Oxidation and Kinetics of Aging in Asphalt Binders *(and so what?)*

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

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Presentation Overview

- Oxidation *kinetics* – fast-rate and constant-rate
- Oxygen *diffusivity* in binders and mastics
- Binder *rheology*: hardening due to oxidation
- *Mixture* hardening and changes to fatigue resistance due to oxidation
- *Modeling* oxidation and hardening in pavements
- References

Oxidation Kinetics

Asphalt Oxidation Kinetics - Our Laboratory -

Previous work: Constant-rate oxidation kinetics

Lau, C. K., K. M. Lunsford, C. J. Glover, R. R. Davison, and J. A. Bullin, "Reaction Rates and Hardening Susceptibilities as Determined from POV Aging of Asphalts," Transp. Res. Rec., 1342, 50-57 (1992).

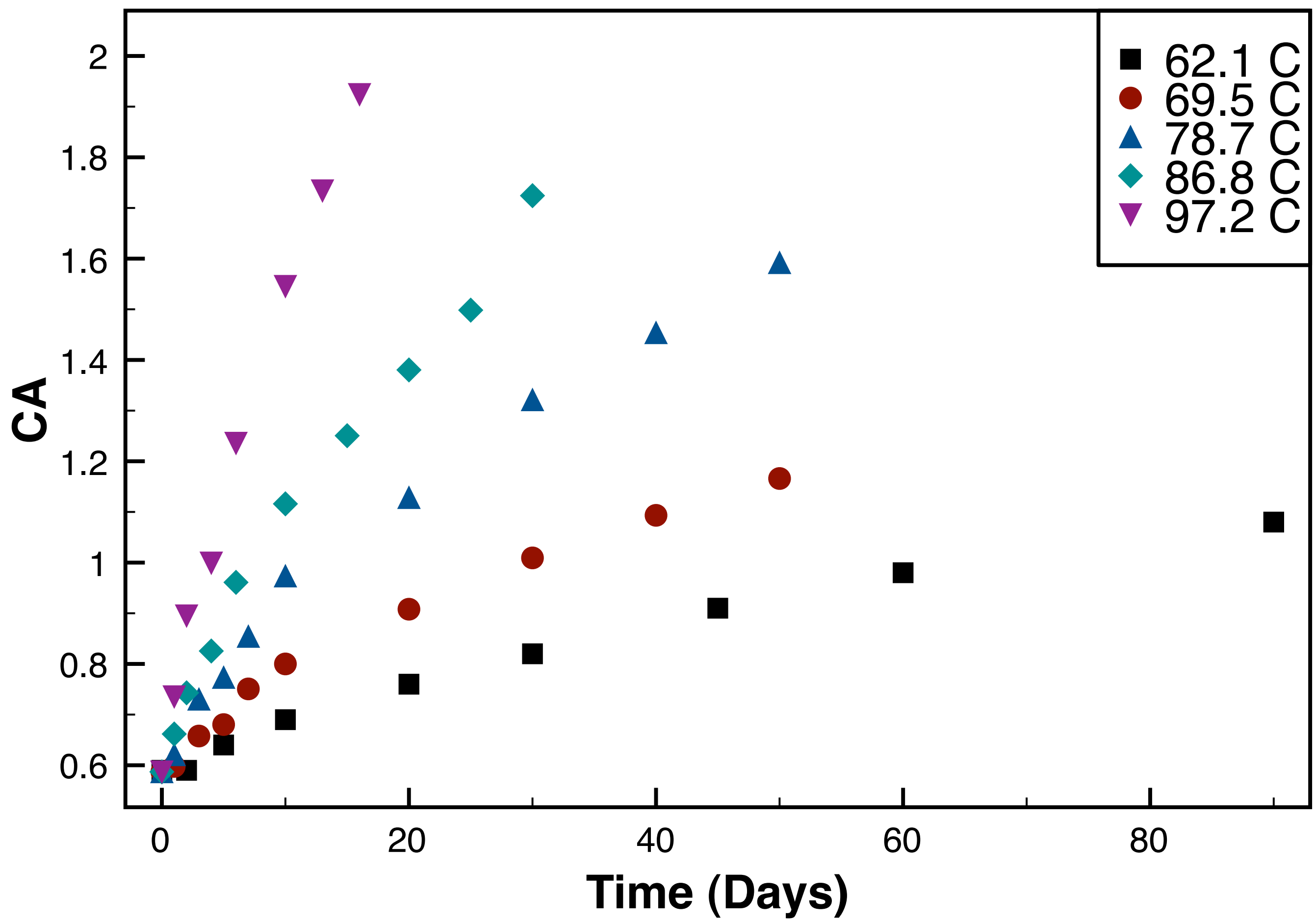
Liu, M., K.M. Lunsford, R.R. Davison, C.J. Glover and J.A. Bullin, "The Kinetics of Carbonyl Formation in Asphalt," AIChE J., 42(4), 1069-1076 (1996). *(Includes pressure effects)*

Domke, C.H., Davison, R.R. and Glover, C.J., "Effect of Oxygen Pressure on Asphalt Oxidation Kinetics," Ind. Eng. Chem. Res., 39(3), 592-598 (2000).

Recent work: Fast-rate; constant-rate oxidation kinetics

Xin Jin, et al., Petersen Asphalt Research Conference

Alon PG64-22
Aged in Air Pressure



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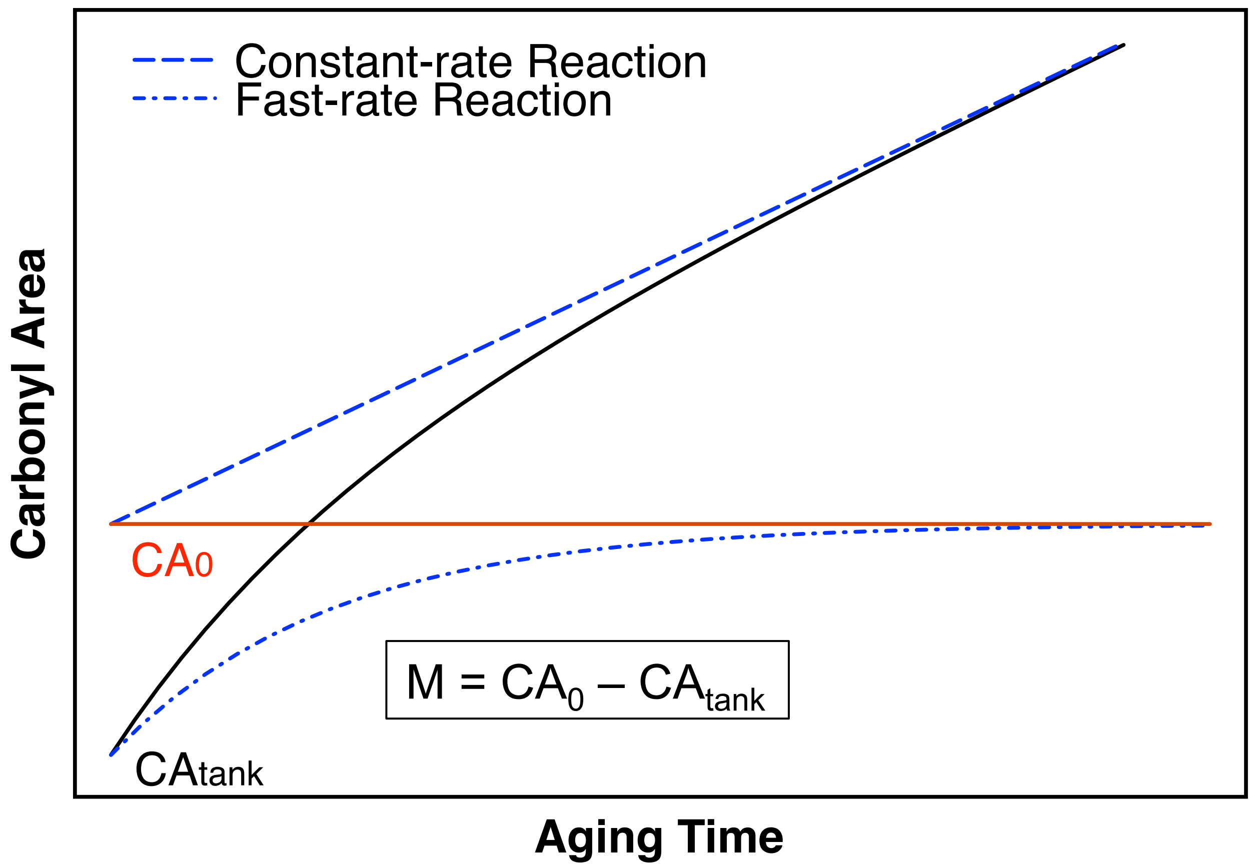
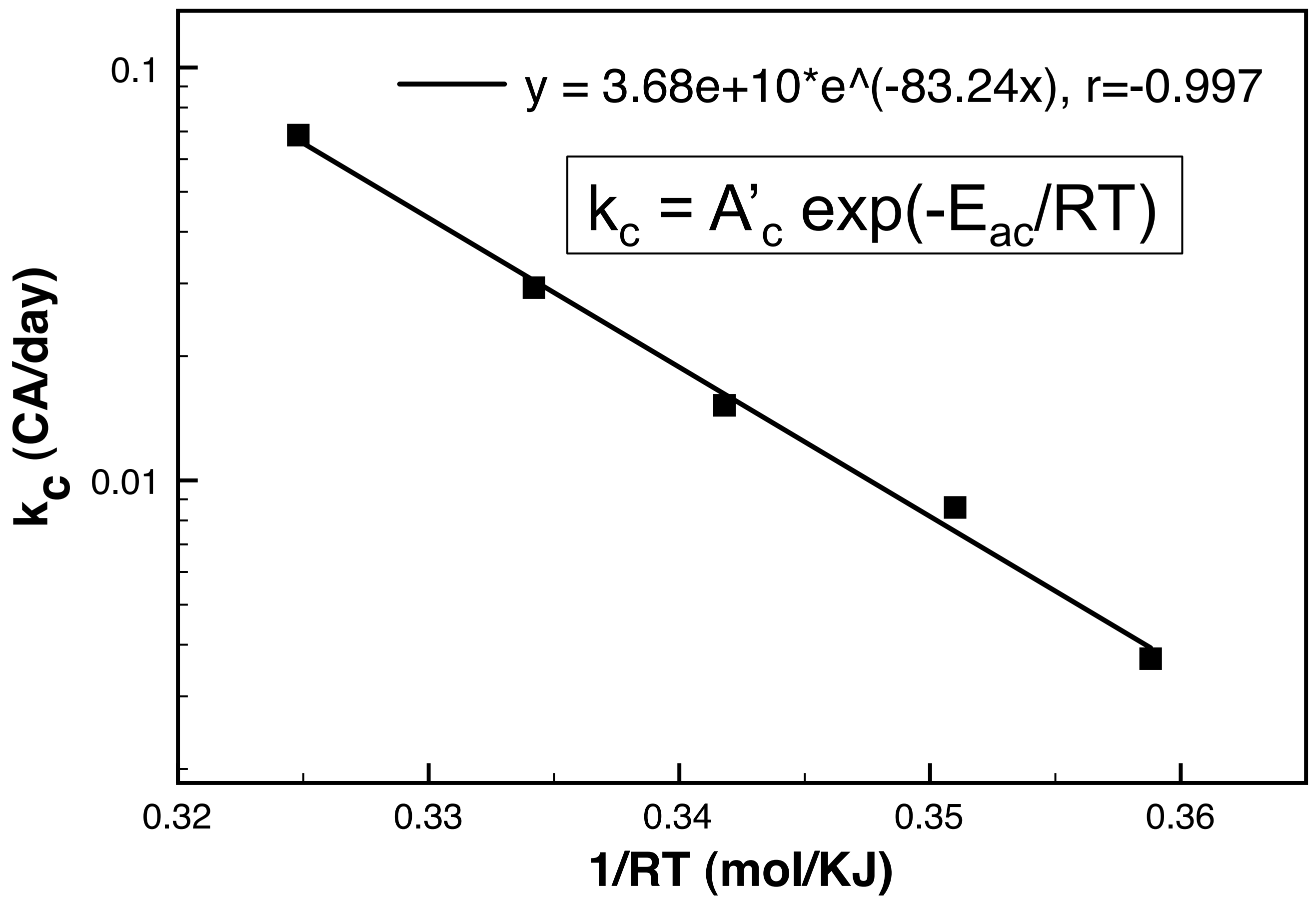
Fast-rate – Constant-rate Kinetics Model

Hypothetical parallel-reaction model in terms of CA:

