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Oxidation simulation of thin bitumen film

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ABSTRACT: Oxidative aging is a complex phenomenon in bitumen and its fundamental understanding is needed to optimize paving materials with long-lasting characteristics. This research reports on a diffuse-reaction model for predicting the oxidation of bituminous binders over time and under different conditions. As known, the oxidation of bitumen is affected by the material chemistry, film thickness and temperature. Thus, these factors were considered in this research to simulate the oxidation of a thin bitumen film. Carbon compounds were assumed as the oxidation index of a model bitumen and analyses were performed enabling prediction of chemical compositional changes. In the future, the current model can be used to simulate the actual oxidative aging in (un)modified binders, such as epoxy modified asphalt, presented in a companion paper (Apostolidis et al., *Kinetics of Epoxy-Asphalt Oxidation*. AM3P).

1. INTRODUCTION

According to Greek mythology, the Cyclops traded one of their eyes with the god Hades in return to be able to foresee the future. However, Hades tricked them by the only vision to see their last day. In comparison with Cyclops, the exact end-of-life of asphalt pavements is unknown, however this did not prohibit the efforts of asphalt scientists to develop a solid research foundation on the aging of bitumen to predict the life of pavement structures.

As everything in nature, aging in bitumen is a simply inevitable process. The chemical composition of bitumen, which depends on their crude oil source and distillation processing, is strongly influenced from oxygen over time through a chemical process named oxidative aging. Oxidative aging leads to chemo-mechanical changes that influence negatively the material performance. In chemistry terms, bitumen can be separated based on differences in solubility and polarity into four primary chemical classes: saturates, aromatics, resins, and asphaltenes. During the oxidation of bitumen, a decrease in aromatic content and subsequently an increase in resins are caused, together with a higher asphaltene content (Petersen & Harnsberger 1998). In mechanics terms, aging is accompanied by stiffening and embrittlement of binders, which contributes to the deterioration of asphalt pavements. Therefore, modelling the oxidation process of bitumen will enable to predict chemical compositional changes and subsequently the degradation of asphalt materials over time.

In this perspective, the scope of this research is to provide insights into the oxidation mechanism of a thin bitumen film by performing multi-physics numerical analyses enabling prediction of changes in material chemistry. In the future, this information could be used as input set of data in a model to couple the oxidative age hardening and ultimately the material failure, in a way to control or prohibit aging, or design asphalt materials with long-lasting characteristics.

2. DIFFUSE-REACTION MODEL

Typically, bitumen oxidation is distinguished in two phases, a non-linear fast-rate reaction and a linear constant-rate reaction phase (see **Fig. 1**) (Van Oort 1956, Liu et al. 1996). Previous works focused on constant-rate kinetics of aging bitumen as well due to the fact that the duration of the fast rate period was speculated to be relatively short and with small impact on long-term asphalt performance (Liu et al. 1996, Domke et al. 1999). For the purposes of this research, a one-step reaction diffuse-reaction oxidation model has been developed and presented herein considering the carbon species as oxidizing species in bitumen.

Particularly, oxidation of bitumen is principally the conversion of carbon groups to carbonyl [C=O] groups. These are the only significant reactions that cause increase in modulus and at longer times, carbonyl formation dominates the stiffening of binder. The oxidized compounds are highly polar

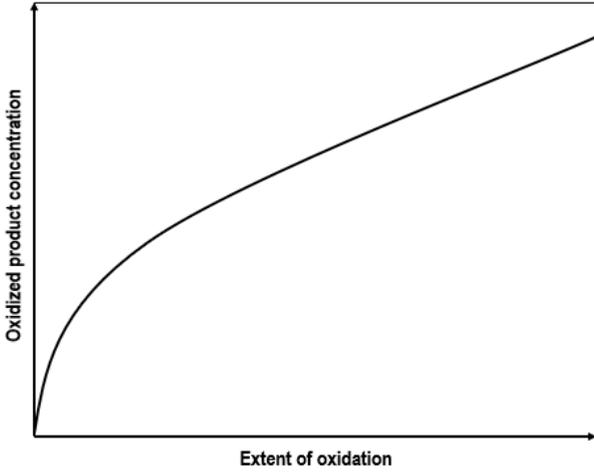
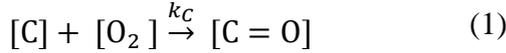


Figure 1. Schematic illustration of typical bitumen oxidation in-service conditions.

