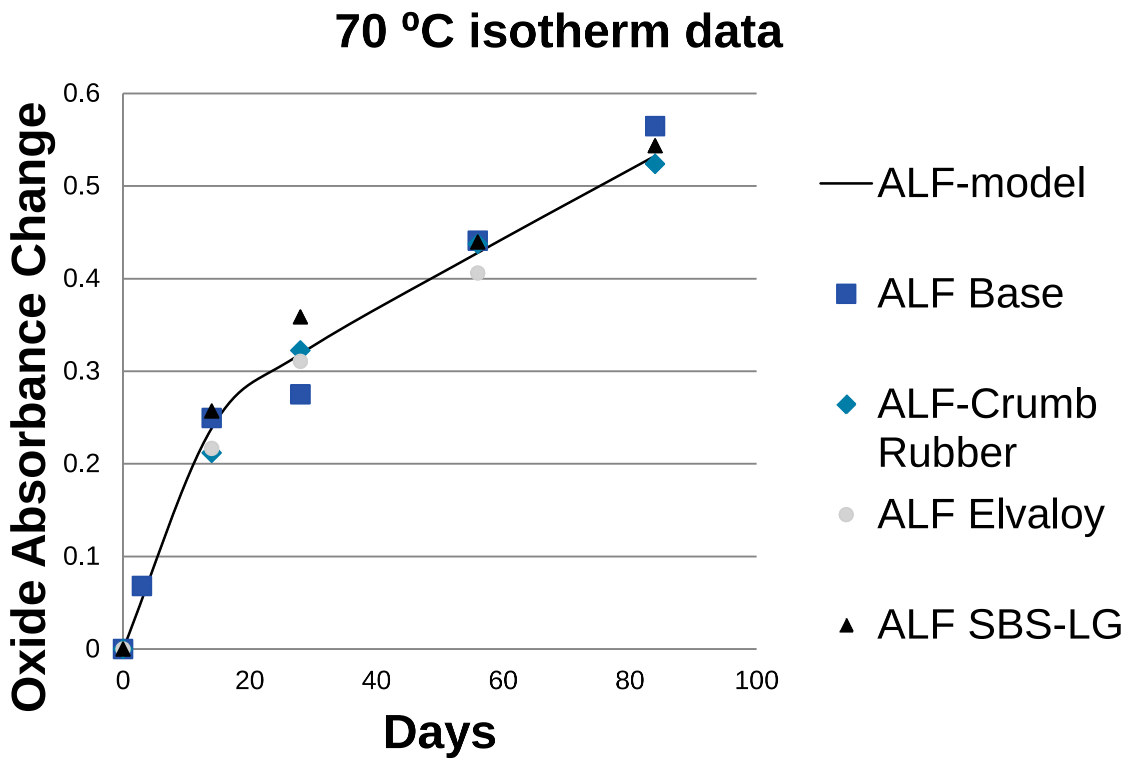
- **Two Arrhenius equations required: same activation energy**
- **Validated for 12 binders oxidized @ 4 temperatures (each point = 12 superposed data points)**

Adjustable parameter Data Fits

- 1 Adjustable Parameter = Amount of Reactive Material in the Rapid Reaction



PMA focus



- **Modified materials follow the same chemical reaction pathways as base binder except time zero absorbencies (polymer functions)**

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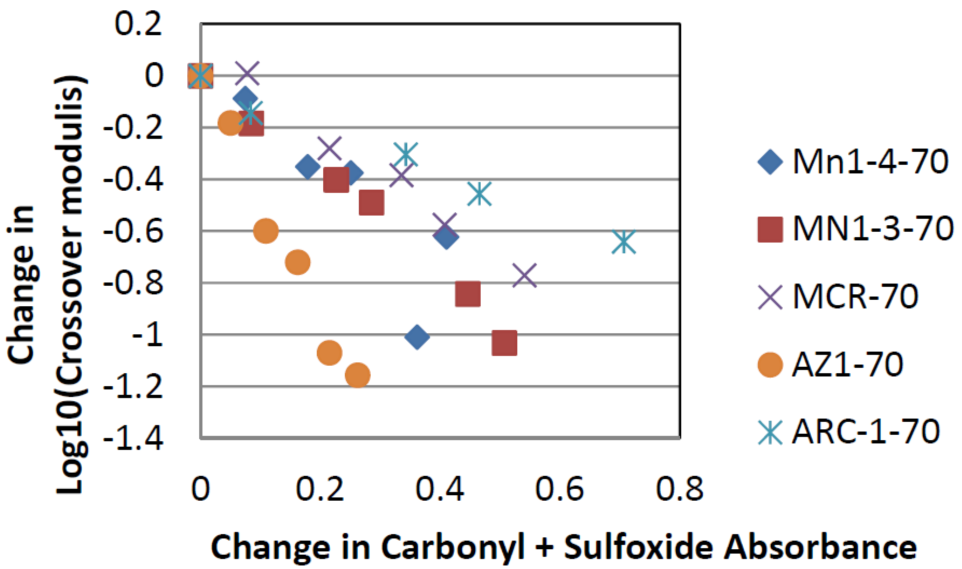
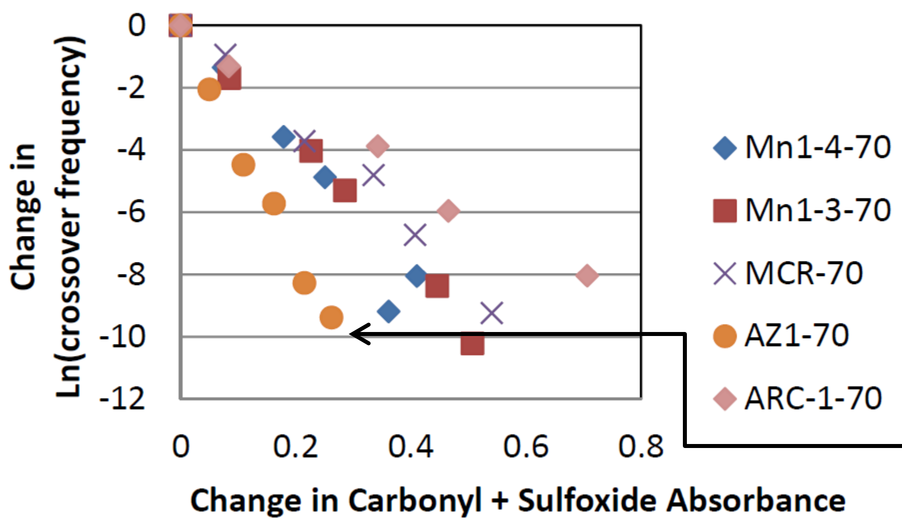
How does oxidation affect rheology?





- **Crossover modulus = mastercurve parameter**
  - **where the material changes from solid to liquid**
- **Binder stiffening upon oxidation**
- **Stiffening rate (with oxidation) depending on binder original state – gel asphalts stiffen “faster” than sol**

AZ1-70 : airblown - gel structure

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Summary - Future Work

- **Asphalt oxidation chemistry is basically the same for all asphalt binders, including PMA's**
  - **Oxidation model using one single adjustable parameter "Reactive material amount"**
- **BUT, oxidation chemistry effect on properties is original binder composition and microstructure dependant**
- **Future work**
  - **Identify, measure and quench (?) M, the reactive material *"let's the SkyFall!"***
  - **Tie changes in chemistry to changes in microstructure to changes in rheology**
  - **Focus on modified binders**
  - **Field validation (ARC test section monitoring, ALF…)**
  - **Input into design models**

Asphalt Testing Miniaturization

Michael J. Farrar
Will Grimes
Steve Salmans
Ryan Boysen

Under

Fundamental Property III FHWA contract and ARC agreement

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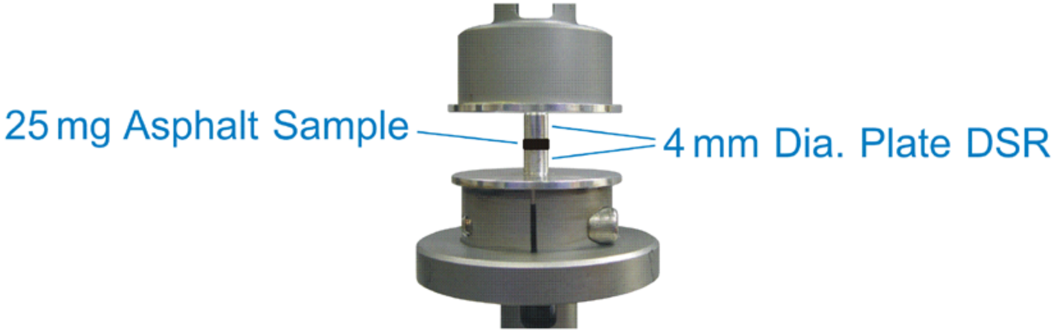
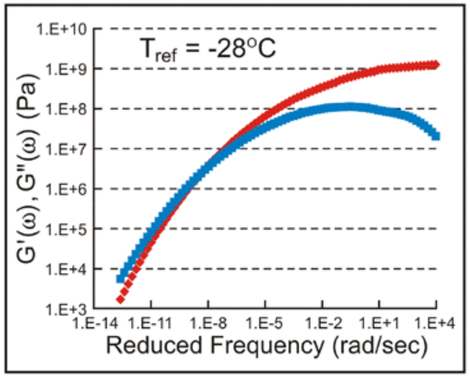
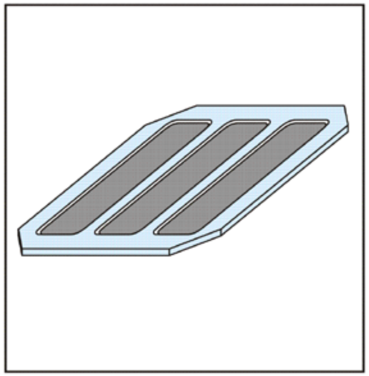
4mm-DSR Spin-Offs







Rheology

Low and Intermediate Temp.