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



Constant-rate Reaction Kinetics



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

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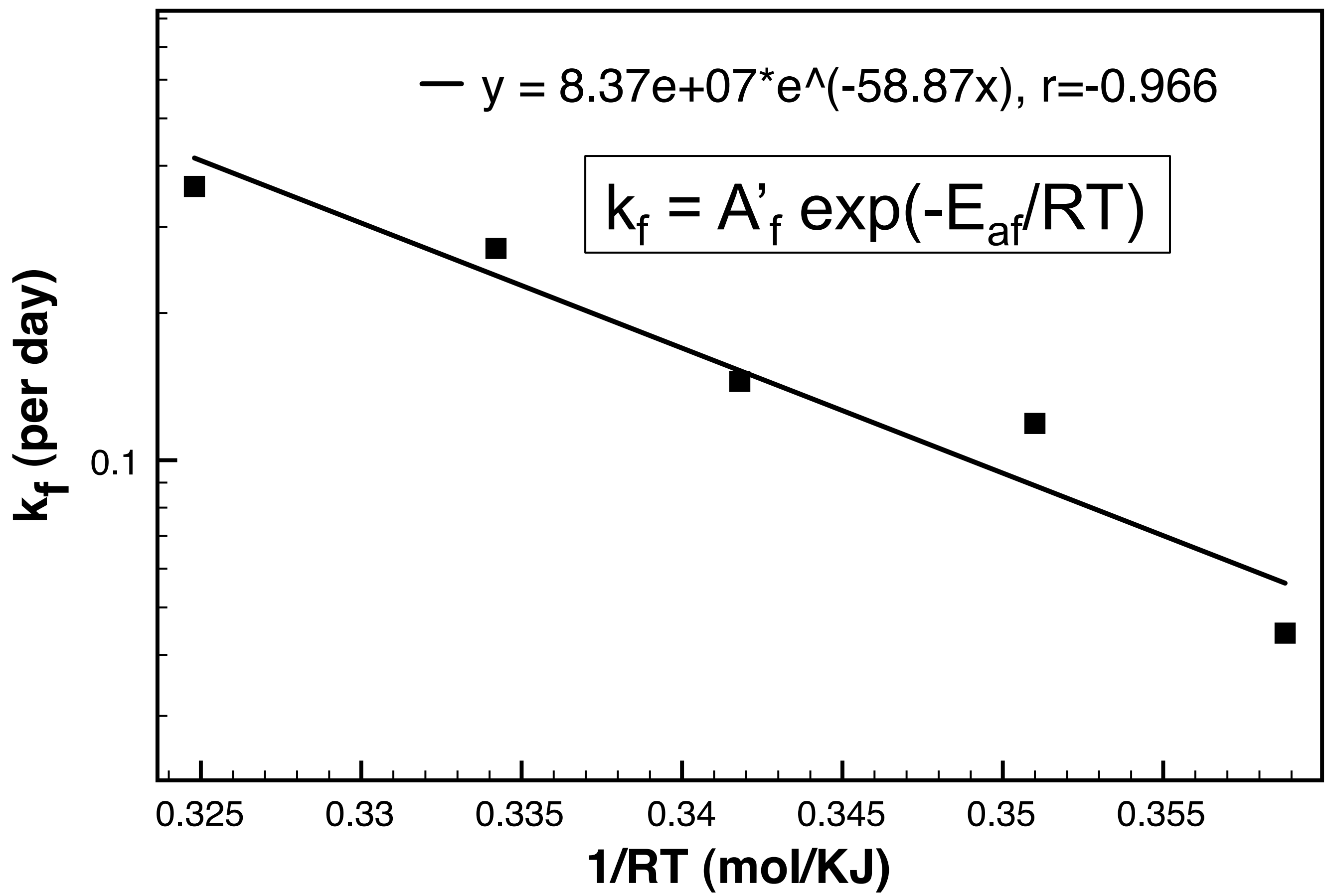
Fast-rate Reaction Kinetics



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

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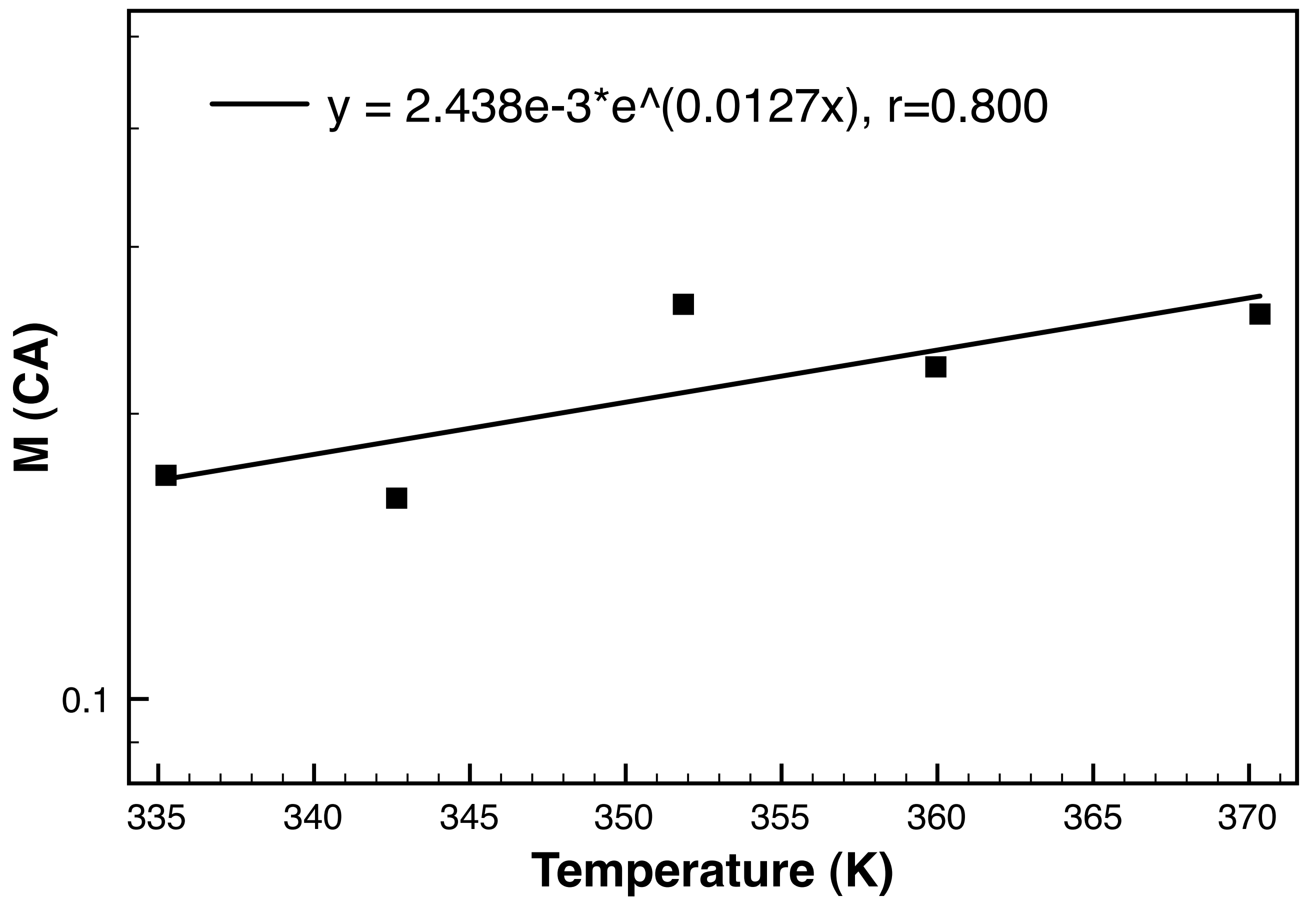
Fast-rate Reaction Kinetics



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

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How well does the model work?

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

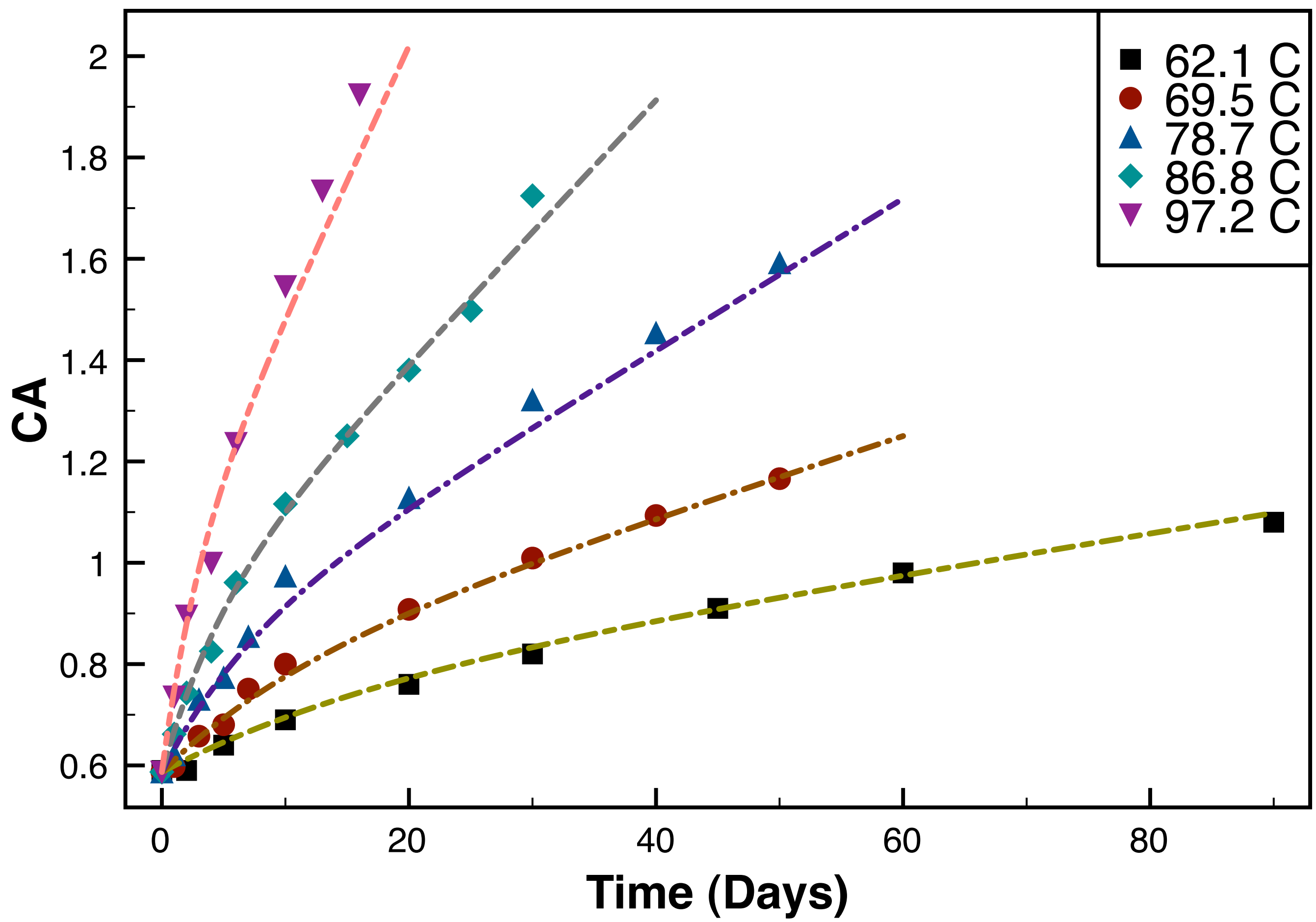

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Table of Kinetics Parameters

	Constant Rate Kinetics		Fast Rate Kinetics	
Binders	A'_c (CA/day)	E_{ac} (KJ/mol)	A'_f (1/day)	E_{af} (KJ/mol)
SEM PG64-22	2.15E+08	68.4	7.97E+05	43.5
SEM PG70-22	9.51E+09	79.4	3.61E+06	48.1
MARTIN PG64-22	9.30E+08	72.2	2.07E+07	52.7
MARTIN PG70-22	2.05E+11	87.7	1.21E+07	58.7
ALON PG64-22	3.68E+10	83.2	8.37E+07	58.9
ALON PG76-22	4.02E+09	77.0	3.07E+05	41.4
Valero-H PG64-22	7.91E+07	65.5		
Valero-H PG70-22	3.38E+07	62.7		
Lion PG70-22	4.77E+08	70.1		

What's The Point?

- With oxidation kinetics parameters known, together with *T(t)* and *P(t)*, one can calculate binder oxidation as a function of time.