species which change the mechanical properties, such as increase of modulus and decrease of phase angle by interacting with other nearby polar groups. The unreacted sited can be exposed to more oxygen to produce higher conversion and thus more inter-molecular interaction. In this research, it was assumed that the concentration-independent chemical reaction of producing carbon oxidized species is defined as



The general expression of such irreversible reaction including the time rate of change of concentration $[C]$ of carbon compound is as

$$\frac{d[C]}{dt} = \sum_{i=1}^M \omega_i k_i \prod_{\omega_i > 0} [C^{\omega_i}] \quad (2)$$

Decomposition of single species produces compounds at a rate proportional to the amount of the decomposing carbon species. Most reactions consist of many simple sub-steps where only pairs of reactants need to be considered. For simplification, a one-step irreversible reaction of reactive species by oxygen (i.e., $[O_2]$) to carbon species (i.e., $[C]$) is considered as a perfect stoichiometric system.

Since the oxidation reactions are affected by the aging temperature, these effects can be incorporated into the reaction rate coefficients by following the Arrhenius approach as

$$k_C(T) = K_{0C}(T) \exp\left(-\frac{E_{aC}}{RT}\right) \quad (3)$$

where K_{0C} denotes the pre-exponential frequency factor (m^3/mol) of the carbon oxidation reaction, E_{aC} is the activation energy (J/mol), R the gas

constant (i.e., $8.314 \text{ J}/(\text{mol}\cdot\text{K})$) and T is the temperature.

The time-dependent mass balance per species, otherwise species transport through diffusion mechanisms, solves the mass conservation equation for carbon species

$$\frac{\partial [C]}{\partial t} + \nabla \cdot (-D\nabla [C]) = Re \quad (4)$$

where $[C]$ is the concentration of product carbon species (mol/m^3), D is the diffusion coefficient (m^2/s), which is modelled herein as in Arrhenius form for the O_2 in bitumen, and Re is a reaction rate for the species ($\text{mol}/(\text{m}^3\cdot\text{s})$). The first term on the left side of **Eq. 4** corresponds to the consumption of the species. The second term accounts for the diffusive transport.

The governing equation of the transient heat conduction within the bitumen is described by

$$\rho c_p \nabla T - \nabla \cdot (k \nabla T) = Q \quad (5)$$

where ρ is the mass density of bitumen, k denotes the thermal conductivity, c_p is the heat capacity, Q represents the endothermic heat source due to oxidative aging (kW/m^3). It was assumed that the convection and radiation heat do not have important impact on the energy balance of the system. The heat absorbed due to oxidation was assumed negligible ($Q=0 \text{ kW}/\text{m}^3$).

3. FINITE ELEMENT SIMULATIONS AND DISCUSSION

The oxidation rate of bitumen is affected by the material chemistry, film thickness and temperature (Herrington 2012). In this study, the parameters of diffusion coefficient (m^2/s) and the initial concentration of oxygen (mol/m^3) and reactive components in bitumen (mol/m^3) were obtained from (Jing 2019). These parameters determined by performing aging studies on a $200\text{-}\mu\text{m}$ film thickness of bitumen and thus a model binder of the same film thickness was simulated herein at 75 , 100 and 125°C as well (see **Table 1**). The reaction rate and the activation energy of the studied model was obtained from the available literature ($1e10 \text{ 1/d}$ and 80 kJ/mol) (Jin et al. 2011). Carbon oxidation was speculated the oxidation as one-step reaction process. As in the reality, oxygen concentration was modelled unlimited by diffusion following the general behaviour shown in **Fig. 1**.

The finite element mesh and predicted profile of oxidized carbon species is shown in **Fig. 2(a)** and **(b)**, respectively. The development of oxidized

species gradients of the model binder film is illustrated in **Fig. 3**^(top) indicating that the oxidation rate over the depth of sample is affected by the applied temperature during oxidation. According to the model prediction of oxidized species depth profiles, the higher the applied temperature, the faster the oxidation reaction over the film thickness (see **Fig. 3**^(top)). In this framework, the modulus gradients are expected to follow the sample pattern as of oxidized species in the model binder, allowing predictions of reasonable precision on the chemo-mechanical response of aged systems. Finally, the oxidation binder was more pronounced at high temperatures, and it was considerably greater at 125°C than that of oxidation after 3000 hrs at 75 and 100°C (see **Fig. 3**^(bottom)).