- Asphalt
- Modified Binder
- Emulsion Residue
- Crack Sealant

Specifications

Asphalt

- AASHTO T 313
- AASHTO R 49-09
- Emulsion Residue
- Crack Sealant

Simple Aging Test

Short and Long-Term

- Asphalt
- Modified Binder
- Warm Mix

Field Sampling

- Hammer Drill
- Rapid Sampling
- Easy Extraction

Low Temperature Rheology Using 4 mm DSR

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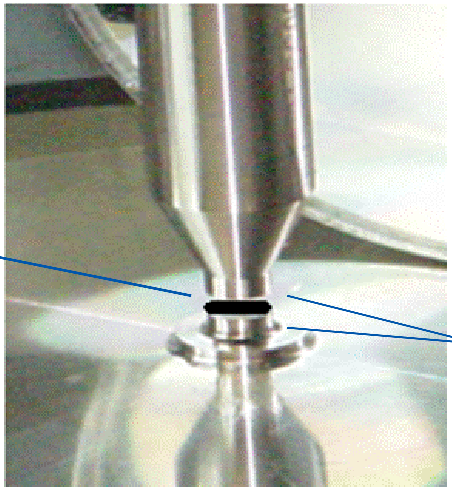

4 mm Dynamic Shear Rheometry (DSR)

- Low Amplitude Oscillatory Shear (-40 to ~ 45°C)
- 4 mm Diameter Parallel Platens
- Instrument Compliance Correction
- Small Sample (25 mg) (1.75 mm gap)
- Low Heat Req. (<60°C) During Sample Prep. on the DSR

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4 mm DSR Status

Standard Method of Test for

Determining the Low Temperature Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)

AASHTO Designation: T XXX-12

- **AASHTO Method, including:**
  - How to manually calculate the DSR compliance correction for G' and G''
  - How to generate a relaxation modulus master curve and determine G(t) slope and magnitude at 60 seconds
  - 8 mm diameter plates in the method
- **Validation**
  - Ruggedness and Round-Robin Testing
  - Binder ETG Task Group on 4 mm DSR
- **Promising Applications**
  - Low and Intermediate Rheology: alternative to BBR and 8mm DSR for Asphalt Binder / Emulsion Residue / Crack Sealant

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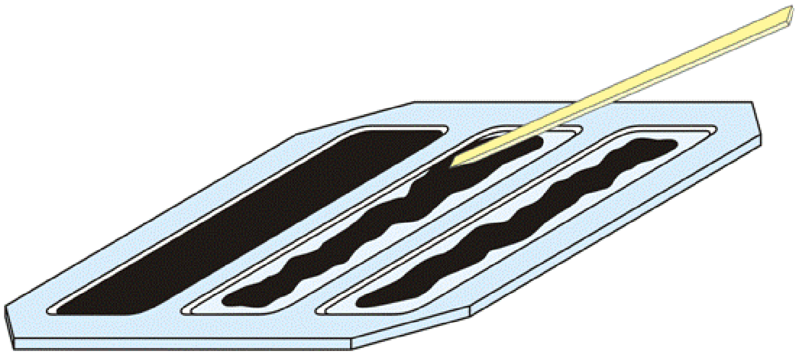
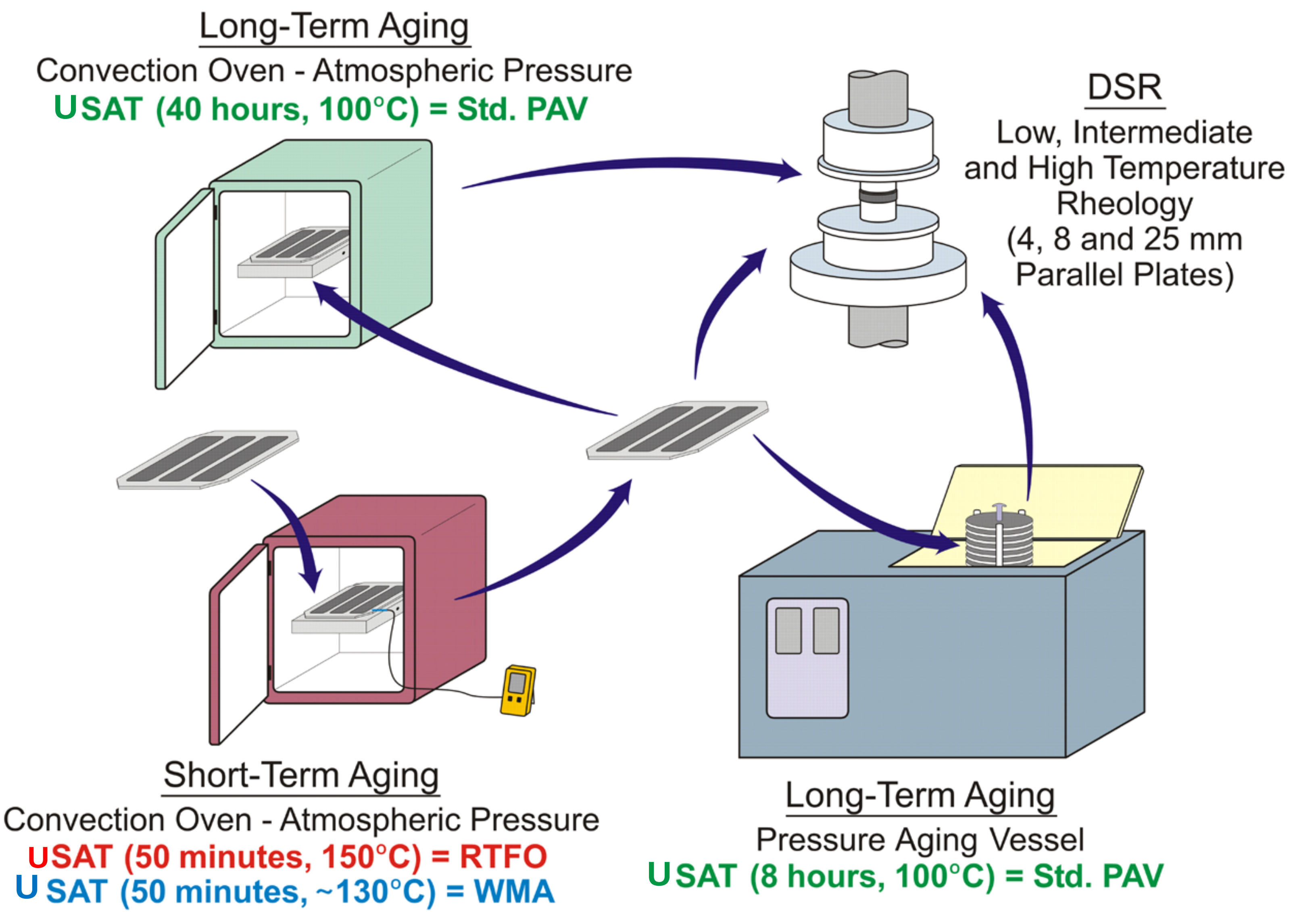
Universal Simple Aging Test - USAT

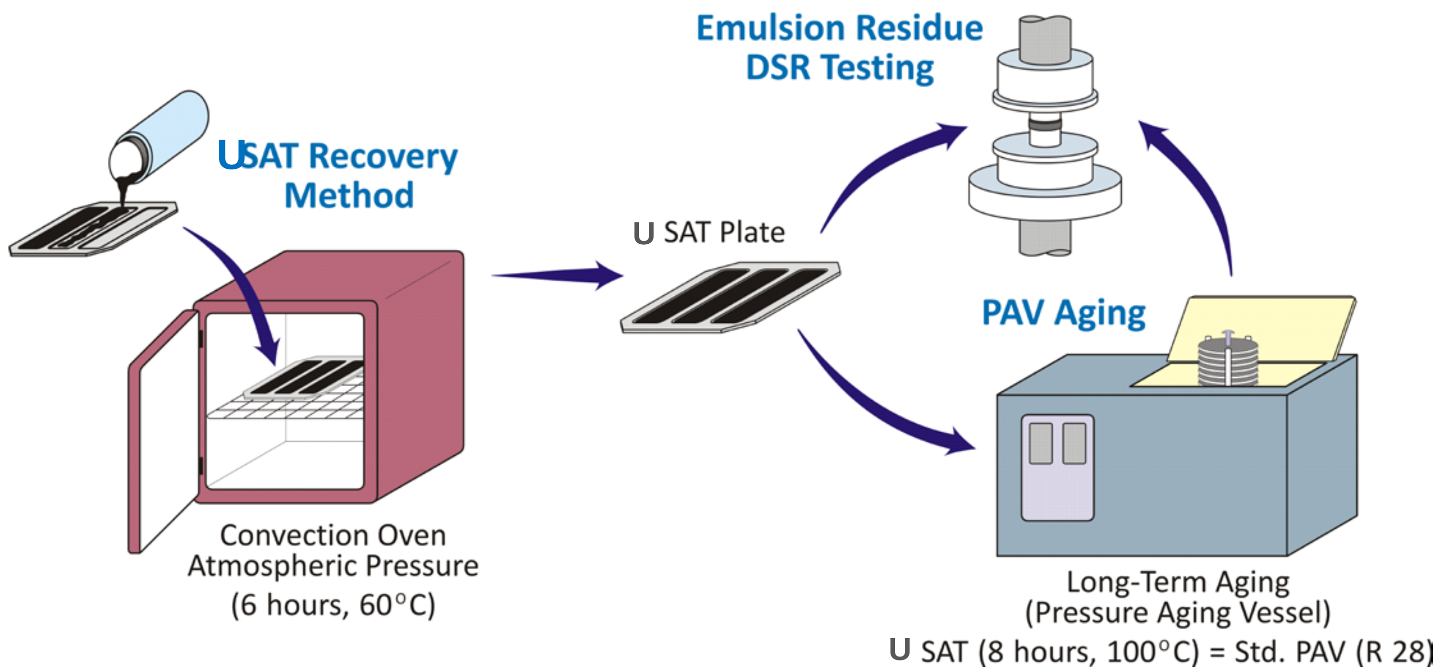


- Short & long-term oxidative aging for WMA or HMA
- Recovery and long-term oxidative aging of emulsion residues
- Preparation
  - Performed in a glove box under nitrogen
  - Hot plate to bring the asphalt to ~120ºC and spread it
  - Small spatula to spread the asphalt to the un-wetted surface
  - Approximately 10 min to prepare one plate

USAT for HMA/WMA binder aging



USAT for Emulsion Residue Recovery & Aging



USAT Recovery Method Advantages as Compared to Method B

- No Silicone Mat
- No Wet Film Applicator
- More Uniform Residue Surface and Thickness (300 µm)
- Designed to Be Placed Directly in the PAV
- PAV Time is Reduced from 20 to 8 Hours

