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R. Jing, D. van Lent, C. Kasbergen, A. Scarpas, X. Liu, S. Erkens

# EXPERIMENTAL AND COMPUTATIONAL INVESTIGATION OF GAS DIFFUSION IN BITUMEN

**Ruxin Jing[1], Diederik van Lent[2], Cor Kasbergen[3], A.(Tom) Scarpas[4], Xueyan Liu[5], Sandra Erkens[6]**

(1) Corresponding author
Section of Pavement Engineering, Delft University of Technology
Stevinweg 1, 2628 CN Delft, the Netherlands
Phone: + 31 (0)15 27 84674
Email: R.Jing@tudelft.nl

(2) Structural Reliability, Netherlands Organizations for Applied Scientific Research (TNO)
Van Mourik Broekmanweg 6, 2628 XE Delft, the Netherlands
Phone:+31 (0)88 86 63132
Email: Diederik.van.lent@tno.nl

(3) Section of Pavement Engineering, Delft University of Technology
Stevinweg 1, 2628 CN Delft, the Netherlands
Phone: + 31 (0)15 27 82729
Email: C.Kasbergen@tudelft.nl

(4) Section of Pavement Engineering, Delft University of Technology
Stevinweg 1, 2628 CN Delft, the Netherlands
Phone: + 31 (0)15 27 84017
Email: A.Scarpas@tudelft.nl

(5) Section of Pavement Engineering, Delft University of Technology
Stevinweg 1, 2628 CN Delft, the Netherlands
Phone: + 31 (0)15 27 87918
Email: X.Liu@tudelft.nl

(6) Section of Pavement Engineering, Delft University of Technology
Stevinweg 1, 2628 CN Delft, the Netherlands
Phone: + 31 (0)15 27 85949
Email: s.m.j.g.erkens@tudelft.nl

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## ABSTRACT

When oxygen diffuses in a bituminous film, it also reacts, simultaneously, with the constituents of the bitumen and as such it is gradually depleted. This depletion process masks the characteristics of the actual diffusion process and complicates the determination of the diffusion coefficient needed for computation of oxygen concentration and its effects on bitumen degradation due to aging. In the present study, experiments were carried out to measure objectively oxygen absorption in bitumen at various temperatures independently of oxygen depletion phenomena. To achieve this, an improved version of van Oort's test set up was utilized and oxygen was replaced by nitrogen. A Laplace transform based numerical technique was developed for processing the test results to determine the diffusion coefficients under various conditions. Once validated, they were used in finite element simulations to demonstrate the influence of time and temperature on gas diffusion and concentration in porous asphalt mixtures.


**Keywords**: Gas diffusion, Laplace transform, theorem of Residues, finite element method, porous asphalt

# INTRODUCTION

The reduced service life of porous asphalt pavements due to ravelling are a major concern [1]. Aging of the bitumen due to oxygen diffusion and oxidation is believed to be one of the major causes. The mechanical and chemical properties of bitumen, as of all organic substances, evolve with time. It is now well documented that ductility and penetration of bitumen are reduced while the softening point and ignition temperature are increased as a response to aging [2, 3]. Ultimately, the viscosity of the bitumen is increased and bitumen becomes stiffer. This may cause the mixture to become excessively brittle and susceptible to fatigue damage at lower temperatures[4].

Gas diffusion in the bitumen of an asphalt mixture is a long term process controlled by various physico-chemical factors such as the chemical composition of the constituents, the film thickness, the porosity of the mix, the temperature and the pressure. The diffusion coefficient of bitumen increases with increasing temperature and decreases with aging [5, 6]. The movement of gas molecules is accelerated with increasing temperature and pressure [7-9].

In the past, several experiments have been carried out to measure the diffusion properties of bitumen films [10-13]. Research has focused primarily on the diffusion of oxygen or air [14-18] and the determination of the corresponding diffusion coefficient necessary for numerical or other predictions. Unfortunately, while the oxygen diffuses in the film, it also reacts, simultaneously, with the constituents of the bitumen and as such it is gradually depleted. This depletion process masks the actual diffusion process and complicates the determination of the aforementioned diffusion coefficient.

In the present study, experiments were carried out to measure objectively gas absorption in bitumen at various temperatures and independent of depletion phenomena due to reactions. An improved version of van Oort's test set up [19] was utilized. On the basis of the experimental results the diffusion coefficients were calculated by means of a Laplace transform based numerical technique. A three dimensional (3D) micromechanical mesh, obtained via X-ray computed tomography (CT) of a porous asphalt (PA) mixture, was used for simulating gas diffusion in a PA mix via the finite element system CAPA-3D. The finite element analyses enable the investigation of the mix characteristics like film thickness, porosity and interconnectivity of pores on the aging process. The research continues with the introduction of reaction phenomena and their influence on oxygen depletion.

# EXPERIMENTAL METHOD

In order to measure accurately the diffusion of gas through bituminous layers, an experimental setup was built, which is an improved version of the instrument developed by van Oort in 1954 [19].

## Experimental setup

The instrument made for this research consists of a 100 $cm^3$ pipet on which the top of the burette was slightly molten over and then double glued together. The 10 $cm^3$ burette is graded into volumes of 0.1 $cm^3$, which gives a precision two times as accurate as the measurements of van Oort who used a 50 $cm^3$ burette graded into volumes of 0.2 $cm^3$.