Table 1. Model parameters for the studied materials (Jing 2019).

aging (°C)	T	initial [O ₂] (mol/m ³)	initial [C] (mol/m ³)	D _C (m ² /s)
75		1.10E-1	38	3.31E-13
100		1.31E-1	38	5.13E-13
125		1.49E-1	38	9.25E-13

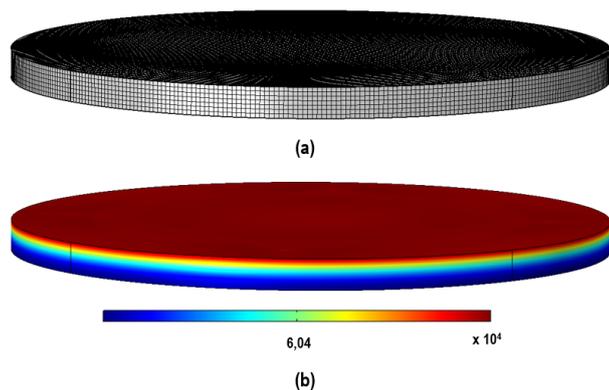


Figure 2. Finite element geometry: (a) mesh (number of elements: 33700 hexahedron and 14800 quad), and (b) predicted concentration of oxidized carbon species in thin bitumen film after 3000 hrs at 125 degC.

The oxidation model presented here was based on a foundation developed after decades of research in the aging-related chemistry of bitumen. The concurrent diffuse-reaction oxidation model developed herein provides an improvement in the implementation on robust predicting schemes of oxidation chemistry of bitumen in a way to be extended to simulate coupling phenomena through the oxidative age hardening in the future. Oxidation studies performed enabling interpretation of the effect of environmental conditions and bitumen film thickness on oxidation rate and oxidized species concentration profiles through aging. The used multi-physics method for the purposes of this study offers a robust modelling tool to simulate the oxidation process in bitumen

considering the diffusion phenomena together with the oxidation reactions.

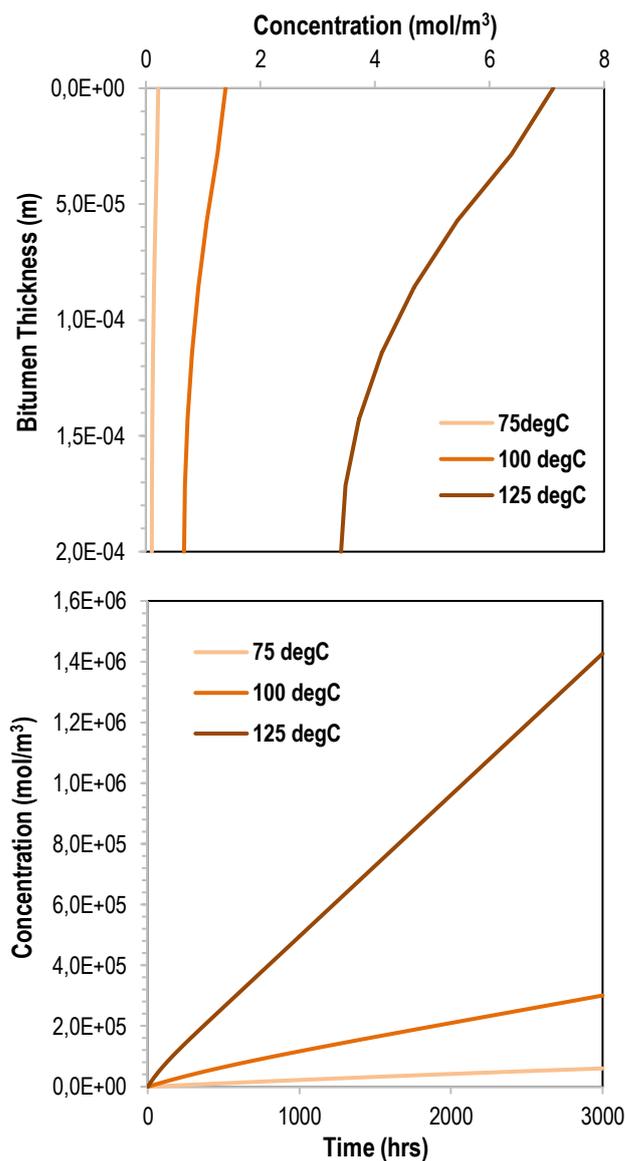


Figure 3. Predicted concentration of oxidized species along the thickness after 3000 hrs (top) and in bitumen (bottom).

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