Farrar, Michael J., Steve Salmans, Jean-Pascal Planche, Recovery and Laboratory Testing of Asphalt Emulsion Residue: Application of the Simple Aging Test (SAT) and 4 mm DSR, TRB 2013

USAT Status

- **HMA/WMA Short and Long-Term Aging**
  - Need to Develop an AASHTO or ASTM Method
  - Evaluate USAT with Polymer Modified Asphalt
  - Confirm Temperature and Time to Simulate WMA
- **Emulsion Residue Recovery and Oxidative Long-Term Aging**
  - Need to Develop an AASHTO or ASTM Method
  - Confirm 6 Hours at 60°C reduces water to Equilibrium Level
  - Establish PAV time and temperature to simulate field aging
- **Binder ETG participation**
  - Create an ETG USAT Task Force
  - Validation
  - Ruggedness Testing
  - Round-Robin Testing

Field Survey: Federal Lands Emulsion Residue Sampling Sites

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- Support of the Emulsion Task Force - Development of Specifications for Surface Treatments
- 5 Projects (National Parks)
  - Polymer Modified Emulsions
- Research
  - Sample Collection (Complete)
  - Testing Underway
    - IR, GPC and AFM
    - Low, Intermediate and High Temperature Rheology,

King, G., J. Johnston, Polymer Modified Asphalt Emulsions - Composition, Uses, and Specifications for Surface Treatments, Publication No. FHWA-CFL/TD-12-004, January 2012

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Field Survey: Collecting Chip Seal Emulsion Residue

Modified Tile Scraper

Putty Knife

Sawzall with Tile Blade

Hammer Drill with Venturi Collector

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Portable Pavement Heating Unit

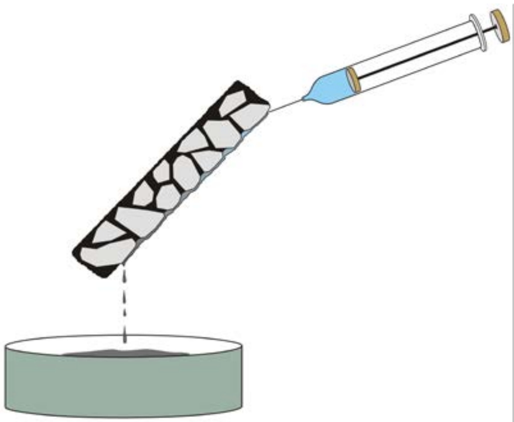
Death Valley
Chip Seal Emulsion Residue

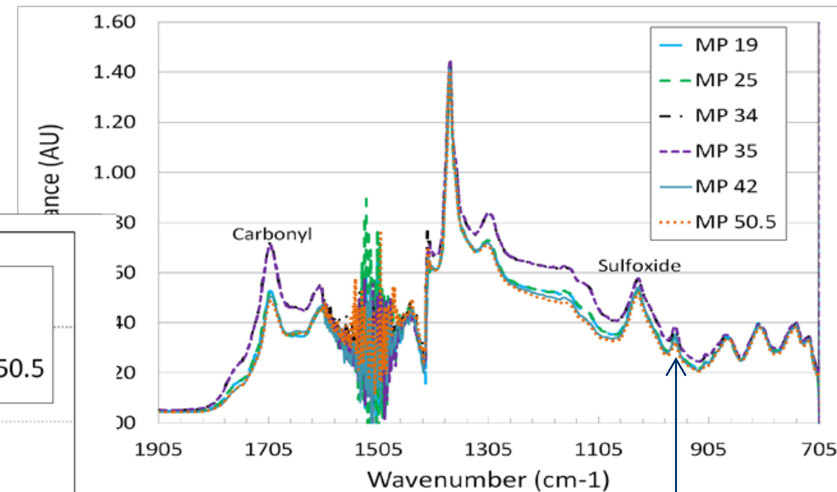
Death Valley National Park

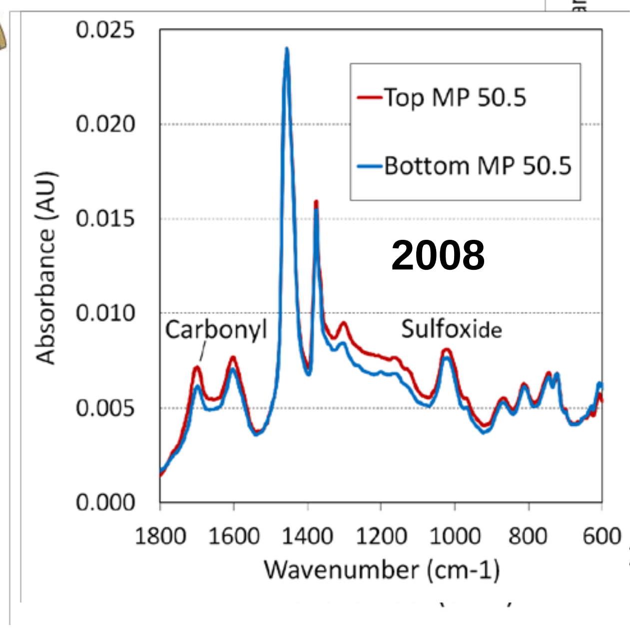
Watch Out for Flash Floods!

Death Valley Chip Seal Emulsion Residue - IR analysis

Surface of Emulsion Residue Removed Using a Solvent Wash

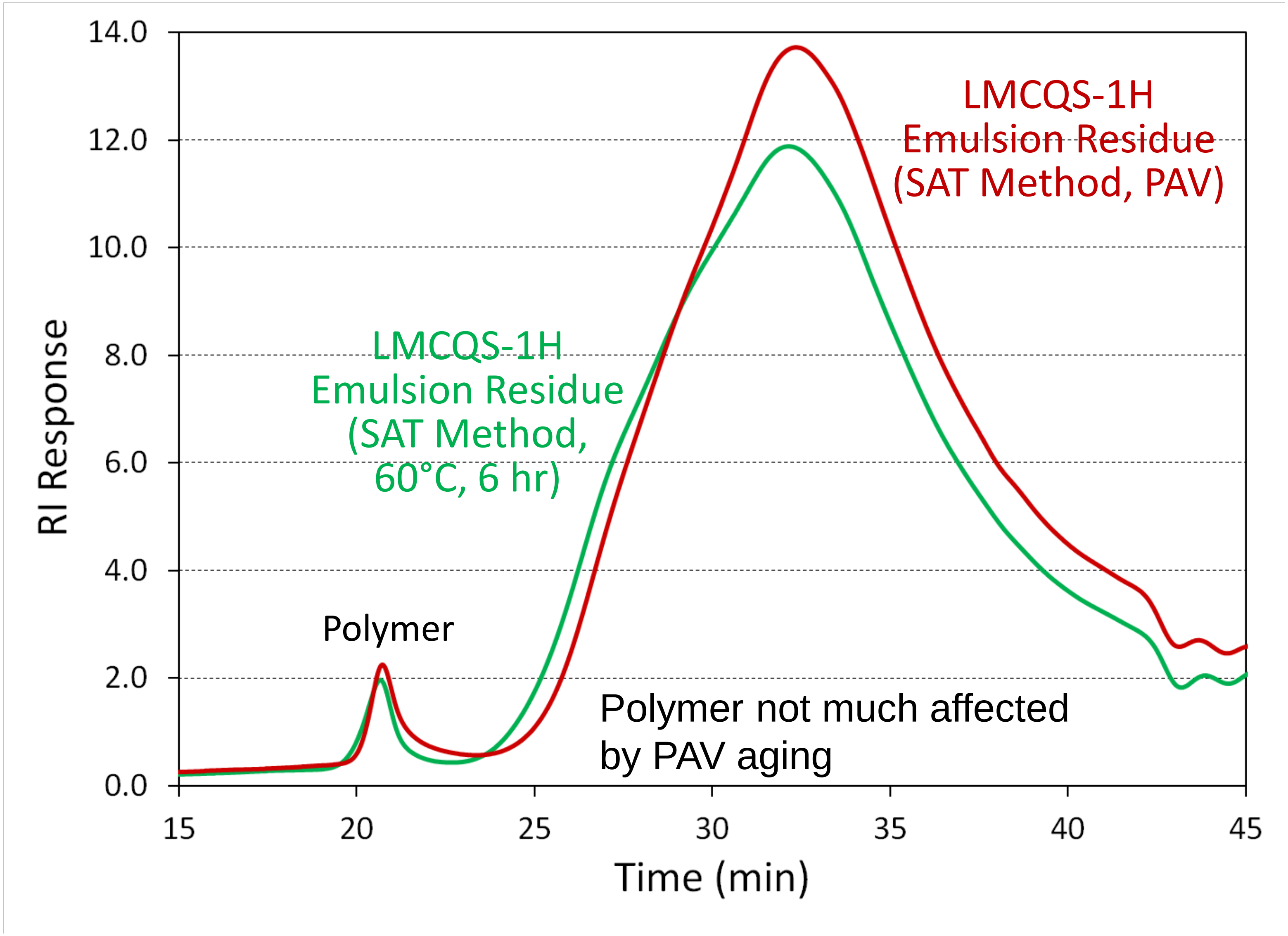




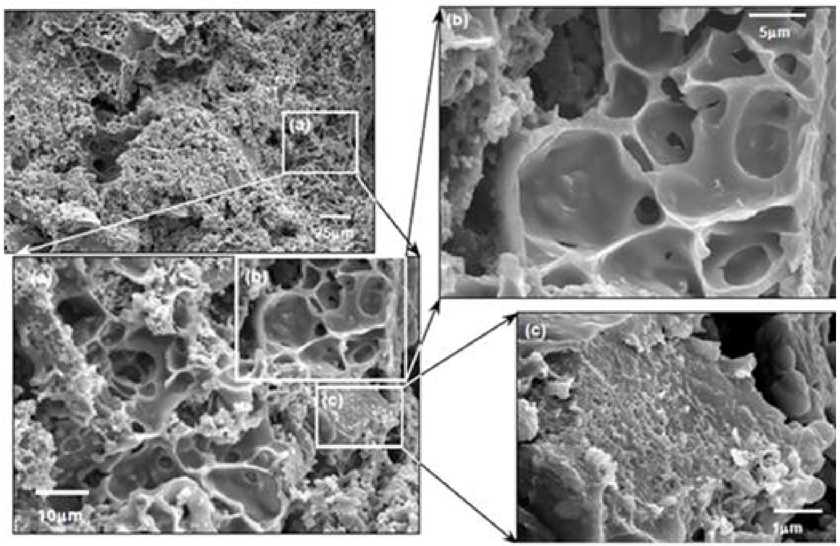


- **Significant amount of oxidation (carbonyl and sulfoxide)**
- **No significant difference between chip seal top and bottom**
- **Presence of SBR (Latex) - limited degradation**