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

$$k_f = A'_f \exp(-E_{af}/RT)$$

$$k_c = A'_c \exp(-E_{ac}/RT)$$

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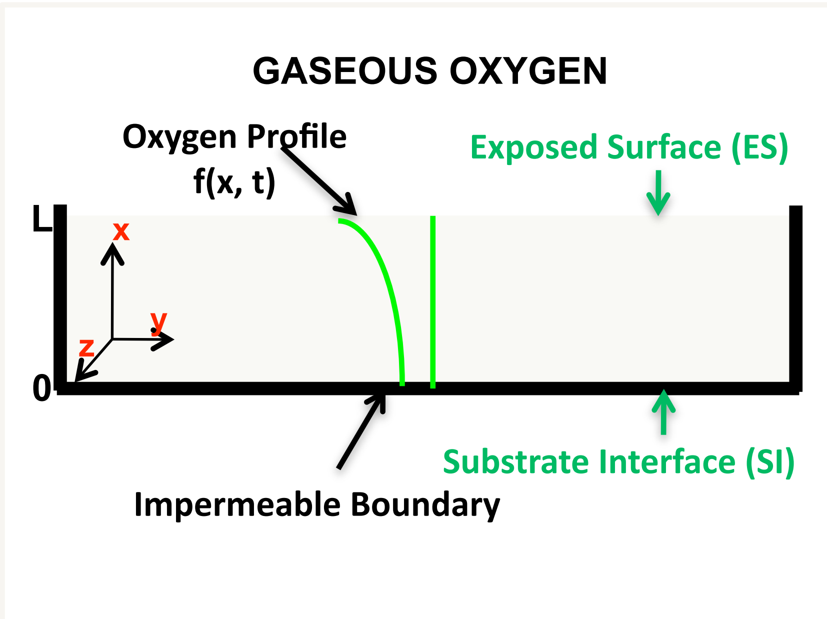
Oxygen Diffusivity in Asphalt

Thin Film Model

Model Concept and Mathematical Expression



Schematic of asphalt thin film model

Governing Equation

$$\frac{\partial P}{\partial t} = \left(\frac{\partial Do_2}{\partial x}\right)\left(\frac{\partial P}{\partial x}\right) + D_{O2}\left(\frac{\partial^2 P}{\partial x^2}\right) - \left(\frac{cRT}{h}\right) r_{CA}$$

$$r_{CA} = AP^{\alpha} e^{-E/RT}$$

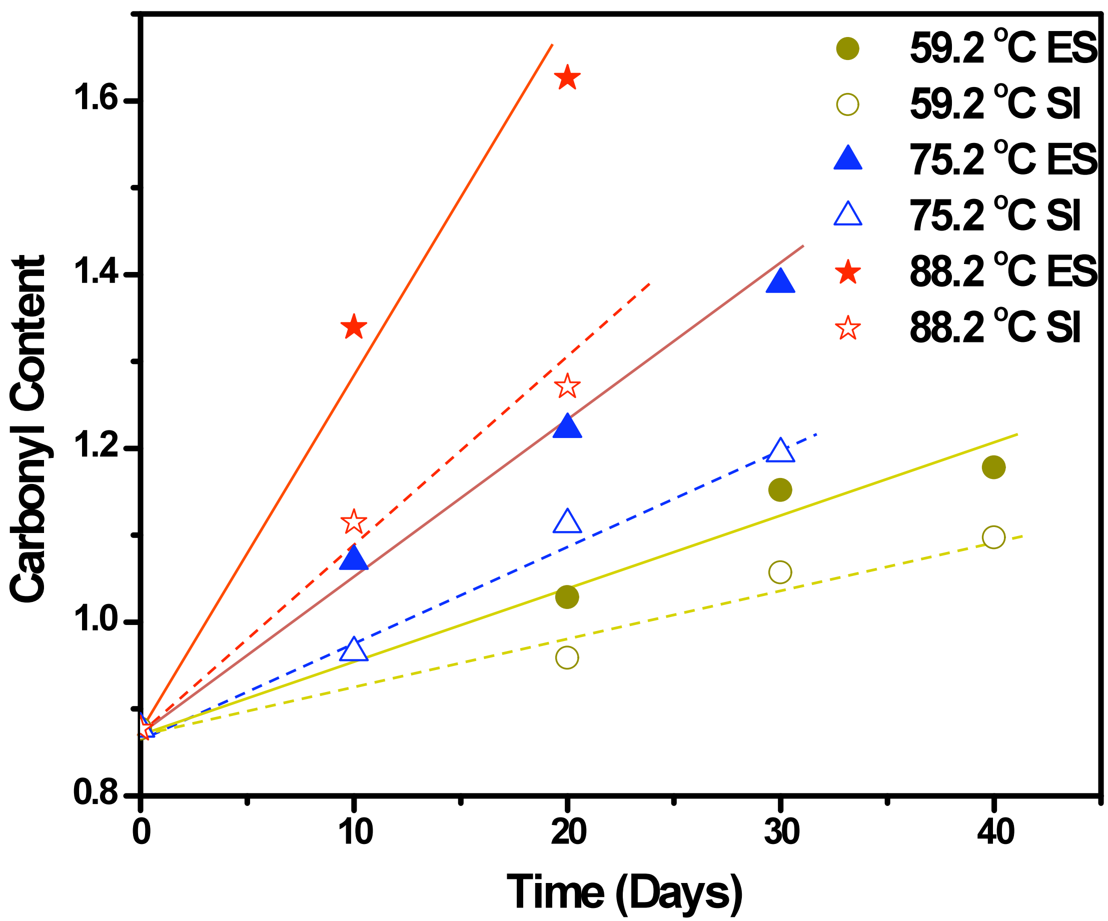
$$h = h_0(1 + 0.00215(T - T_r))$$

BCs & IC

$\left(\frac{\partial P}{\partial x}\right) = 0$	at x=0	**Substrate Interface**
$P = P_{gas}$	at x=L	**Exposed Surface**
$P = 0$	at t=0	**Initial Condition**

Thin Film Model

Calculation of a Value and Time for P_{SI}



P_{SI} Value

$$r_{CA} = AP^{\alpha} e^{-E/RT}$$

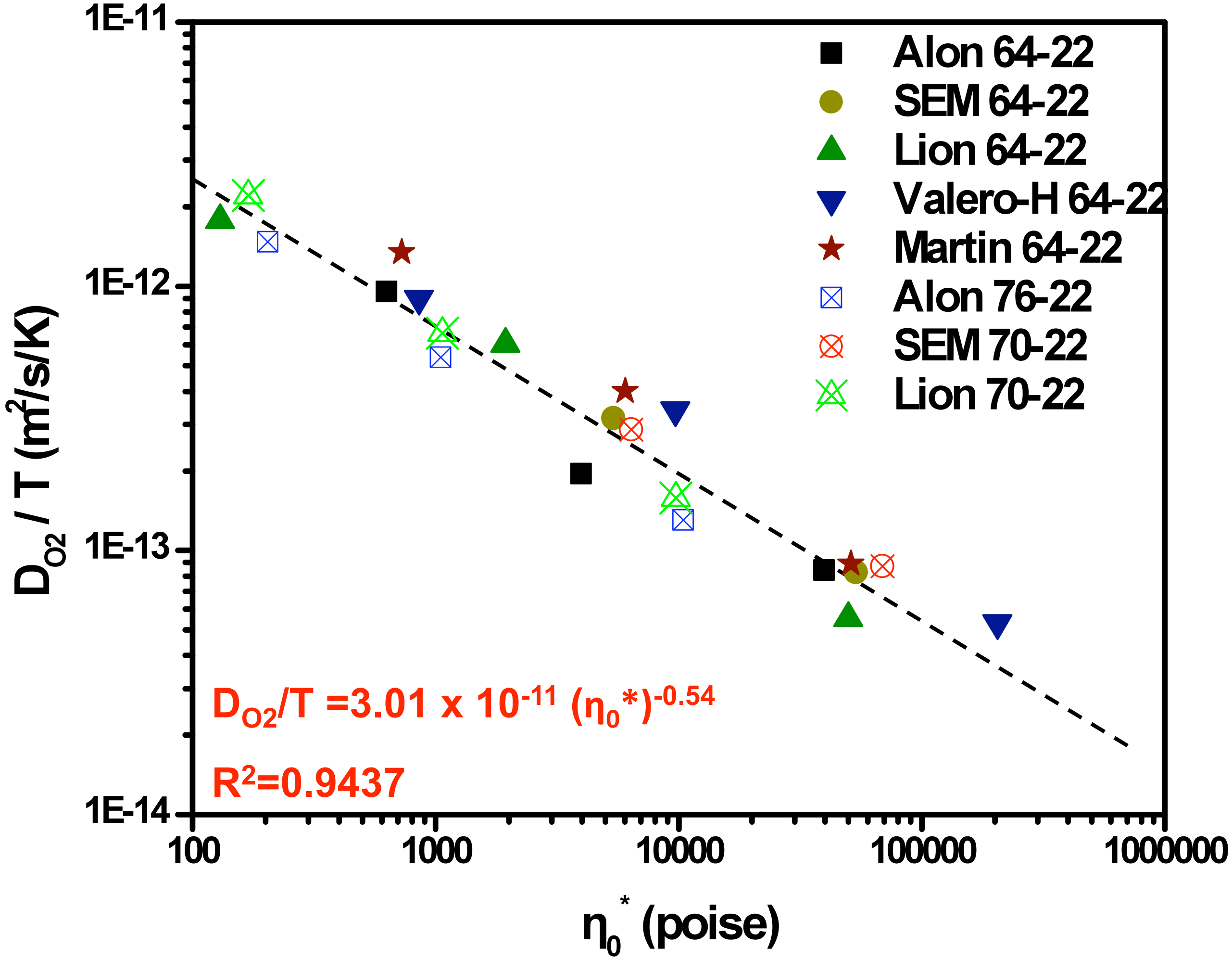
$$P_{SI} = P_{ES} \left(\frac{r_{SI}}{r_{ES}} \right)^{1/\alpha}$$

P_{SI} Time

Close to medium point of testing time

Values of D_{O2}

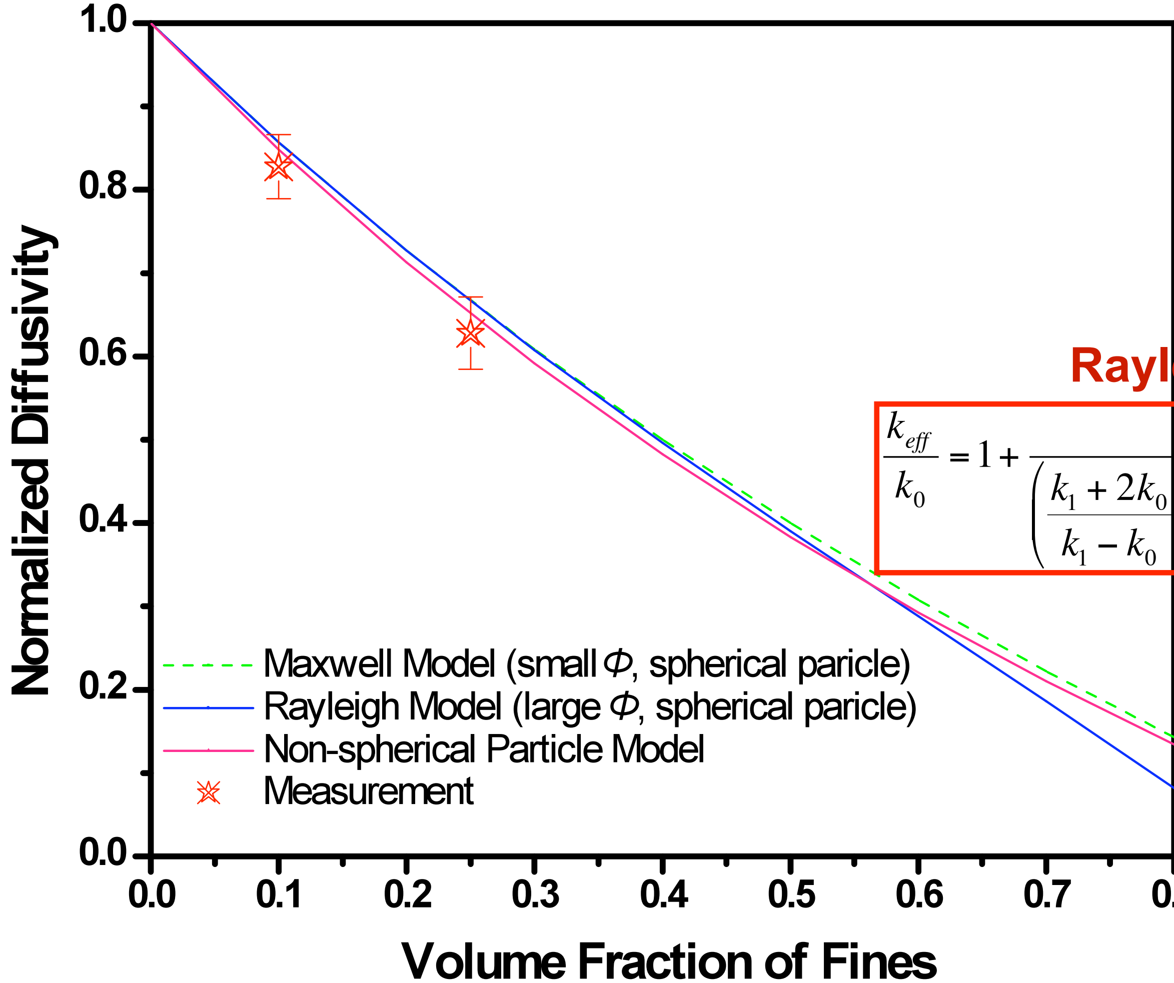
D_{O2}/T and (η_o*): Empirical Correlation



