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The Asphalt Binder Oxidative Aging Chemo- Mechanical Model

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Rationale for Asphalt Binder Oxidation Studies

The concept of designing perpetual pavements has obvious economic advantages when lifecycle costs are evaluated. The realization of extended pavement life resulting in reduced cost requires developing technologies to monitor and/or mitigate the effects of asphalt binder oxidation, which stiffens and embrittles the binder.

A fundamental understanding of the phenomena causing asphalt oxidation may suggest ways to control or stop it, either through material design or pavement design. A fundamental understanding of oxidation is also beneficial for designing cost-effective monitoring protocols for pavement to rationally assess when and what maintenance measures should be applied. An understanding of the oxidation processes is also essential to producing robust pavement performance models for use in pavement design.

The rheological properties of asphalt binder change with oxidation, and these changes must be predicted over the service life of the pavement. The oxidized binder is stiffer, and stresses relax more slowly at comparable temperatures. The oxidized binder and the pavement it holds together accumulate stresses due to temperature drops much more quickly and at higher temperatures than the freshly placed binder. This shifts the effective performance grade to warmer values. Not only does the pavement accumulate stresses more readily in a given climate with oxidized binders compared with recently placed pavements, but the extent of oxidation is also more severe at the surface than deeper in the asphalt concrete, causing higher stress concentrations at the surface than would be expected if the pavement oxidized uniformly

with depth. Oxidation also changes the pavement failure strength. Without being able to understand these changes in nearly quantitative terms, pavement performance models cannot accurately predict the behavior of aged pavements.

Overview

The asphalt oxidative aging model presented here is based on a foundation of decades of research by the asphalt research community and represents a significant improvement in the understanding of how oxidation occurs in asphalt binders and how oxidation affects the rheological properties of the binder.⁽¹⁾

The asphalt oxidative aging model is actually two models: a fundamental-based model that describes the oxidation chemistry (oxidation chemistry rate model) and a semi-empirical model that relates the level of oxidation to changes in the rheological properties (master curve change model).

The oxidation model is derived from fundamental chemistry, and the semi-empirical rheological model describes the changes in the Christensen-Andersen complex modulus master curve model parameters.⁽²⁾ This combination of models can predict the oxidation behavior and the resulting changes in rheology from data obtained by aging a binder sample at a single temperature for two durations and collecting an infrared spectrum and a rheological master curve from each duration sample.

From these data, the complex modulus master curve of the binder can be predicted at any level of aging. Once the rheological properties are known, stress and strain responses can be computed. The level of aging to expect in an actual pavement will require knowledge of the thermal history of the pavement and

degree of oxygen depletion with depth in the pavement. This information would have to be determined from either field observations or mass- and heat-transfer models of the pavement in its target environment.

The master curve change model can also be employed to easily monitor the oxidation condition and rheological properties of aging pavements using inexpensive small-sample infrared methods, replacing expensive methods requiring large core samples and expensive rheological testing.

Oxidation Chemistry Rate Model

This oxidation rate model was derived from fundamental chemistry in differential form based on chemical reaction steps believed to be occurring so that it can be directly applied to a wide variety of thermal histories and geometries. Unlike prior art models determined from curve fits of isothermal laboratory data, this model includes terms for dissolved oxygen concentrations, reactive moieties in the asphalt, and intermediate species, which are currently assumed to be free radicals.

Consequently, this model can be used as a means of interpreting data for laboratory-aged binders or for binder aging in a pavement with thermal and oxygen partial pressure gradients, if those gradients are known. The Petersen dual-reaction mechanism was used with a rate limiting step simplification to cast the governing differential equations, but other reaction path schemes can be imagined that produce the same mathematical form.⁽³⁾

Extensive laboratory testing shows that this model can very accurately describe the course of oxidation in 34 different binders, both modified and unmodified, using only a single adjustable parameter

representing a reactive material chemical species concentration. The calculation of reactive material concentrations in blends has been shown to be sufficient to predict the course of oxidation in those blends. Thus, the rate of oxidation of recycled asphalt asphalt/virgin blends can be estimated. The model has been shown to predict rates for very different binders in high-pressure environments using a simple, uniform pressure correction. The correlation coefficients (R^2) range between .95 and .98 in all laboratory testing to date. An example of the model fits to oxidation data from the Accelerated Load Facility (ALF) unmodified binder at the Federal Highway Administration's Turner-Fairbank Research Center is shown in figure 1. The material was aged at ambient pressure in Laramie, WY.