Gel Permeation Chromatography (GPC)



“Quest to the Honeycomb” Latex Modified Emulsion Residue



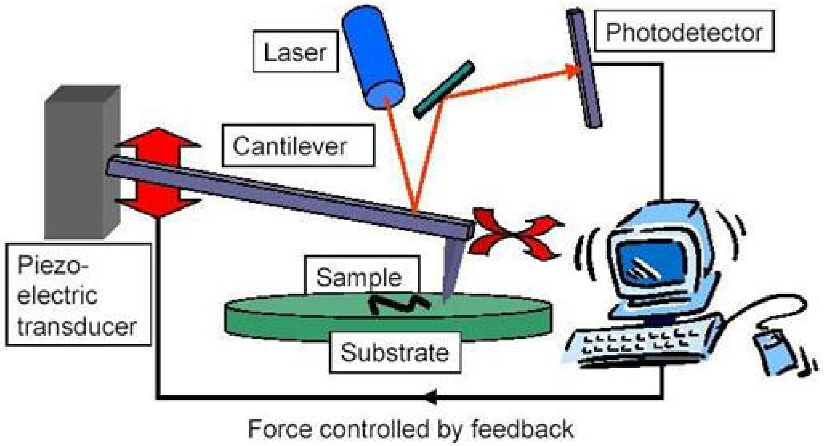
SEM photographs of the cured microsurfacing specimen demonstrating (b) SBR polymer honeycomb formed around asphalt particles and (c) some polymers also adhere on the aggregate surface

From Takamura, K. Chris Lubbers, Comparison of Emulsion Residues Recovered by Forced Airflow and RTFO Drying.
Dr. Takamura at the AEMA/ARRA/ISSA an. meeting March 13-16, 2000

- Field aging & residue recovery at high temperature may damage the honeycomb structure / formation
- Does solvent extraction disrupt the honeycomb structure?
- Attempt to capture the polymer morphology before and after extraction using atomic force microscopy (AFM)
- Evaluation of differences in rheology before and after extraction

AFM Images

- **AFM Images of latex-free (CRS-2) and latex-modified (LMCRS-2) asphalts**
  - Samples provided by Utah DOT.
  - Emulsion Residue Recovered Using the USAT Plate (60°C, 6 hr)
- **Topography & phase images**
  - Topography: color contrast = changes in the relative height of the surface features
  - Phase: color contrast = phase shift between incident and reflected waveform of the oscillating cantilever, due to differences in the relative stickiness and/or hardness of the corresponding features
- **Images collected in (non-contact) tapping mode**
- **Samples rinsed with n-heptane to more clearly expose any structures**



Schematic from TNO

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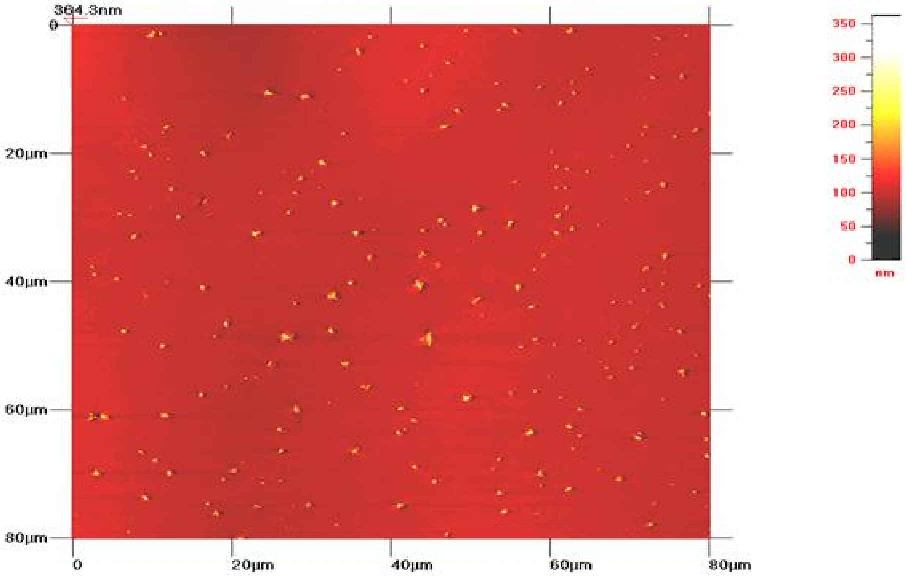
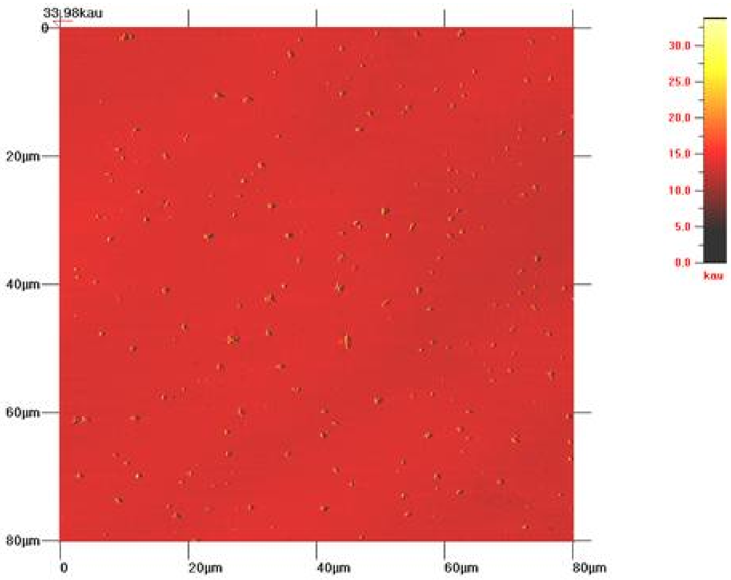
AFM - No latex, rinsed



Topography image



Phase image

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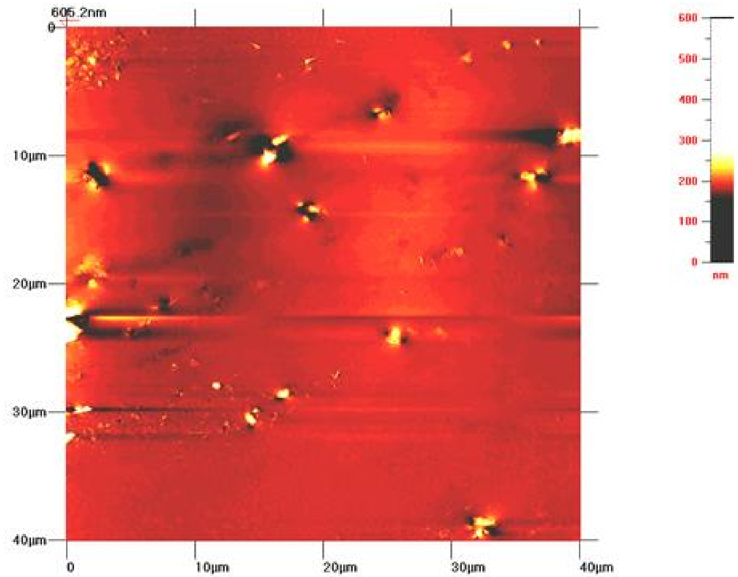
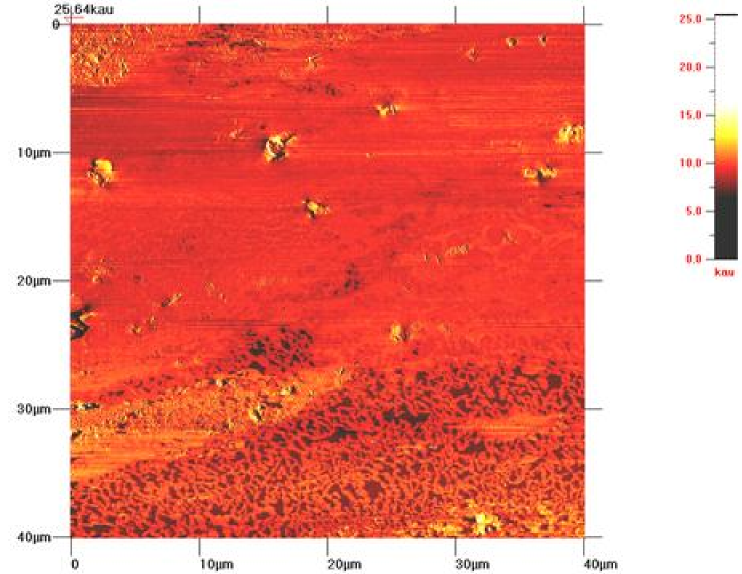
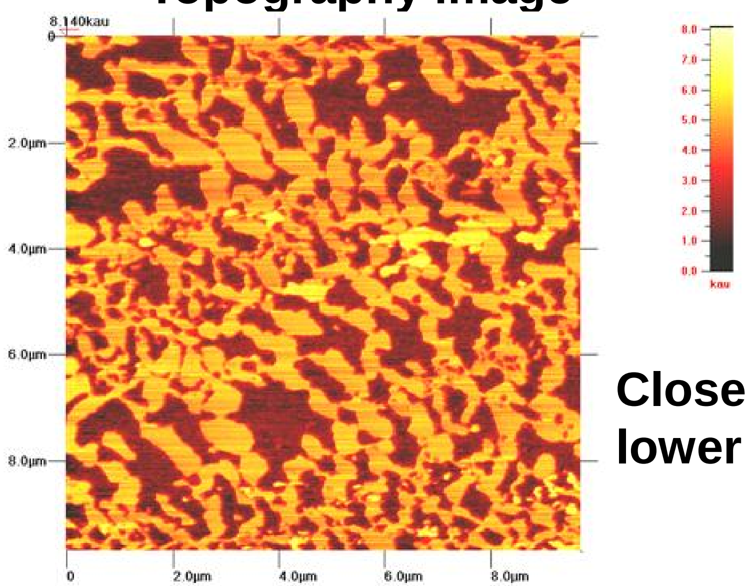
AFM- Latex modified, not rinsed