D_{O2} in Mastics

D_{O2} in Mastics

Effect of Φ of Aggregate Fines on D_{O2}



Maxwell Model

$$\frac{k_{eff}}{k_0} = 1 + \frac{3\phi}{\left(\frac{k_1 + 2k_0}{k_1 - k_0}\right) - \phi}$$

Rayleigh Model

$$\frac{k_{eff}}{k_0} = 1 + \frac{3\phi}{\left(\frac{k_1 + 2k_0}{k_1 - k_0}\right) - \phi + 1.569\left(\frac{k_1 - k_0}{3k_1 - 4k_0}\right)\phi^{10/3} + \bullet\bullet\bullet}$$

Non-spherical Model

$$\frac{k_{eff}}{k_0} = \frac{(1-\phi) + \alpha\phi(k_1 / k_0)}{(1-\phi) + \alpha\phi}$$

$$\alpha = \frac{1}{3}\sum_{k=1}^{3}\left[1 + \left(\frac{k_1}{k_0} - 1\right)g_k\right]^{-1}$$

Diffusivity Conclusions

- Oxygen diffusivity in asphalt materials is highly dependent on temperature and viscosity of asphalt; A correlation was established between log D_{o2}/T and log (η_0^*).

- Oxygen diffusivity in mastics decreases with an increase of volume fraction of aggregate fines; this effect of fines on oxygen diffusivity can be estimated using conventional prediction models

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Effects of Oxidation on Asphalt Rheology

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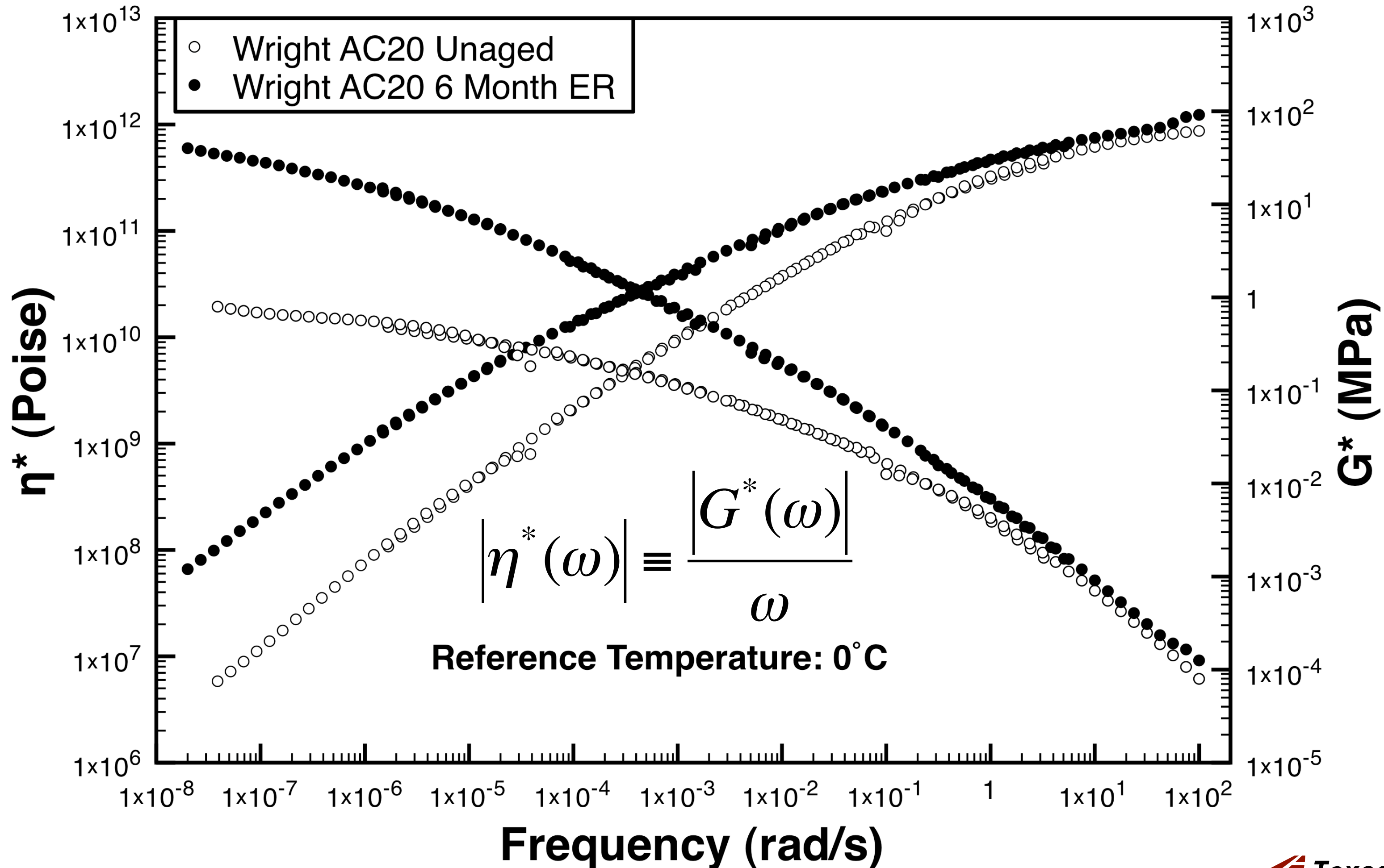
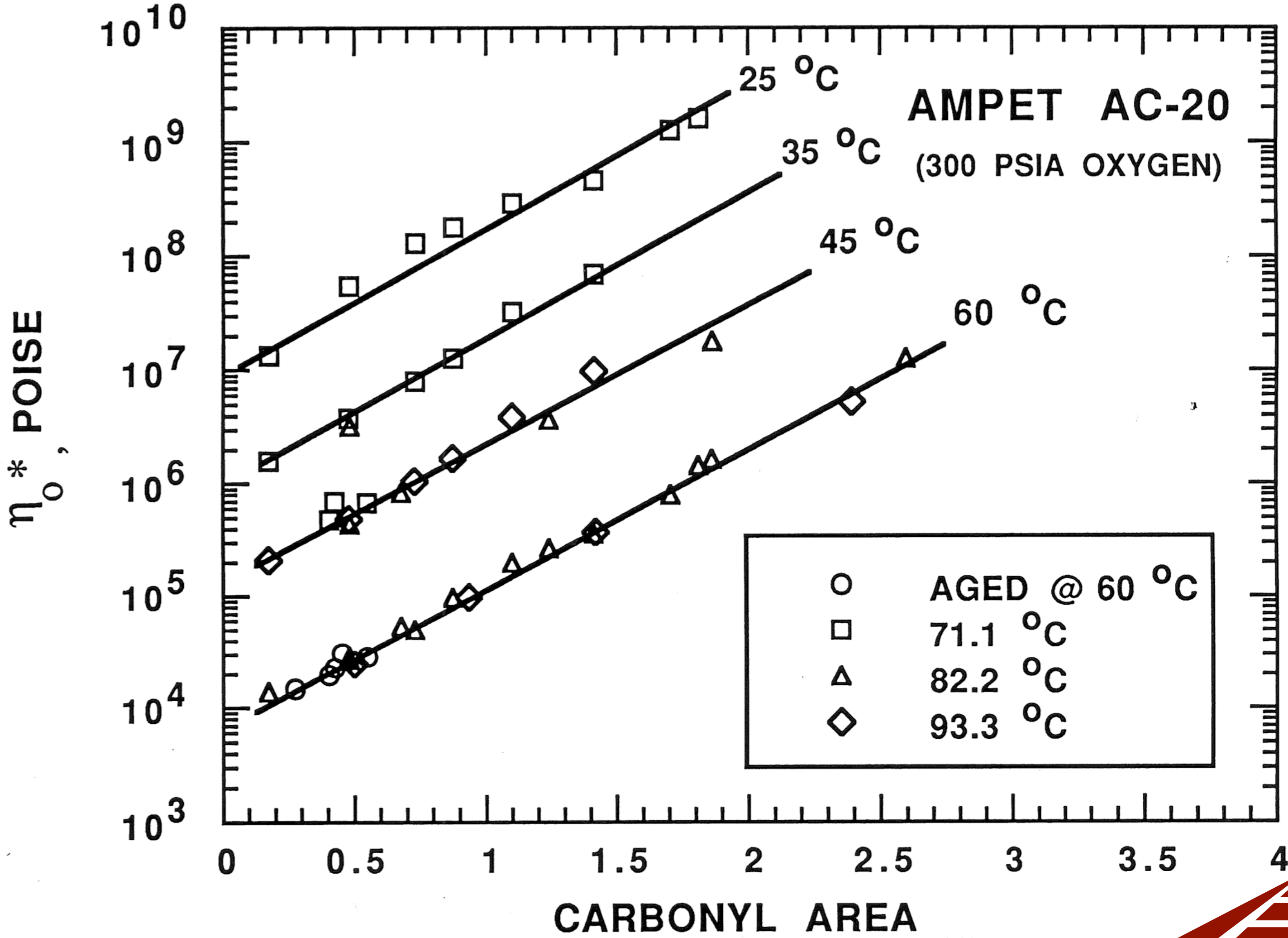
Asphalt Master Curves



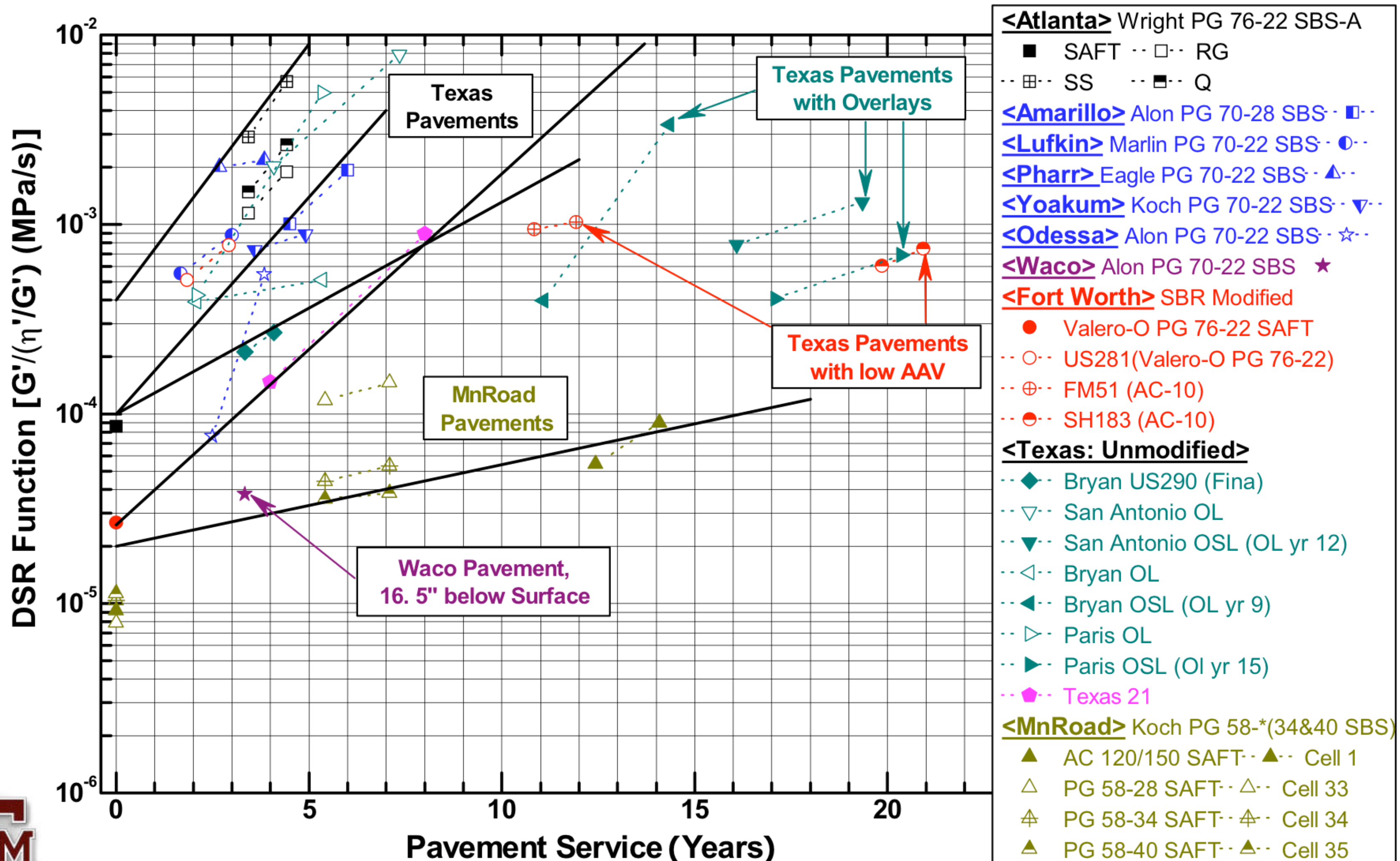
Ruan, PhD Dissertation, data from Figs V-1, V-5 (2002)