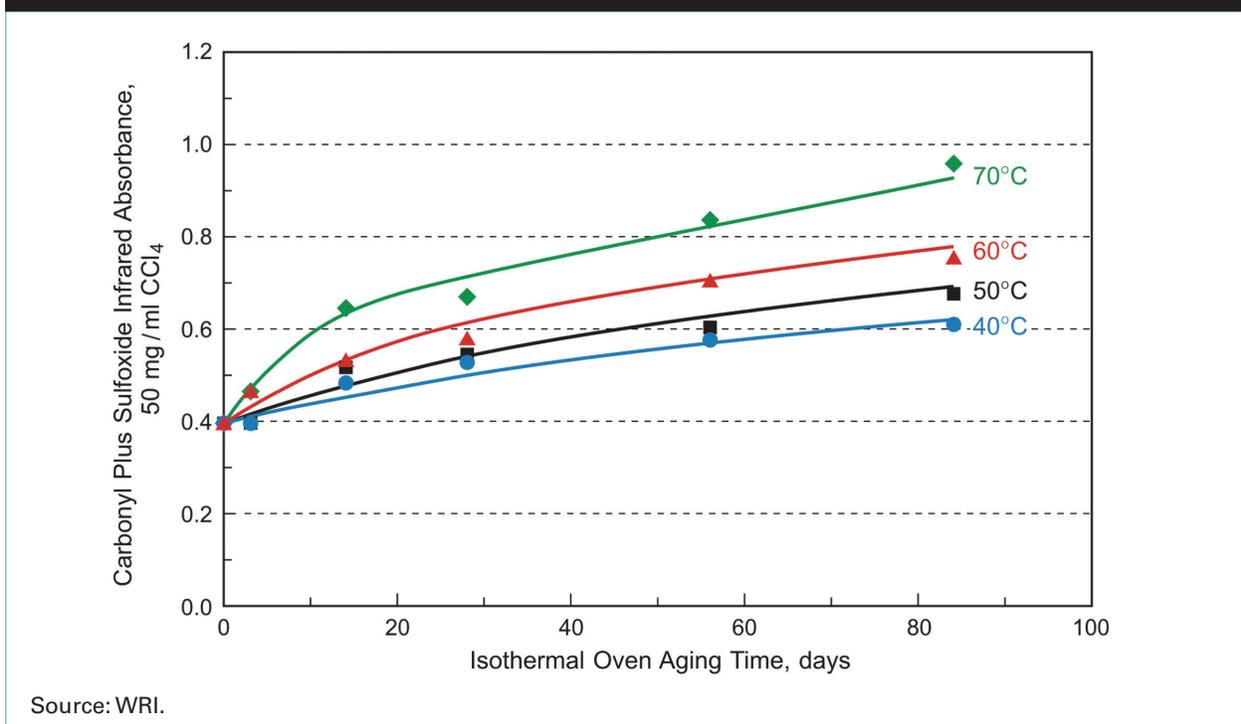
Chemical Mechanism

The chemical mechanism assumed in the rate model is based on the more detailed

dual-reaction mechanism proposed by Petersen.⁽³⁾ Two dominant reaction paths occur in parallel. An important advancement in this model is the recognition that these reactions are coupled. The two reactions consist of a fast reaction that consumes a highly reactive material producing oxidation products, predominantly sulfoxides and ketones in subsequent steps, and also free radical species.

Although Petersen's sequence does not specifically illustrate the possible role of organo-metallic catalysts, these kinds of materials may participate in the reaction path through an activation process. At the same time, the slow reaction proceeds with an induction period depending on the generation of radicals in the fast reaction following a well-established hydrocarbon oxidation reaction sequence. The fast-reaction radicals abstract hydrogen from benzyl carbons and sulfides, producing reactive radicals that eventually become predominately ketones

Figure 1. Graph. Oxidation model fits to isothermal oxidation infrared absorption data for the ALF unmodified binder.



and more sulfoxides if sufficient sulfide is available. The slow reaction produces additional free radicals in amounts that appear to be nearly balanced to those consumed. Again, organo-metallic catalysts could be involved and produce similar mathematical descriptions.

One important behavior of this model is that it recognizes that the rate-limiting steps are earlier and slower than the generation of the predominant oxidation products. Defining the extent of oxidation in terms of oxygen uptake by the binder, instead of the formation of a single species such as the ketone carbonyl functional group, results in consistent activation energies for both reaction paths, contrary to the findings in other studies that monitored carbonyl alone.⁽⁴⁾ Once it was recognized that the slow reaction rate was governed by the extent of fast reaction through the bi-molecular effect of the free radical concentration, truly fundamental reaction rate constants could be determined from the isothermal studies, and these rate constants produced nearly identical reaction rate temperature dependencies of classical Arrhenius form.