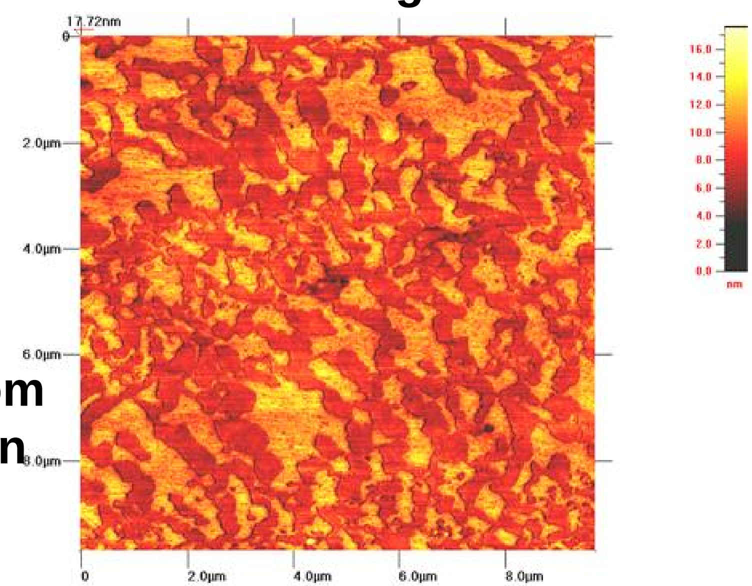
Topography image



Phase image



Close up from lower portion



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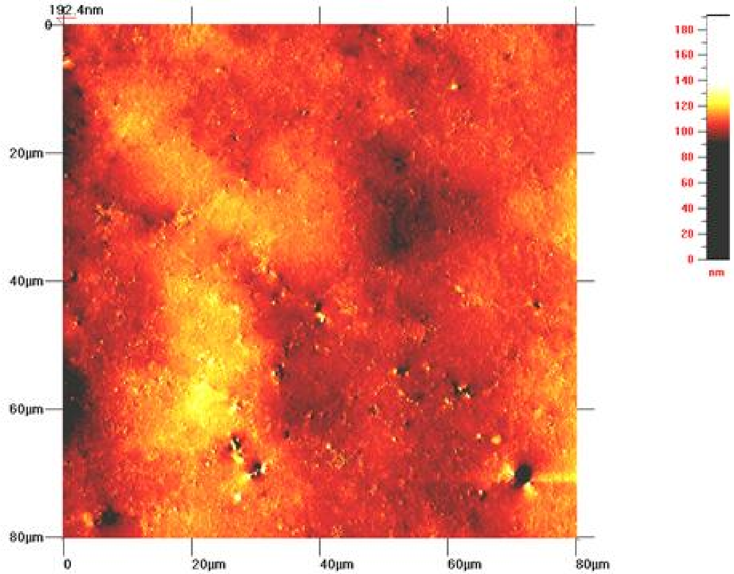
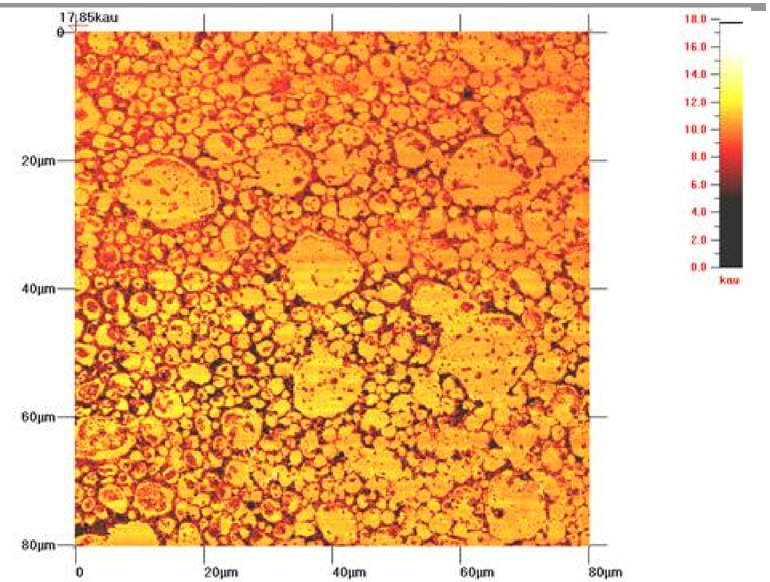
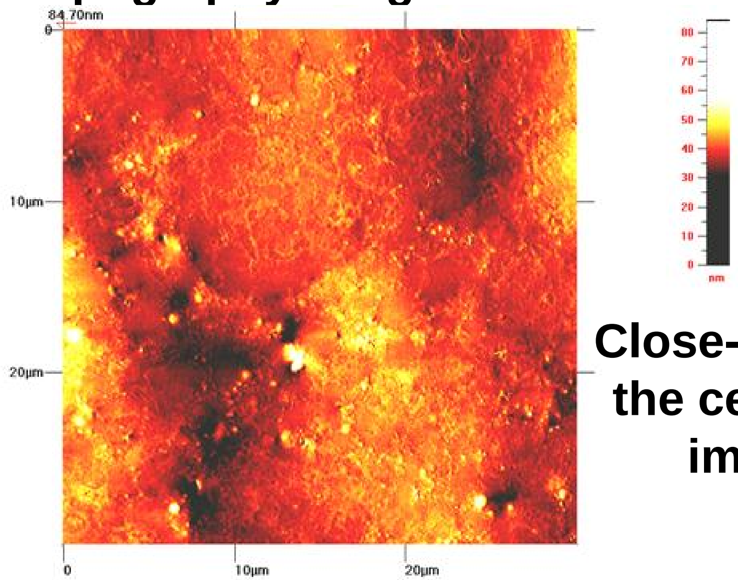
AFM - Latex modified, rinsed



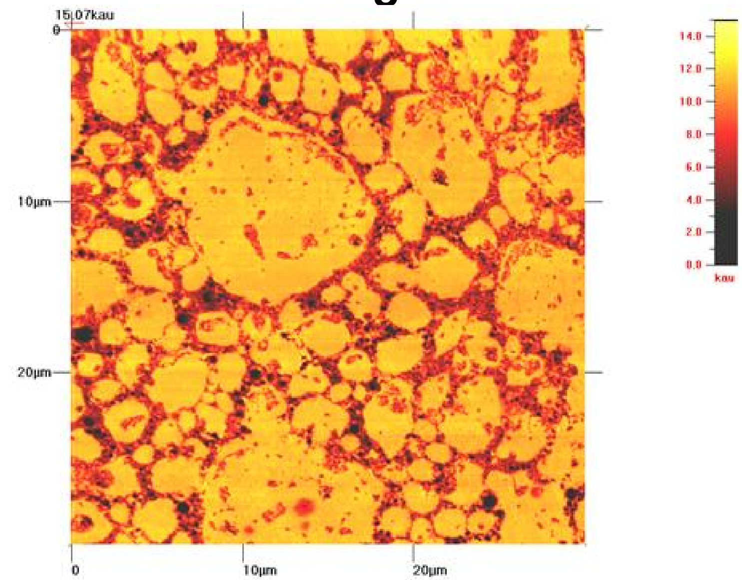


Topography image

Phase image



Close-up from the center of image



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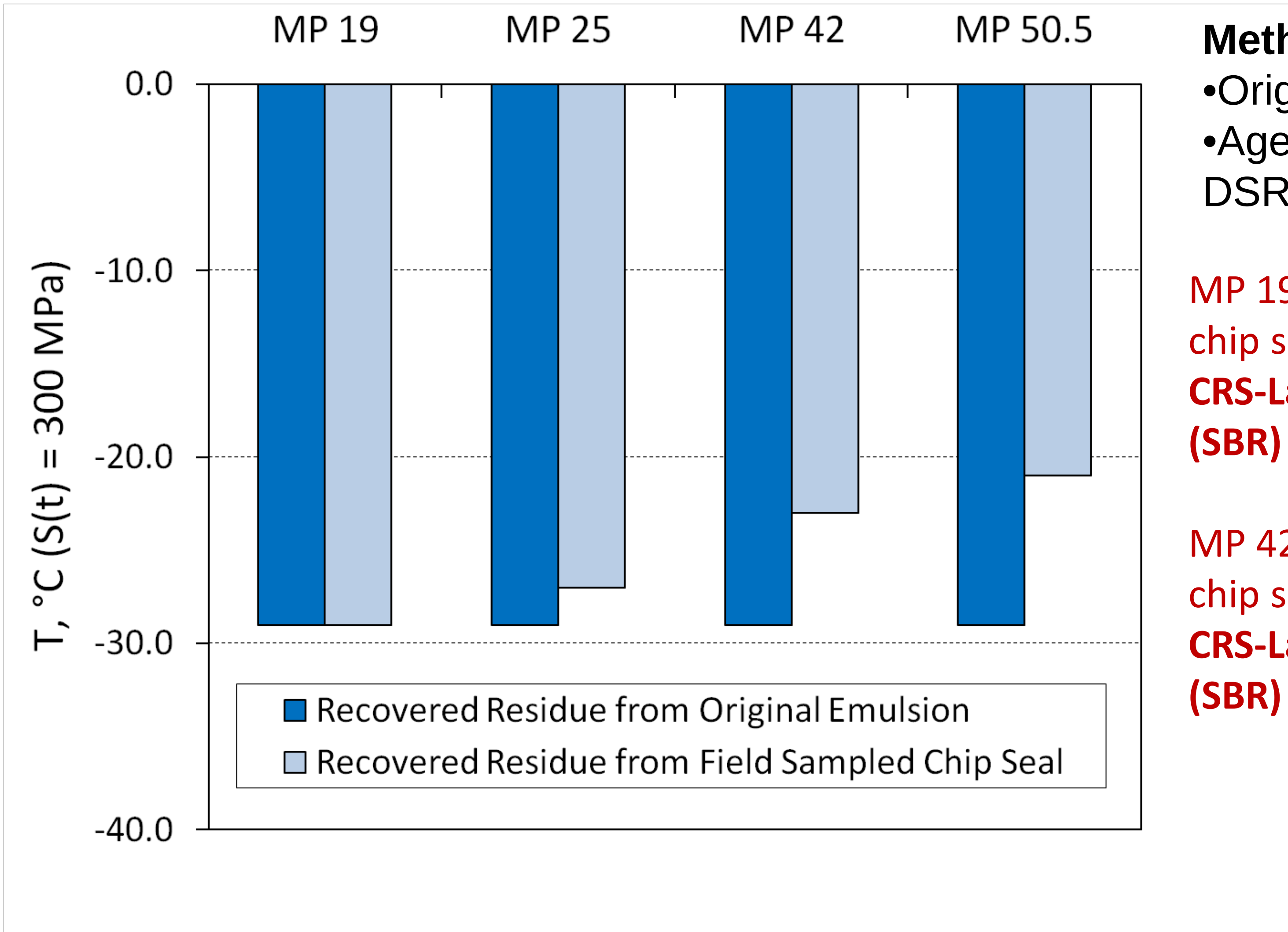
Death Valley Recovered Residue Low temperature S(t)