Hardening Susceptibility



Lau et al., TRR 1342, 50-57 (1992)

Field Binder Aging



Woo et al., FHWA/TX-07/0-4688-1, 5-38 (2007)

So what? Pavement Performance Depends upon:

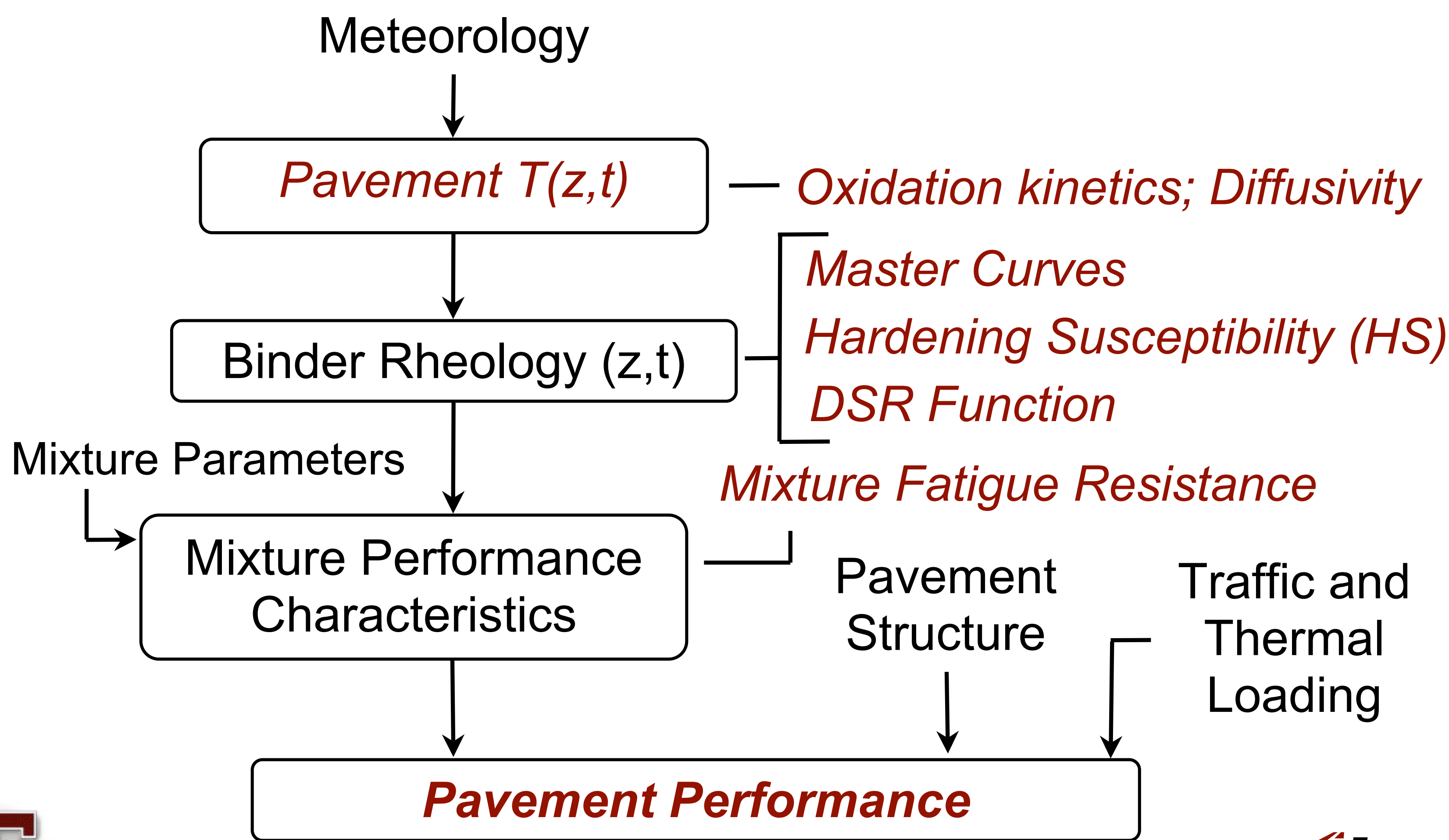
- Pavement Structure
- Mixture Parameters:
  - Aggregate type/gradation
  - Binder Content
  - Compaction
- Traffic Loading
- Thermal Loading

Cont'd…

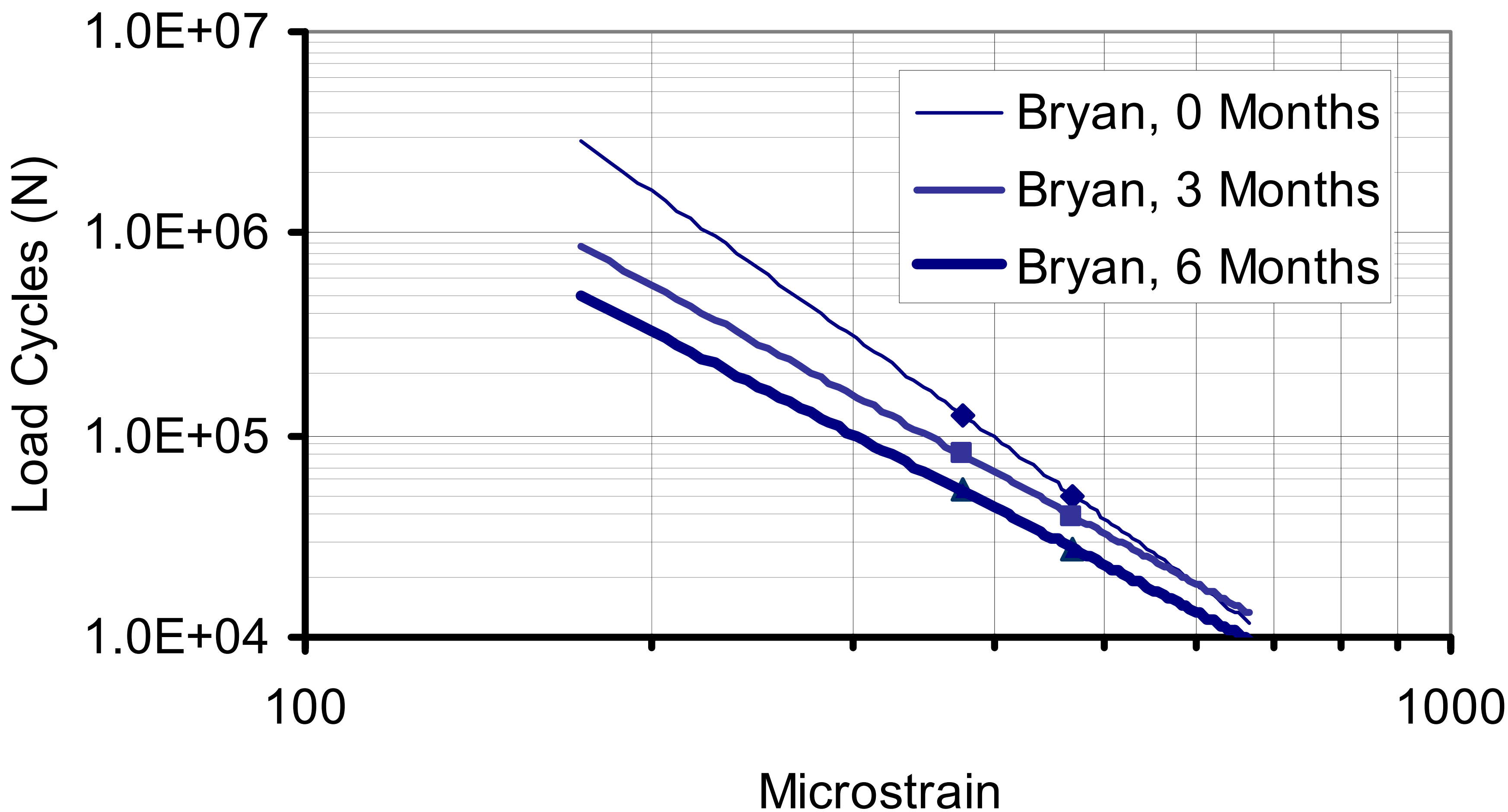
Pavement Performance Depends upon:

- Binder Properties
  - Rheology
    - Temperature – TTS shift factor
    - Oxidation
      - Hardening Susceptibility
      - Temperature
      - Diffusivity
  - Water Susceptibility
  - Healing

Pavement Performance Depends upon:



Mixture BB Fatigue Cycles-to-Failure vs Strain



Walubita et al., FHWA/TX-05/0-4468-2, 169 (2005)