Monitoring only one product, instead of oxygen uptake, results in highly variable source-dependent results because the various product reaction paths compete with each other (predominantly forming sulfoxide and carbonyl). Because it is key to obtain consistent rate constants for the determination of thermal rate dependency, the research team needed to know that the slow reaction rate was controlled by the amount of reactive material available.

The slow reaction rate depends on the amount of free radicals produced in the fast reaction, which is determined by the reactive material consumed in the fast reaction. The quantity of reactive material is source dependent and is the single adjustable variable needed to evaluate the

oxidation behavior from a given source of asphalt binder. Not accounting for the fast reaction rate effect on the slow reaction resulted in widely varying apparent rate constants and highly variable activation energies in prior art studies. In its studies, the team found that the combination of sulfoxide and carbonyl infrared absorbencies correlate well with direct oxygen uptake measurements, and this substitution provides a convenient cost-effective method for tracking the course of oxidation.

The two reaction pathways can be simplified to reaction 1 (figure 2) and reaction 2a and 2b (figure 3 and figure 4, respectively).

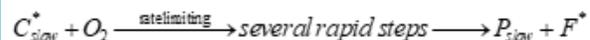
Figure 2. Equation. Reaction 1: The fast reaction.



Figure 3. Equation. Reaction 2a: The slow reaction hydrogen abstraction.



Figure 4. Equation. Reaction 2b: The slow reaction oxygen interaction.



C_{fast} represents the reactive material, currently unidentified, for the fast reaction. C_{slow} represents the reactive material for the slow reaction, generally assumed to be benzyl carbons.⁽⁵⁾ F^* is a generic symbol for any species of effective radicals produced. P_{fast} and P_{slow} represent the products produced, which are assumed to be proportional to the sum of the carbonyl and sulfoxide concentration as

determined from infrared analysis. To do the mathematics properly, the distinction between the product origins must be kept in mind, but once the isothermal integration is completed, these terms can be combined to obtain the values that can be measured. It is critical to understand that the concentration of the reactive material for the slow reaction (benzyl carbon radical) is proportional to the fast reaction product concentration.

The basic rate equations can be written as shown in figure 5 and figure 6.

Figure 5. Equation. The fast reaction rate expression.

$$\frac{dP_{fast}}{dt} = k'_1 [C_{fast}] [O_2] = k_1 [C_{fast}]$$

$$= k_1 [C_{fast,0} - P_1]$$

Figure 6. Equation. The slow reaction rate expression.

$$\frac{dP_{slow}}{dt} = k'_2 [C_{slow}^*] [O_2] = k_2 [P_1]$$

Here, $C_{fast,0}$ represents the fast reaction reactive material at the beginning of the aging experiment. The slow reaction reactive material is assumed to be a benzyl radical produced in proportion to the products of the fast reaction. During the course of the slow reaction, additional radicals are produced to replace the radical consumed in the hydrogen abstraction of benzyl carbons. Integration of the rate equations in figure 5 and figure 6 produces the isothermal equation used to fit the data.

Figure 7 is used to fit the isothermal data to determine the rate constants and amount of reactive material for each binder studied. The dissolved oxygen concentration is combined with the fundamental rate

constants in figure 7. In a pavement or diffusion-limited bitumen film, oxygen consumption will reduce the partial pressure of oxygen.

Figure 7 assumes isobaric conditions. Expanding the apparent rate constants to include the dissolved oxygen concentration results in the more general equations, which also correct for oxygen concentration order not being restricted to 1, which is useful for mapping accelerated aging methods to pavement conditions. The expanded model also has the Arrhenius temperature dependence included as shown in figure 8 and figure 9.

Figure 7. Equation. The integrated overall oxidation rate expression.

$$P = P_{fast} + P_{slow} = C_{fast,0} \left(1 - \frac{k_2}{k_1}\right) (1 - e^{-k_1 t}) + k_2 C_{fast,0} t + P_o$$

Figure 8. Equation. The fast reaction temperature dependence.

$$k'_1 = A_1 e^{\frac{-E_{a,1}}{RT}}$$

Figure 9. Equation. The slow reaction temperature dependence.

$$k'_2 = A_2 e^{\frac{-E_{a,2}}{RT}}$$

The Arrhenius parameters, pre-exponential constants, $A_{1\&2}$, and activation energies divided by the gas constant, $\frac{-E_a}{R}$, are the same for all binders studied. The generalized fast and slow reaction rate expressions are shown in figure 10 and figure 11.

The isothermal kinetic model can be written as shown in figure 12.