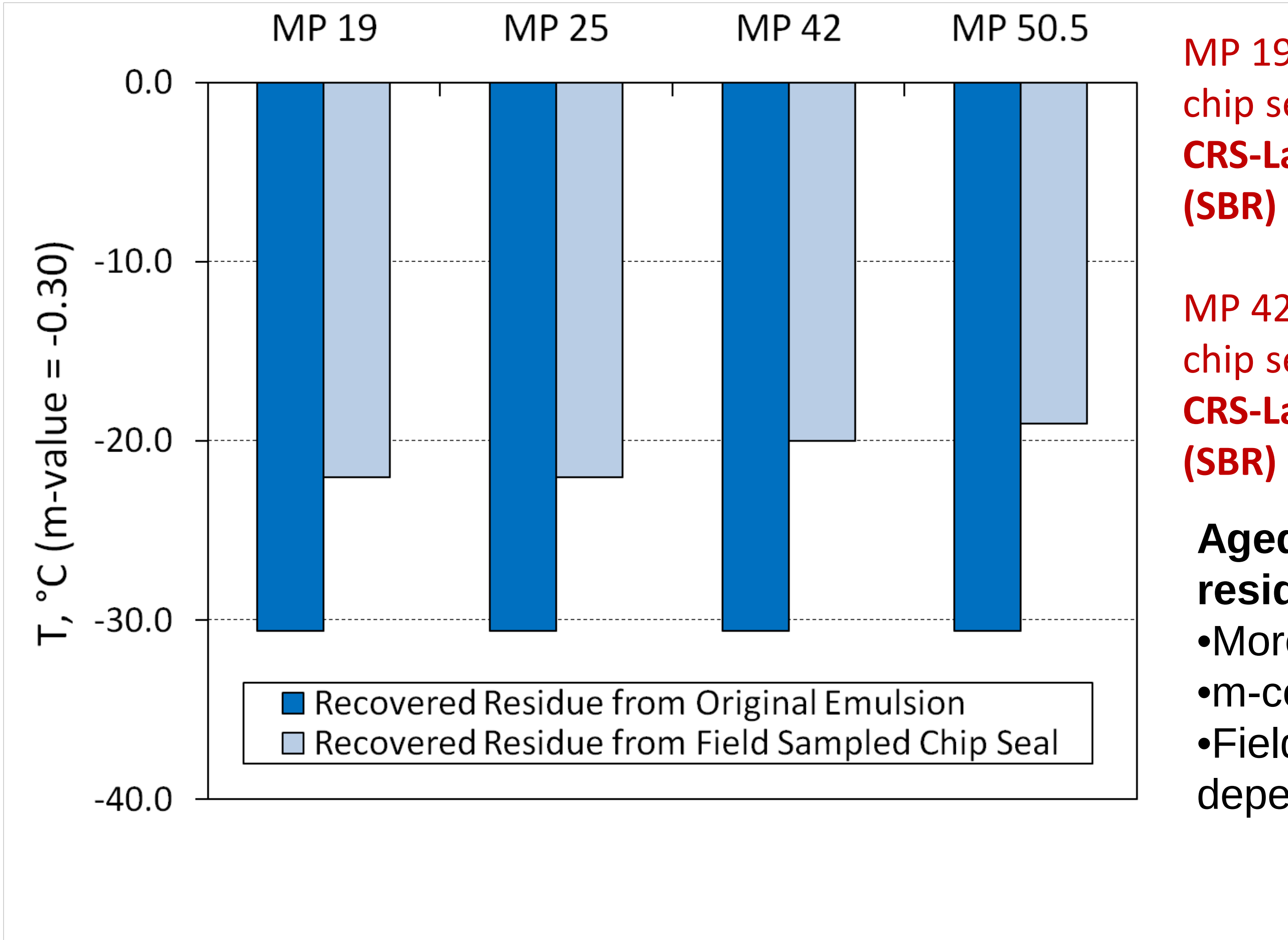
Method

- Original by BBR
- Aged extracted by DSR-4mm

MP 19 and 25
chip seal placed 2010,
CRS-Latex Modified (SBR)

MP 42 and 50.5
chip seal placed 2008,
CRS-Latex Modified (SBR)

Death Valley Recovered Residue Low temperature m-value



MP 19 and 25
chip seal placed 2010,
CRS-Latex Modified (SBR)

MP 42 and 50.5
chip seal placed 2008,
CRS-Latex Modified (SBR)

Aged recovered residues low T:
- More brittle
- m-controlled
- Field aging time dependant

Death Valley Recovered Residue DSR High Temperature Rheology

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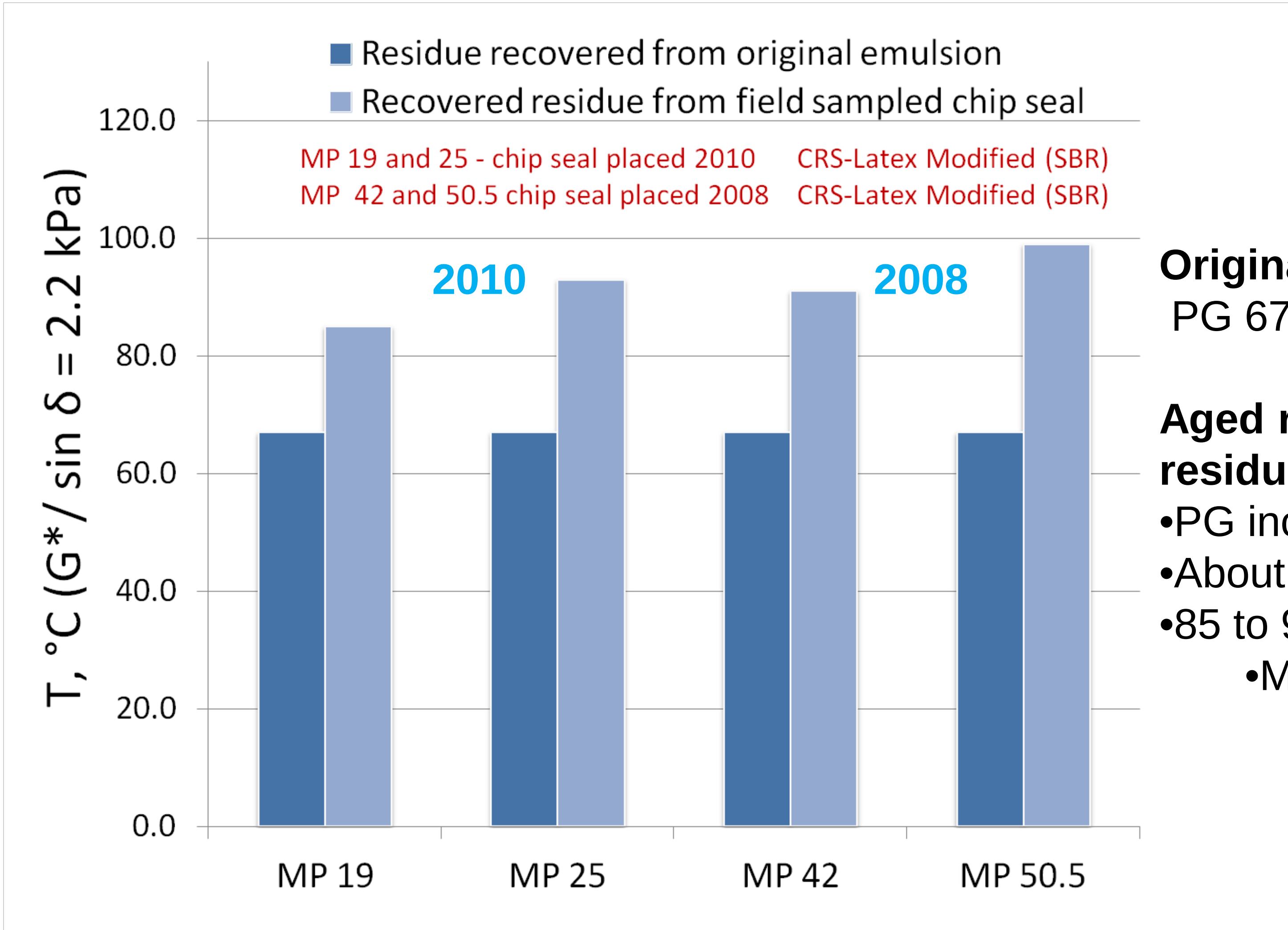
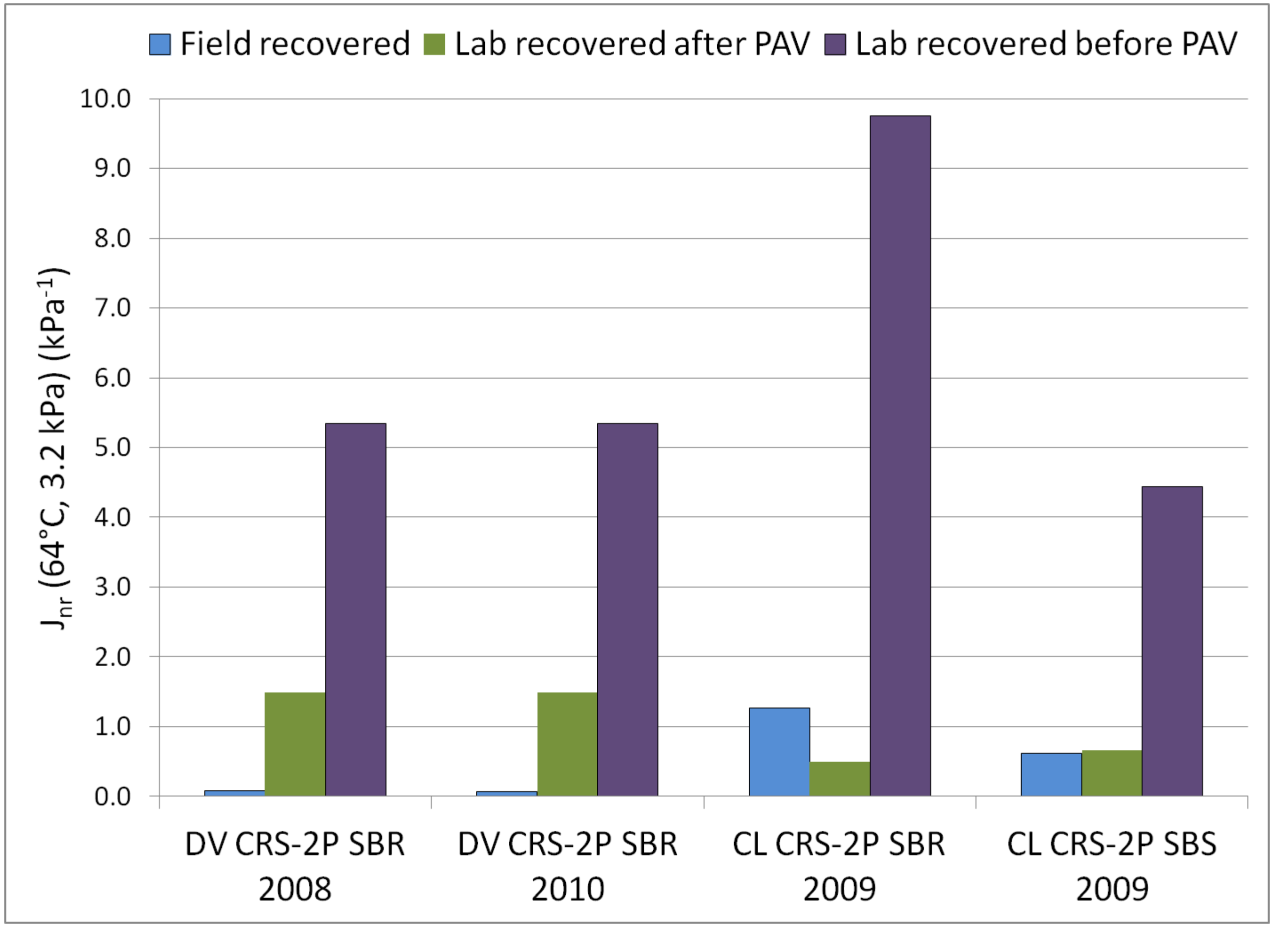