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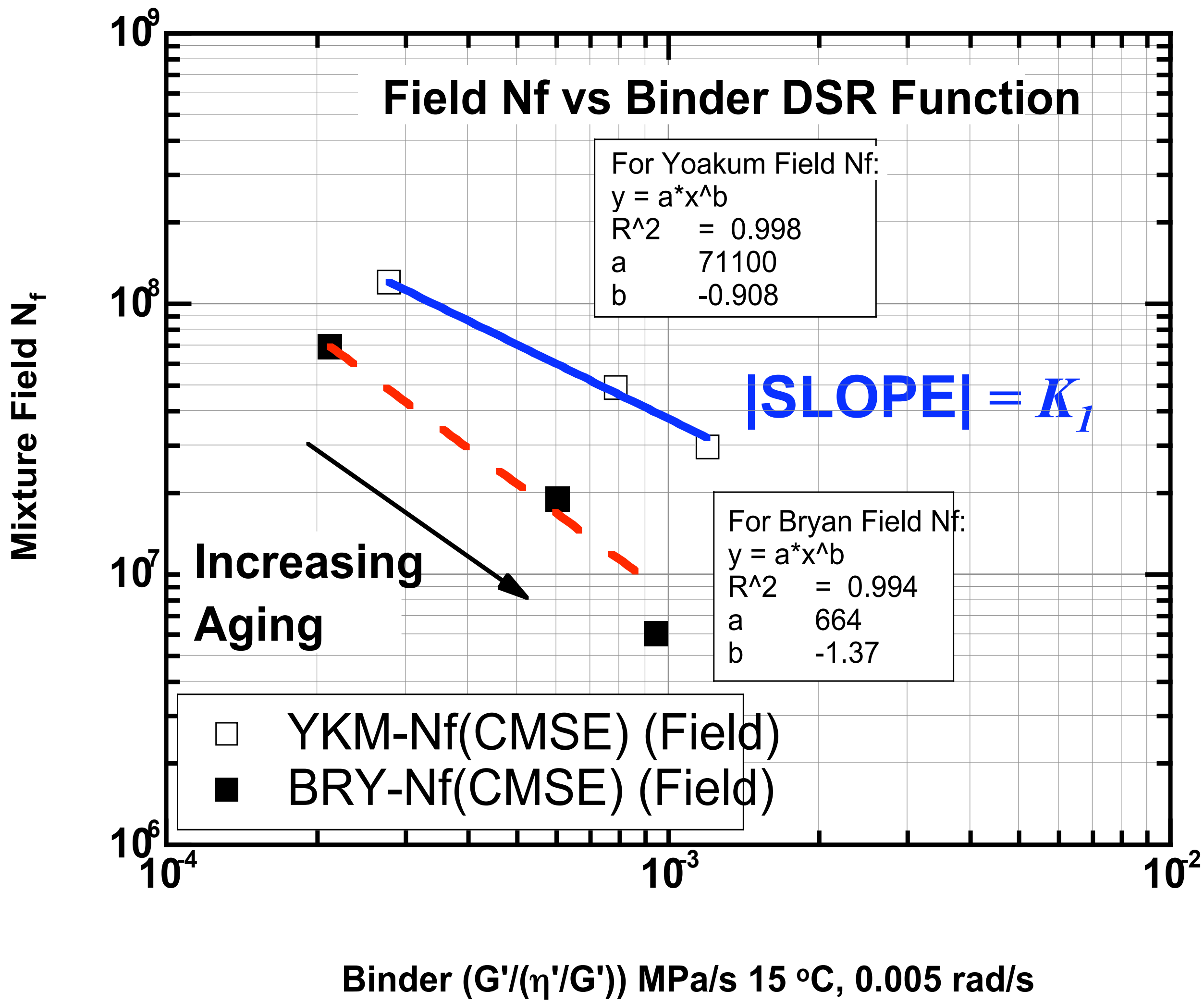
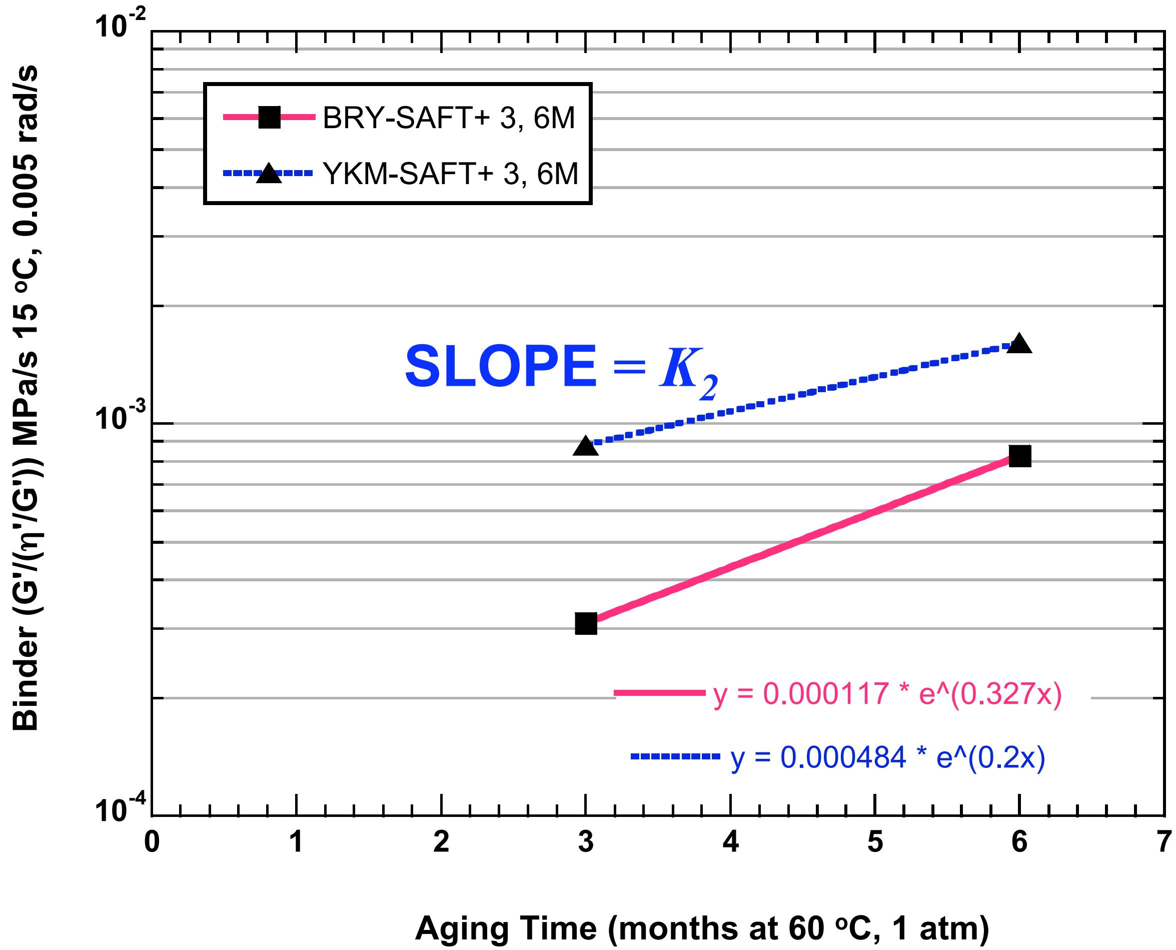
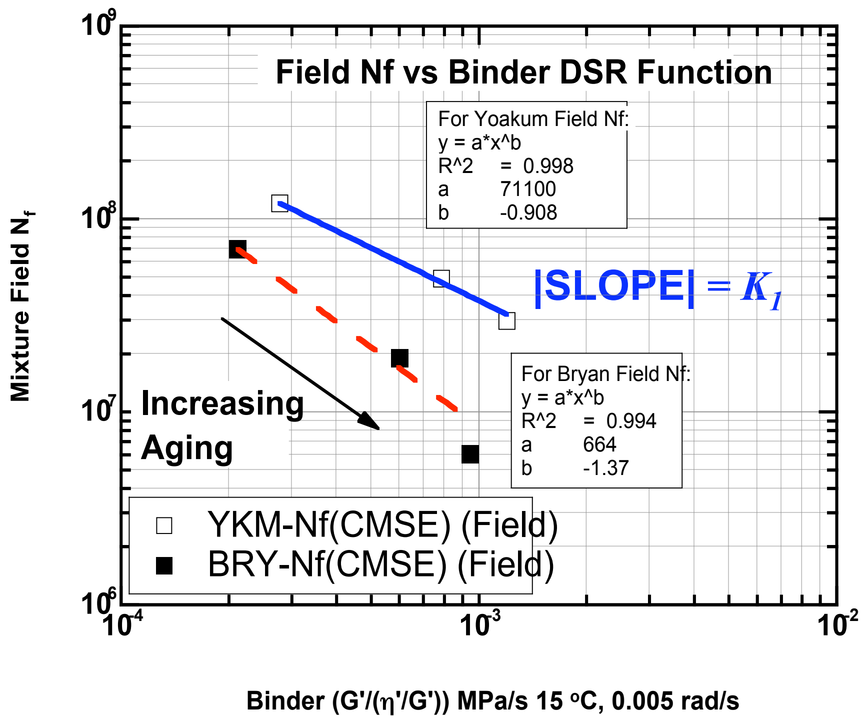
Mixture Fatigue

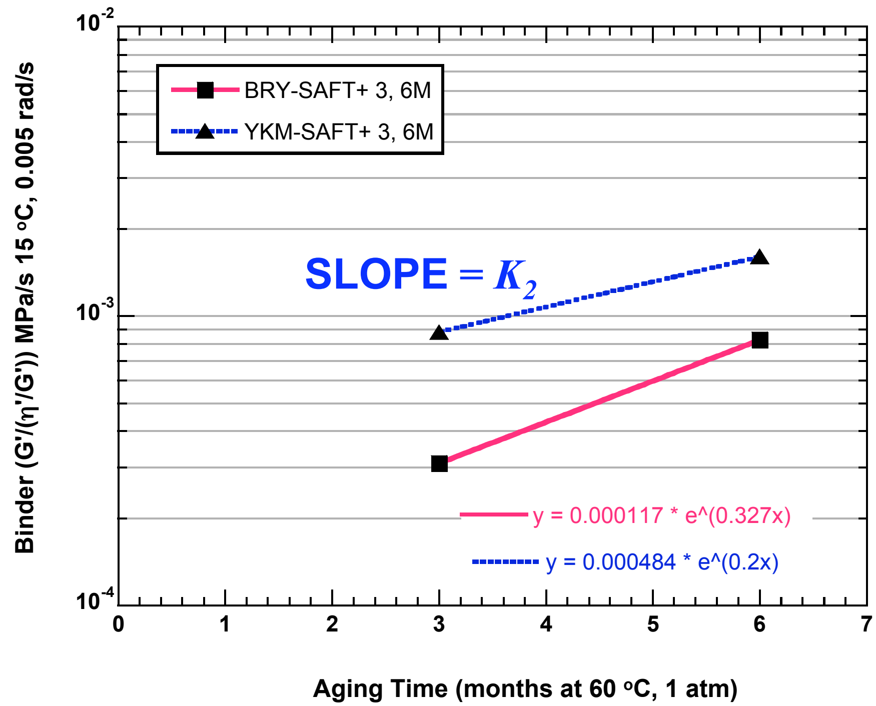


Mixture Fatigue



Fatigue Life
Decline With Aging





$$N_f(t) = N_{f0} e^{-K_1 K_2 t}$$

FATIGUE LIFE

DEFINITIONS

$$N_f = \text{Field Fatigue Life - Cycles, ESALs}$$

$$R_L = \text{Pavement Loading Rate, ESALs/yr}$$

FOR CONSTANT N_f

$$N_f \;/\; R_L = \text{Field Fatigue Life - Time, years}$$

Fatigue Life

FOR $N_f(t)$ A FUNCTION OF TIME:

$$\text{Fraction of Life Expended During Time } dt = \frac{dt}{N_f(t)\ /\ R_L}$$

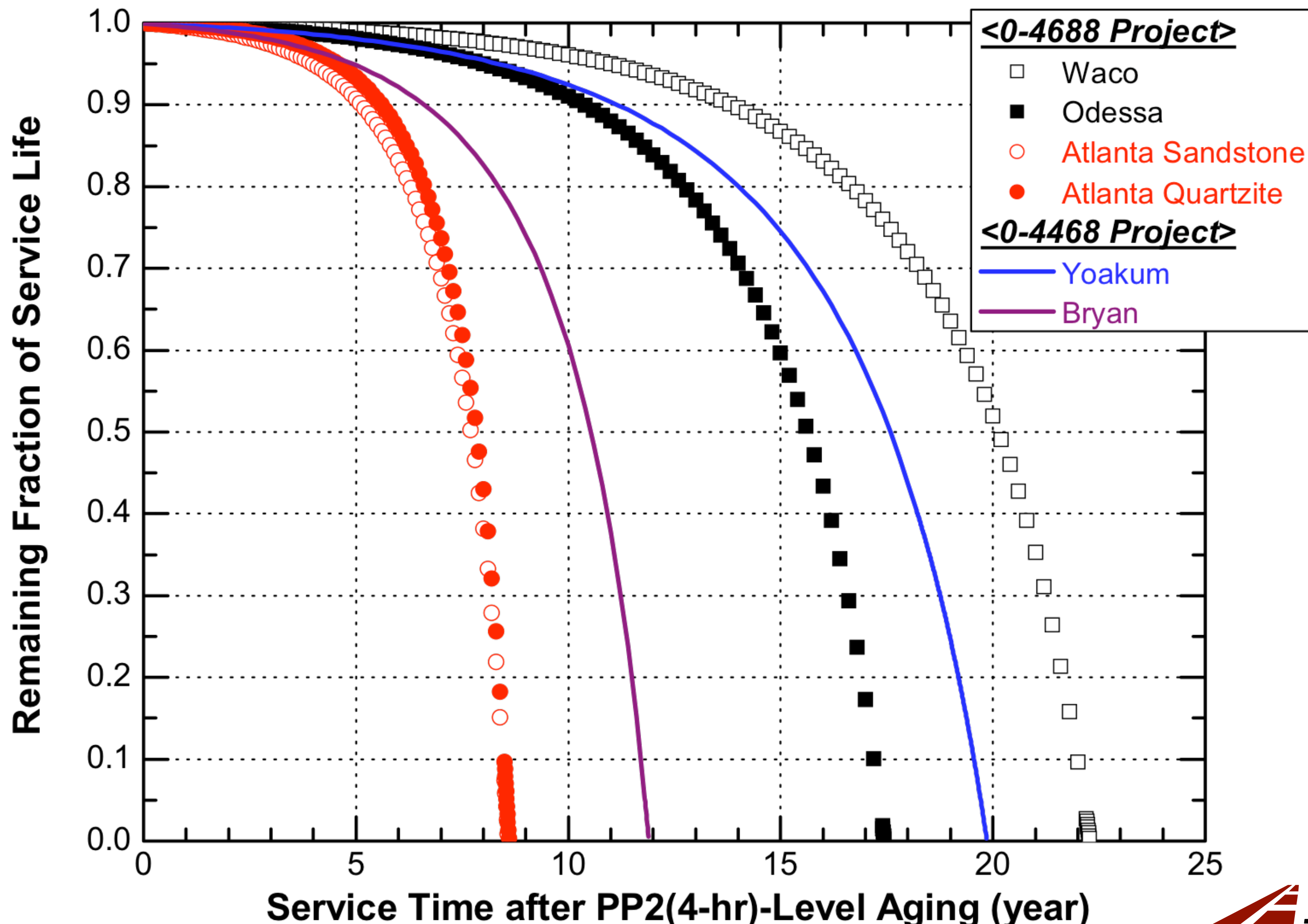
CUMMULATIVE DAMAGE:

$$\text{At life's end, fractions sum to 1:} \quad \int_0^{t_{\text{end}}} \frac{dt}{N_f(t)\ /\ R_L} = 1$$

$$N_f(t) = N_{fo} e^{-K_1 K_2 t}$$

$$t_{\text{end}} = \frac{\ln(K_1 K_2 N_{fo}\ /\ R_L + 1)}{K_1 K_2} = \text{Service Life}$$