Figure 10. Equation. The fast reaction rate expression generalized for pressure and temperature.

$$\frac{dP_1}{dt} = A_1 e^{\frac{-E_{a,1}}{RT}} [O_2]^n [C_{fast,0} - P_1]$$

Figure 11. Equation. The slow reaction rate expression generalized for pressure and temperature.

$$\frac{dP_2}{dt} = A_2 e^{\frac{-E_{a,2}}{RT}} [P_1][O_2]^m$$

Figure 12. Equation. The overall oxidation reaction with pressure dependence.

$$P = C_{fast,0} \left(1 - \frac{k_2 P_{O_2}^n}{k_1 P_{O_2}^m} \right) \left(1 - e^{-k_1 P_{O_2}^m t} \right) + k_2 P_{O_2}^n C_{fast,0} t + P_0$$

Where:

P = The extent of oxidation metric, usually sulfoxide and carbonyl absorbance sums.

P_0 = The rolling thin film oven-aged time-zero value of P .

$C_{fast,0}$ = The reactive material concentration for the fast reaction.

k_2, k_1 = The slow and fast reaction rate constants for isothermal aging, temperature dependent according to the Arrhenius equation.

$P_{O_2}^n$ = The partial pressure oxygen; n is the pressure exponent for the slow reaction.

$P_{O_2}^m$ = The partial pressure oxygen; m is the pressure exponent for the fast reaction.

In the equations shown in figure 2 through figure 12, sulfoxide and carbonyl concentrations are usually assumed to be proportional to oxygen incorporation

into the binder as oxidation proceeds and provides the metric for P . Other measurements could be used, such as direct oxygen determination for the binder as it ages. For non-isothermal use and geometrical length scales where diffusion has a significant effect on rate, the model must be integrated numerically and coupled to heat and mass transfer results, either model results or direct measurement.

The basic rate equations can be written as shown in figure 13 and figure 14.

Figure 13. Equation. The general non-isothermal and non-isobaric fast reaction rate expression.

$$\frac{dP(x,t)_1}{dt} = A_1 e^{\frac{-E_{a,1}}{RT(x,t)}} [C_{fast,0} - P(x,t)_1] [O(x,t)_2]^n$$

Figure 14. Equation. The general non-isothermal and non-isobaric slow reaction rate expression.

$$\frac{dP(x,t)_2}{dt} = A_2 e^{\frac{-E_{a,2}}{RT(x,t)}} [C_{slow}^*(x,t)] [O(x,t)_2]^m$$

In this most general version of the model, concentrations and temperatures are functions of both time and depth from the gas-binder interface. The experimental results indicate that the pressure exponents are not in agreement, indicating that our model remains an approximation for the true bimolecular process.

Master Curve Change Model

The well-known and widely used Christensen-Andersen model that describes asphalt complex modulus master curves was used to correlate the changes in the model parameters with the extent of oxidation in 19 unmodified binders.⁽²⁾

The glassy modulus was assumed to be 1.5 gigapascals. The other two model parameters, the crossover frequency and crossover modulus, were found to change in a log-linear fashion as asphalt binder ages (figure 15 and figure 16). The behavior of polymer modified materials had not been studied at the time of this report.

Figure 15. Equation. The change in crossover modulus correlation.

$$\ln(G_c^* / G_{c,0}^*) = A_g \Delta([C=O] + [S=O])$$

Figure 16. Equation. The change in crossover frequency correlation.

$$\ln(\omega_c / \omega_{c,0}) = A_\omega \Delta([C=O] + [S=O])$$

Where:

G_c^* = complex modulus at phase angle = 45 degrees.

$G_{c,0}^*$ = complex modulus at phase angle = 45 degrees; time = 0.

ω_c^* = frequency at phase angle = 45 degrees.

$\omega_{c,0}^*$ = frequency at phase angle = 45 degrees; time = 0.

$[C=O] + [S=O]$ = sum of absorbencies of sulfoxide and carbonyl.

$\Delta[C=O] + \Delta[S=O]$ = change in sum of absorbencies of sulfoxide and carbonyl.

A_g = crossover modulus fit coefficient.

A_ω = crossover frequency fit coefficient.

While the binders all provide good fits, with regression coefficients typically exceeding 0.9, the fit parameters were found to

depend on source. Obtaining this empirical relationship from test data will require rheological data from the sample aged for two oxidation extents. The team found no significant change in the shift functions as the binder ages, but, of course, each binder has its own shift function.

Summary

The asphalt binder oxidative aging chemo-mechanical model provides a significant improvement in the understanding of asphalt binder oxidation chemistry. It offers a more consistent mathematical description of the oxidation process and provides evidence that greatly simplified testing methods can be developed to describe the oxidation behavior of asphalt binders for the interpretation of pavement monitoring and for use in pavement performance prediction models. This model is also compatible with diffusion studies because the role of oxygen concentration in determining the oxidation rate is explicitly described.

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