Original residues
PG 67 at 1.0kPa

Aged recovered residues high T:
- PG increase
- About 100C at 1 kPa
- 85 to 95C at 2.2 kPa
    - More relevant?

Recovered Residue DSR High Temperature - MSCRT



- DV – Death Valley and Cl – Crater Lake
- Lab recovery – low temperature evaporative, Standard PAV,
- Field recovered toluene extraction

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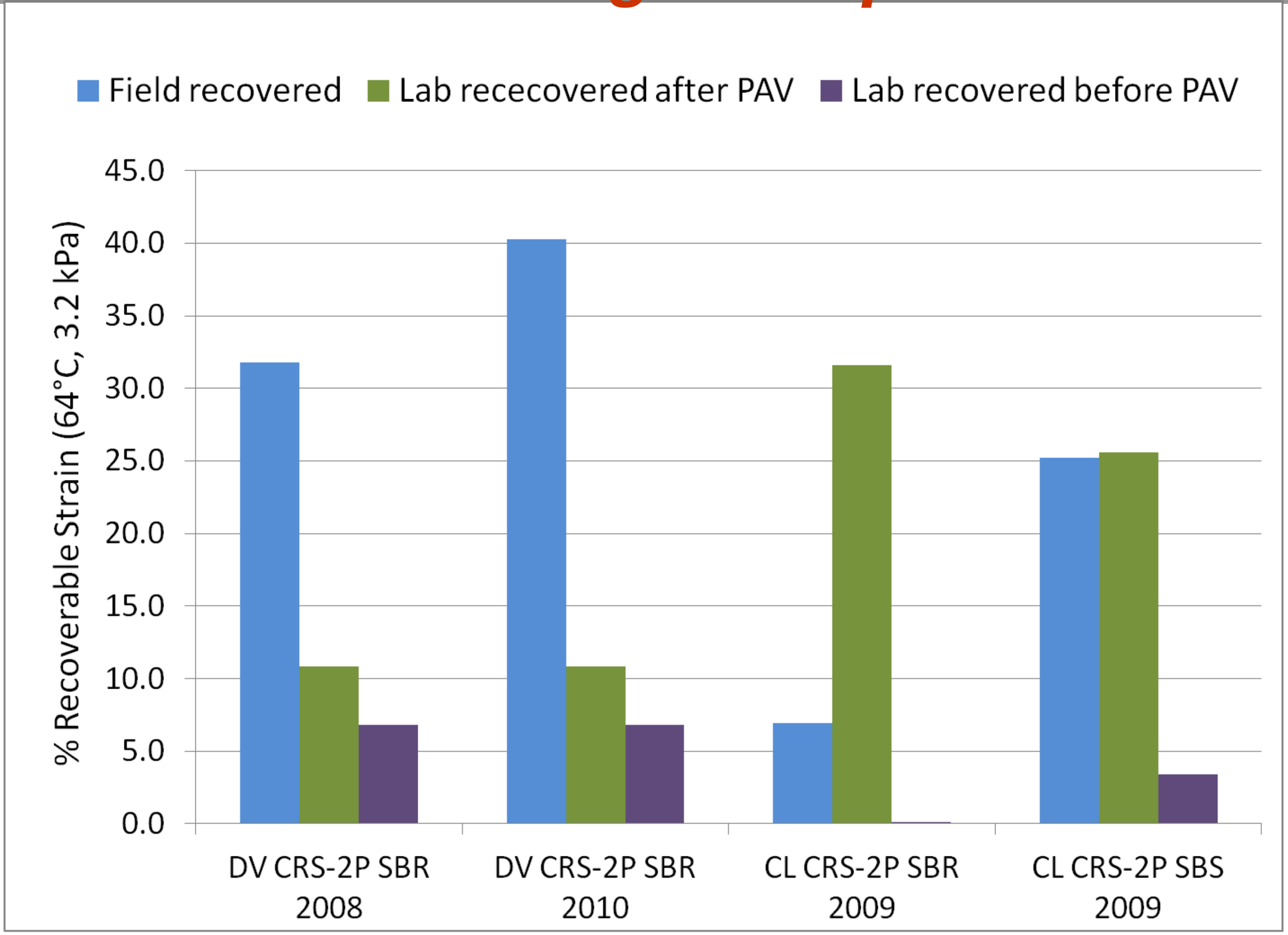
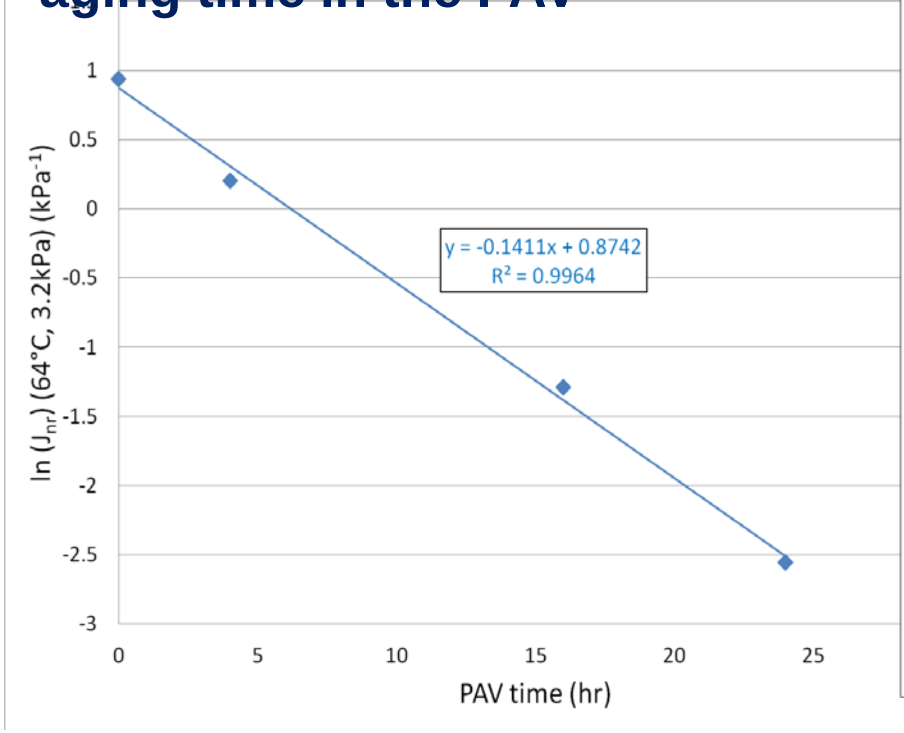
Recovered Residue DSR High Temperature - MSCRT

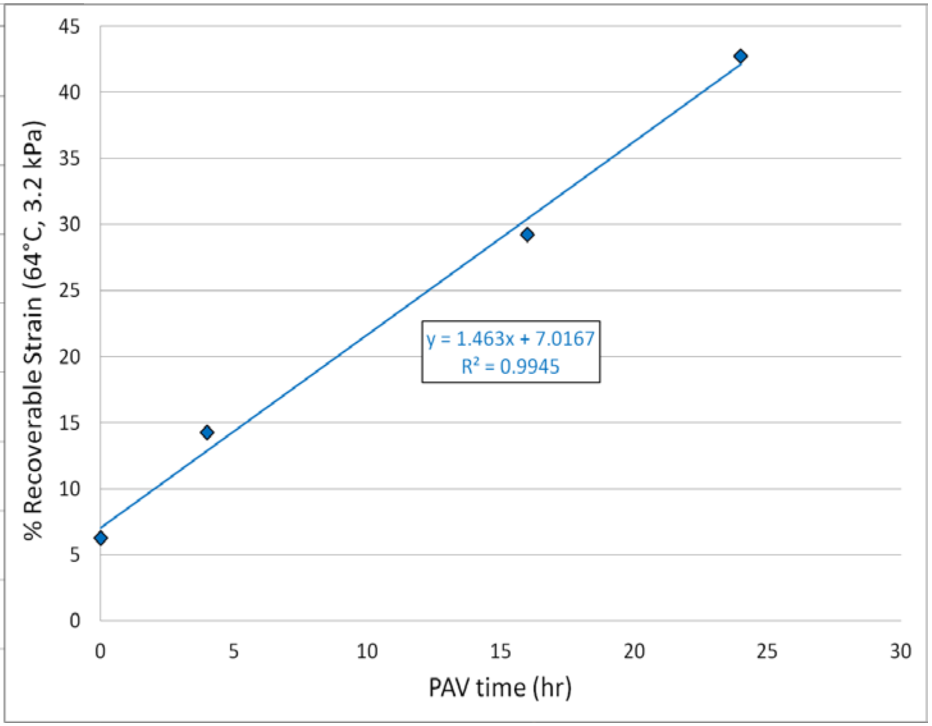


- •DV – Death Valley and Cl – Crater Lake
- •Lab recovery – low temperature evaporative, Standard PAV,
- •Field recovered toluene extraction