Pavement Fatigue: Remaining Service Life



Woo et al., FHWA/TX-07/0-4688-1, 7-20 (2007)

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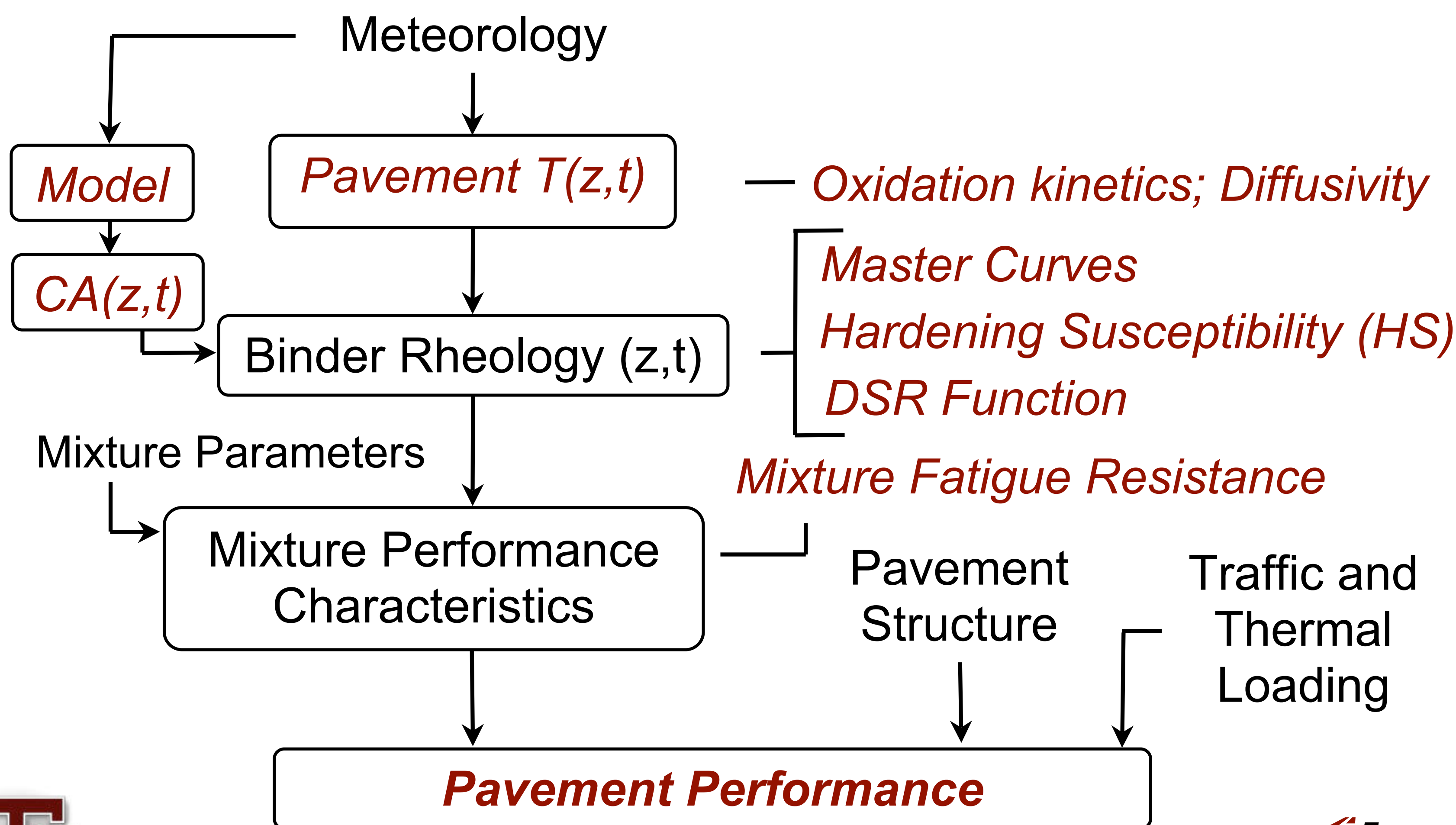
Pavement Performance Depends upon:



TRANSPORT MODEL CALCULATIONS OF BINDER HARDENING IN PAVEMENTS

- Calculation of hardening is based on fundamentals: oxidation kinetics, diffusivity, HS, DSRFn, master curves
- Oxygen in pavements appears to be ubiquitous – little evidence that oxygen supply to pavements is very restricted (tentative hypothesis); pores allow air permeation
- Includes effect of binder oxidative hardening on mixture properties, fatigue resistance decline, e.g.

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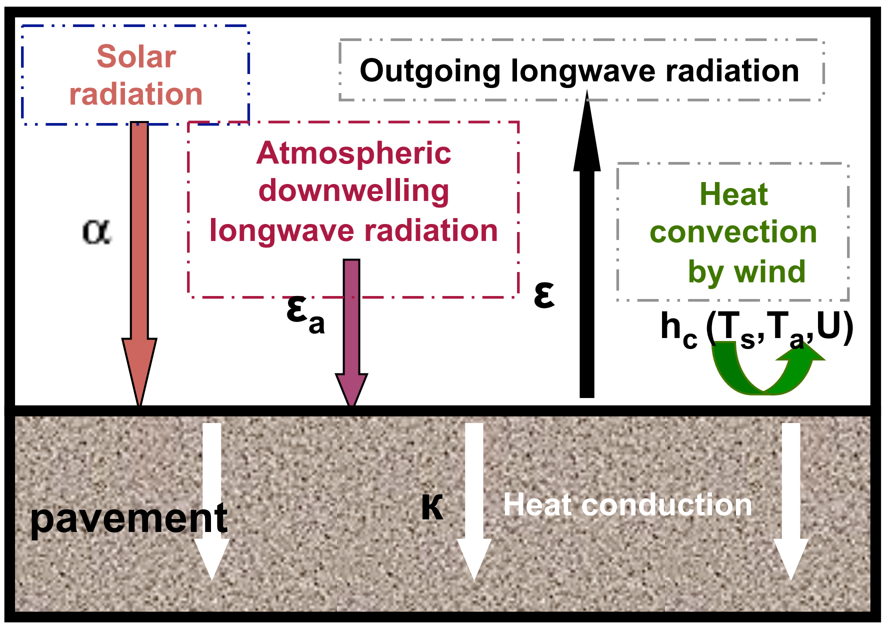
Thermal Transport

Temperature Modeling concept and mathematical expression

Modeling Concept



Mathematical Modeling

- **Surface Boundary Condition: Hourly Heat Flux Balance**

$$\rho C \frac{\Delta x}{2}\frac{\partial T_s}{\partial t} = (1-\alpha)q_s + \varepsilon_a \sigma T_a^4 - \varepsilon\sigma T_s^4 - h_c(T_s - T_a) + k\frac{\partial T_s}{\partial x}$$

α: Stefan-Boltzmannn constant; **T_s**: Surface temperature
ε: emissivity coefficient; **T_a**: Air temperature
ε_a: absorption coefficient; **q_s**: Solar radiation
h_c: heat convection coefficient; :Albedo

- **Heat Conduction inside Pavement**

$$\frac{\partial T}{\partial t} = \boxed{\frac{k}{\rho C}}\frac{\partial^2 T}{\partial x^2}$$

k: Thermal conductivity
ρ: Density
C: Heat capacity
Κ : Thermal diffusivity

- **Bottom Boundary Condition:** Depth Independent heat flux based on field measurement

THERMAL TRANSPORT

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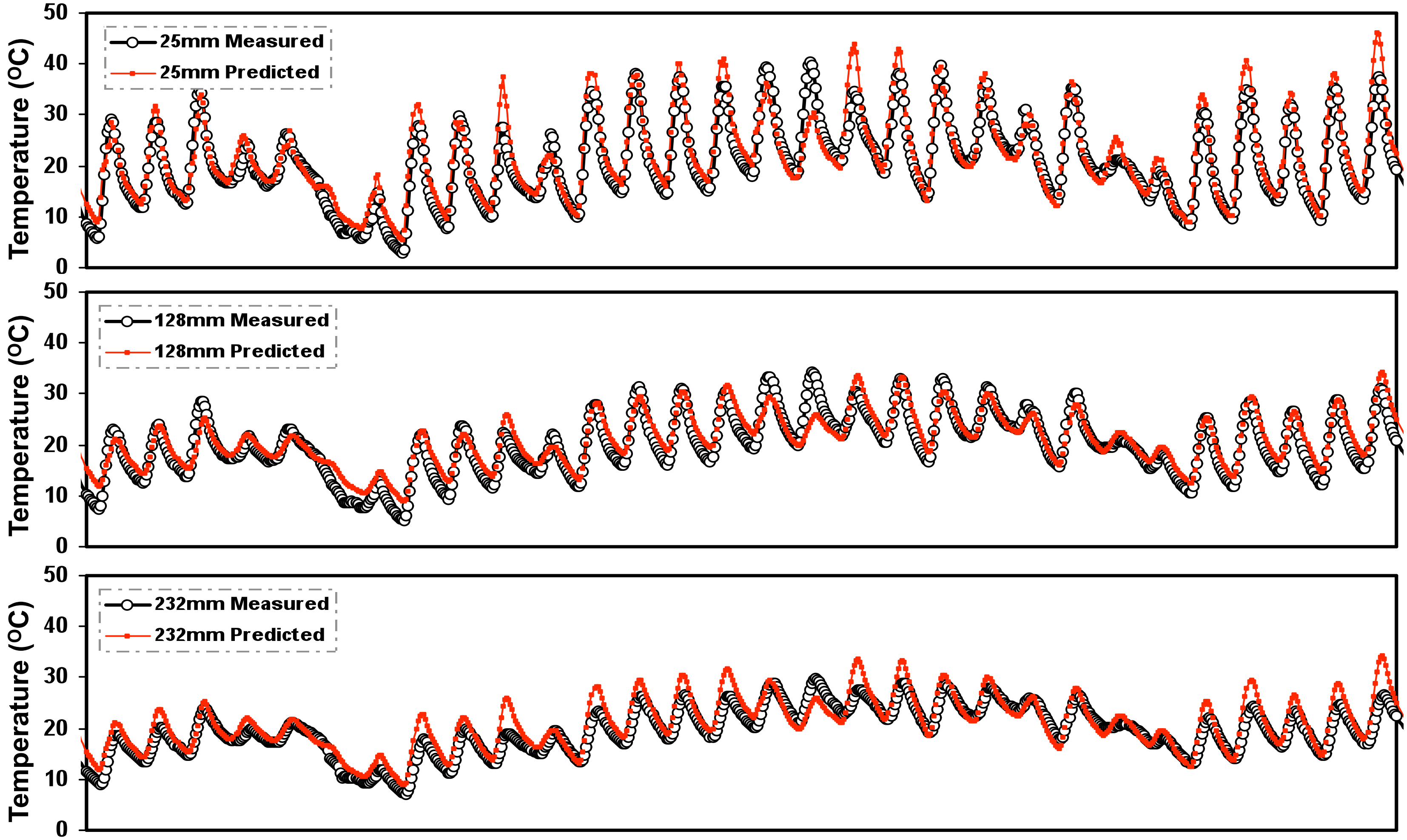
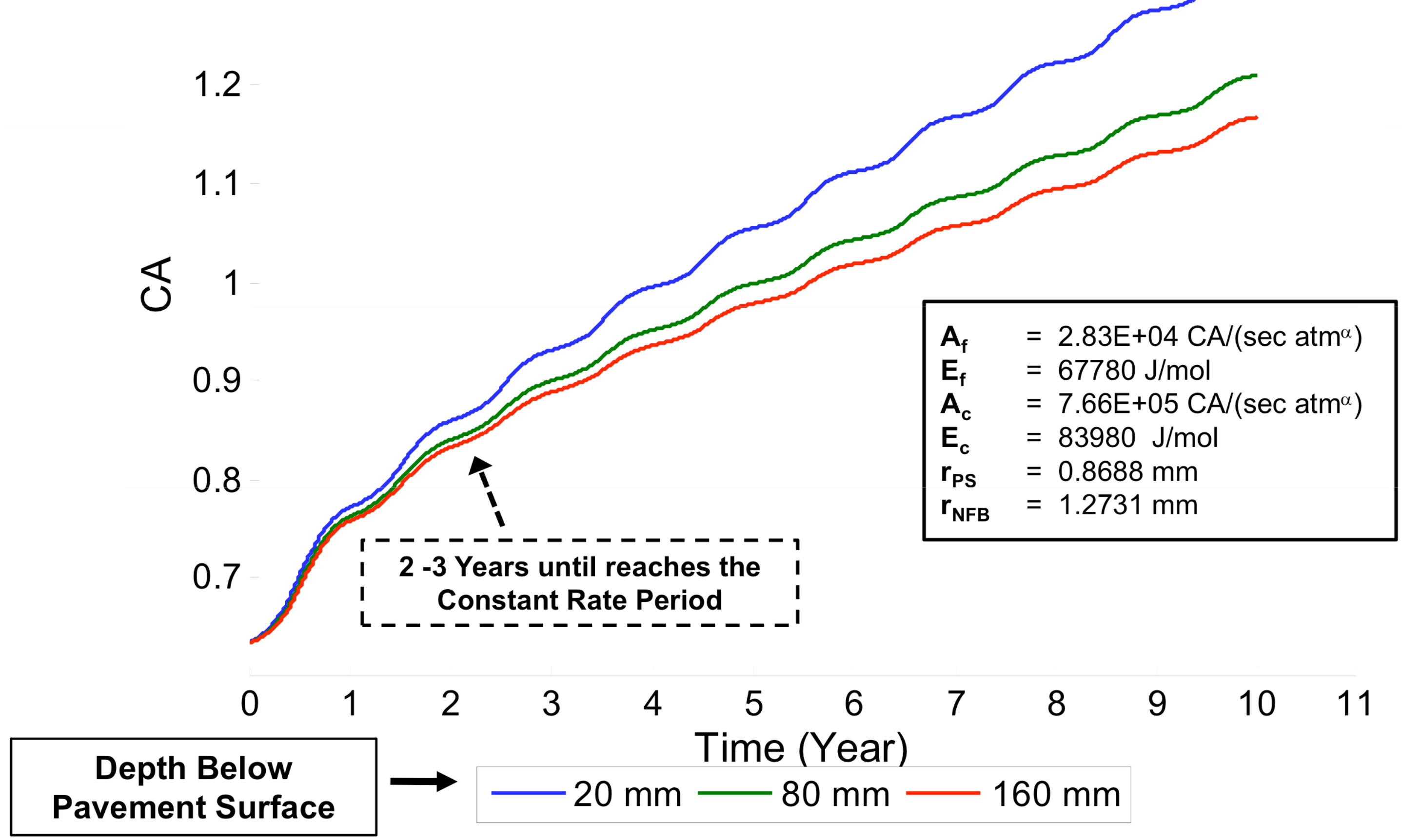
Comparison of sample calculations with field measurements, pavement 48-1068, Mar-1994.



Han, Rongbin, Xin Jin, Charles J. Glover, *Modeling Pavement Temperature for Use in Binder Oxidation Models and Pavement Performance Prediction*, JMCE, *in press*.

Transport Model Calculations of Binder Oxidation in Pavements (Texas)

$$\frac{\partial P_{O_2}}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r D_{O_2}\frac{\partial P_{O_2}}{\partial r}\right) - \left(\frac{cRT}{h}\right) r_{CA}$$

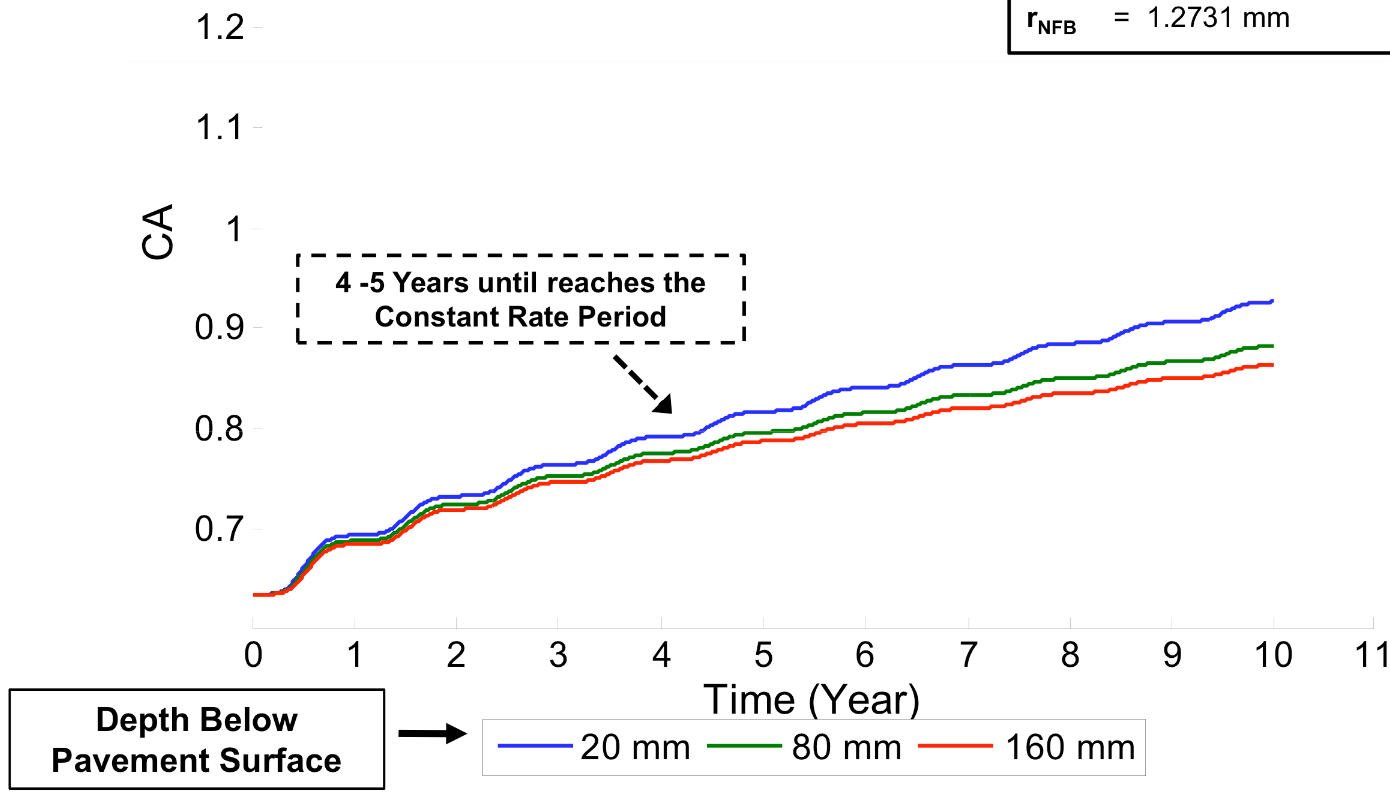


Model from: Prapaitrakul et al., Rd Mtls and Pvmt Des, 10, 95-113 (2009)

Transport Model Calculations of Binder Hardening in Pavements (Minnesota)

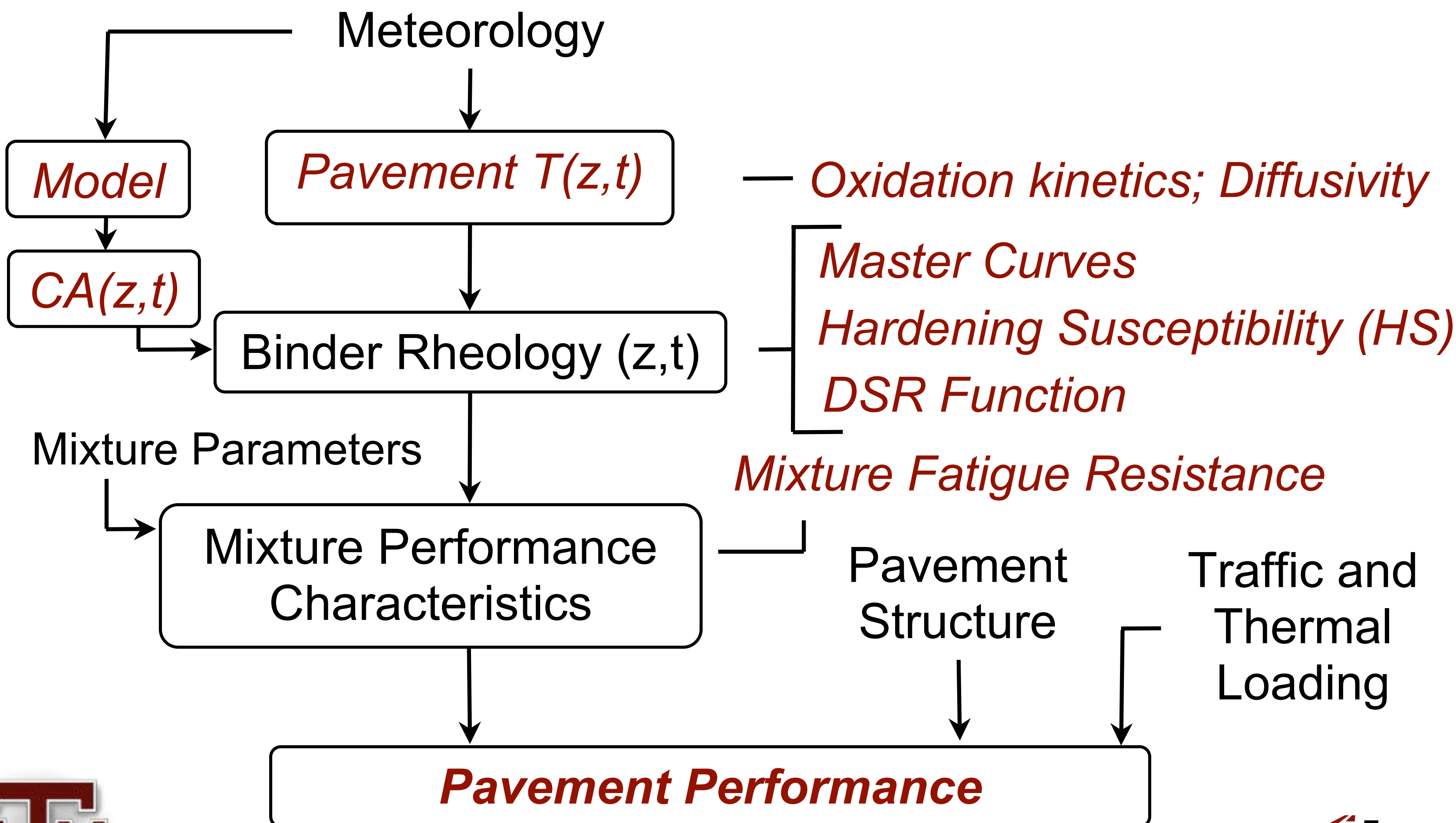
$$\frac{\partial P_{O_2}}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r D_{O_2} \frac{\partial P_{O_2}}{\partial r} \right) - \left(\frac{cRT}{h} \right) r_{CA}$$

A_f	=	2.83E+04 CA/(sec atm$^{\alpha}$)
E_f	=	67780 J/mol
A_c	=	7.66E+05 CA/(sec atm$^{\alpha}$)
E_c	=	83980 J/mol
r_{PS}	=	0.8688 mm
r_{NFB}	=	1.2731 mm



Model from: Prapaitrakul et al., Rd Mtls and Pvmt Des, 10, 95-113 (2009)

Pavement Performance Depends upon:



Summary

- Binder oxidation occurs in pavements
- Oxidation kinetics can be described by parallel fast-rate and constant-rate reactions
- The fast-rate reaction is product limited; the constant-rate reaction proceeds indefinitely
- Oxygen diffusivity correlates well to *T* and binder viscosity (base binder for PMA). Fines affect diffusivity in accordance with common models
- Oxidative hardening adversely affects mixture fatigue life and thus pavement durability
- A transport model serves as a foundation for pavement performance predictions

Acknowledgments

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- Texas Transportation Institute
- Artie McFerrin Department of Chemical Engineering

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