MSCRT properties to assess aging time (1/3)

Preliminary ! Jnr decreases log-linearly as a function of aging time in the PAV

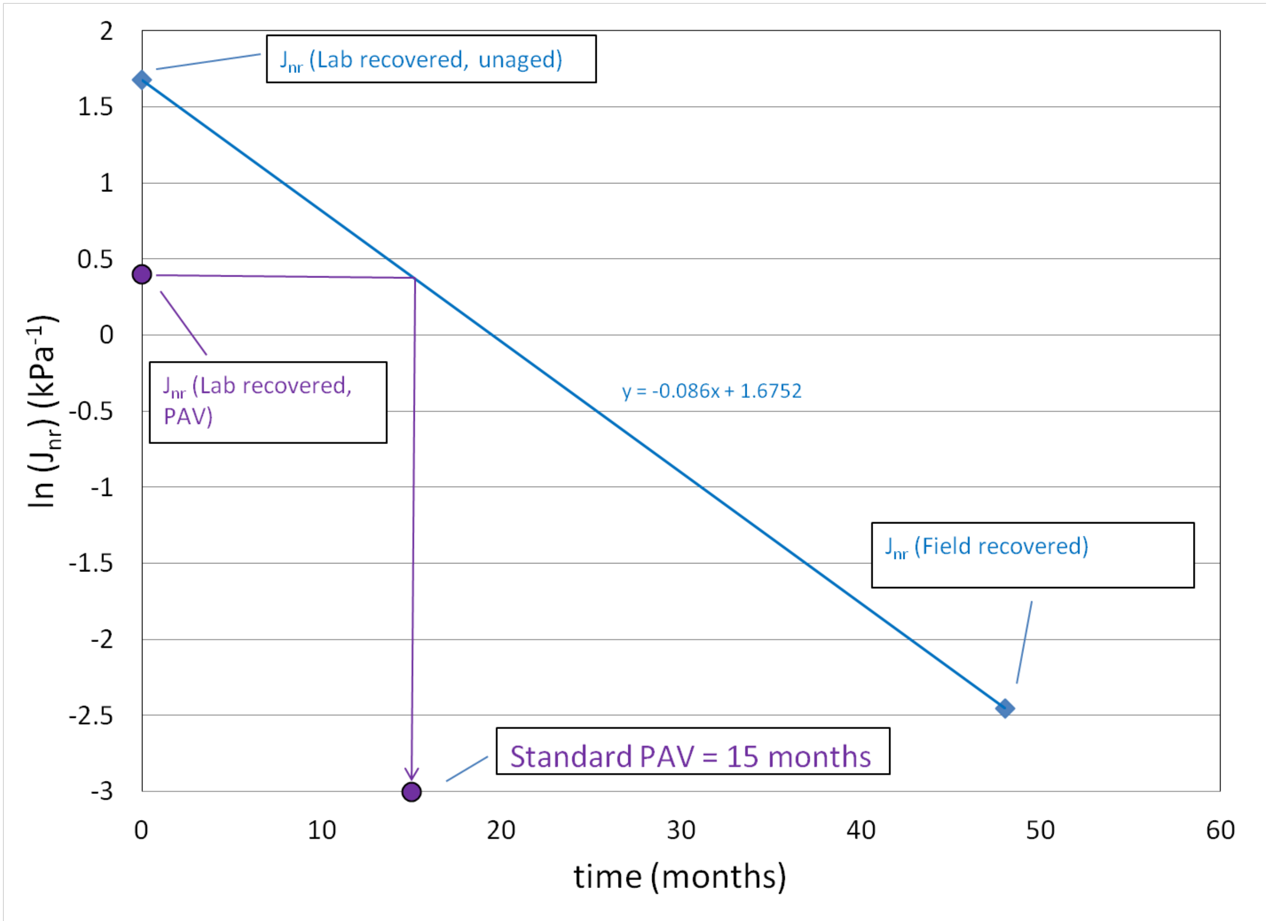




- Yellowstone NP, SBS modified Asphalt
- USAT short term aging (50C, 50 min) = time 0
- Then USAT PAV aging (100C, 300 psi) up to 24hrs

MSCRT properties to assess aging time (2/3)

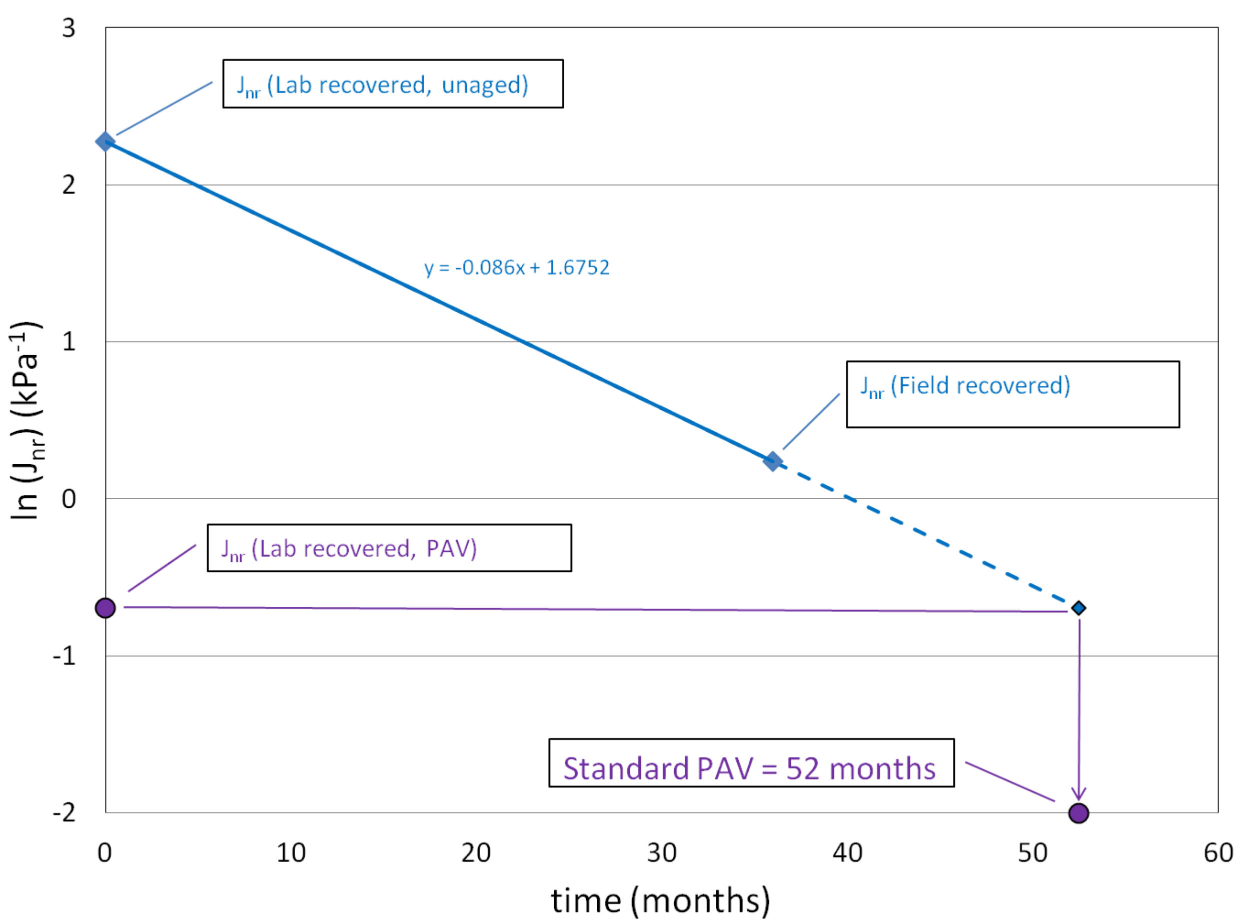
Preliminary !



- Death Valley 2008 SBR Latex,
- Lab recovery – low temperature evaporative
- Standard PAV

MSCRT properties to assess aging time (3/3)

Preliminary !



- Crater Lake 2009 SBR Latex,
- Lab recovery – low temperature evaporative
- Standard PAV

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Chip Seal Field Survey Summary & Next steps

- Successful collection of emulsion residues from chip seal projects - No contamination with the underlying pavement
- First analyses (IR, GPC) show SBR still present after some years - AFM can capture the latex honeycomb (aging effect?)
- Rheological evaluation with 4 mm DSR and MSCRT, show huge field stiffening depending on climatic conditions (DV>>CL)
- Karl Fischer titration indicates the moisture content after recovery similar for the 3 methods evaluated
- **Next Steps**
    - Complete sample characterization
    - Evaluate the binder aging level by comparison with original binders, under various climatic conditions, and integrate the results in WRI aging model.
    - Participate in the Emulsion TF discussions on PG grading criteria for emulsion residues

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Conclusions

- **A lot is going on Asphalt Research at WRI**
  - Fundamental research, such as asphalt oxidation…
  - Applied research, very much highway industry oriented
    - RAP / RAS / Emulsions / Micro sampling and testing
  - Cross-fertilization with Heavy Oils analytical breakthrough
- **Stay tuned!** WRI papers and presentations at
  - Binder and Mix ETG
  - TRB 2013 papers
  - PARC 2013
  - ACS 2013
  - RILEM and ISAP 2013 conferences in Europe
  - … and ***this AMAP Annual Meeting!***

Thank you !

Summer 2013

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