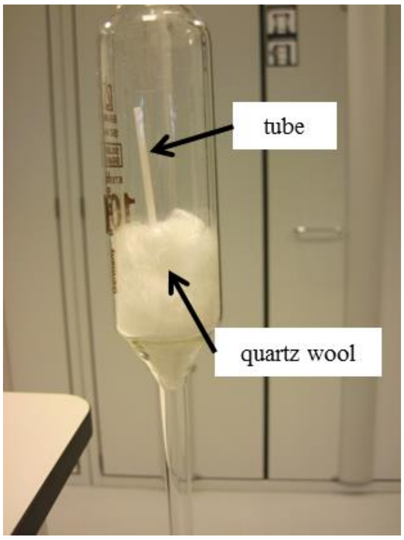
Similar to van Oort's experimental setup, the burette was open at the bottom end. On the opposite side of the burette there is a filling opening with a ground-in stopper. A wad of quartz wool was placed in the passage from the bulb of the pipet to the burette, Figure 1 (a). The quartz wool was densely packed in order to prevent drainage of the bituminous material through the quartz wool down the burette.

During the measurement, in order to level out the pressure change in the top of the pipet due to the absorption of gas into the bituminous sample, a small tube was installed at the bottom of the quartz wool up until the top of the bulb of the pipet, Figure 1 (a). This small tube ensures that the change in pressure of the burette was the same as the change of the pressure of the bulb. The measurements of the change in pressure of the burette thus represent the absorption from both sides of the bituminous material.

For the sample, the tube with an internal diameter of about 35 mm, was filled with 20 grams of bitumen (PEN 70/100). Then the dripping bitumen formed a 20 mm thick flat layer on top of the wad of quartz wool under influence of gravity, Figure 1 (b). As both oxygen and nitrogen are diatomic molecules and their van der Waals radii are very similar ($N_2$; $150\times10^{-12}$ m, $O_2$; $140\times10^{-12}$ m), the diffusion coefficient of nitrogen can be used to simulate oxygen diffusion, but without any aging effects.

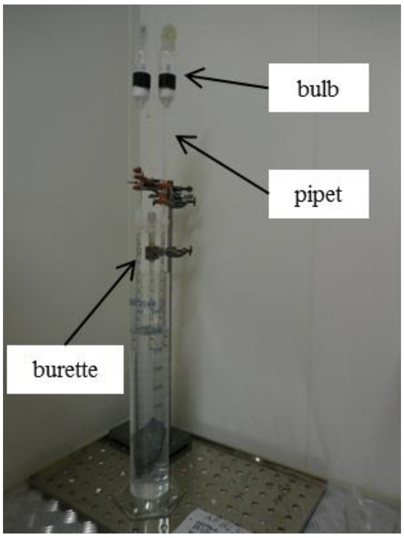
In this research absorption into bituminous material was measured with nitrogen at 20 ℃ and 60 ℃, respectively. After the bituminous material formed a layer on top of the quartz wool, the top of the pipet was connected to a supply of pure nitrogen. The nitrogen from the supply would dispel the air mixture from the top of the pipet through the small tube installed in the quartz wool, down the burette and is leaving the instrument at the bottom end of the burette. The instrument was connected to the nitrogen supply for over an hour. After this, the top of the pipet was also sealed with a cork and then additionally glued with silicone sealant.

The filled and closed pipets were put in a water tube in which the water level was maintained at the same level at all time, Figure 1 (c). The whole measuring instrument was then put in a temperature and humidity controlled environment, Figure 1 (d). This gave more accurate results than van Oort's, who performed measurements for a long time at room temperature with a variation of about 4 °C. At the elevated temperature of 60 °C, light viscous oil was used instead of water to prevent evaporation of the measuring liquid. To rule out the influence of changes in outside air pressure, a reference pipet-burette system without bitumen was installed. The changes in outside pressure could then be easily subtracted from the measurements to find the real absorption of the bitumen.



(a) Small tube balances pressure change


(b) Bituminous material filling




(c) Measuring instrument

(d) Temperature controlled environment

**Figure 1 Experimental setup**

During the experiment, the water/oil level in the burette was measured regularly from which the volume of the gas that was absorbed in the bituminous material can be calculated.

## Results and Discussion

The resulting absorbed nitrogen from the recordings at different temperatures are presented in Figure 2. The increasing rate of absorption over time was larger at the beginning and decreased later. It can be seen that the absorbed nitrogen at 60 °C is more than at 20 °C. This shows that gas absorption at this elevated temperature is faster than at lower temperatures.

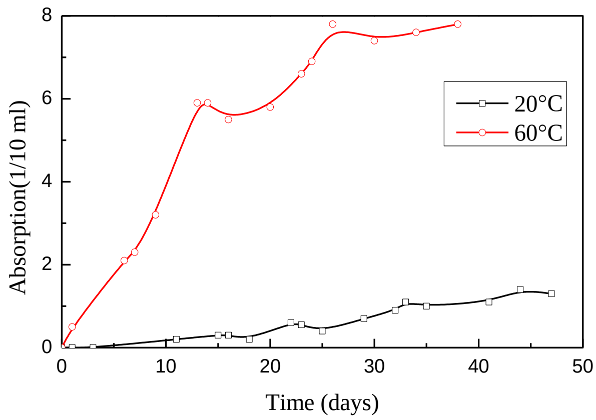



**Figure 2 Absorbance of nitrogen over time at different temperatures**

## SOLUTION OF THE GAS DIFFUSION EQUATION

By assuming the diffusion coefficient to be independent of the amount of gas locally bound, the differential equation of gas diffusion can be written as follows:

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \tag{1}$$

where $D$ is the diffusion coefficient, $c$ is the concentration of free gas, $x$ is the coordinate, and $t$ is the time. The boundary conditions and initial conditions of Equation (1) can be written as:

$$\begin{aligned} x = 0 \quad & \frac{\partial c}{\partial x} = 0 \\ x = a \quad & c = c_0 \end{aligned} \qquad (2)$$

$$t = 0, x > 0 \qquad c = 0 \qquad (3)$$

where $a$ is the layer thickness and $c_0$ is the concentration of free gas at the boundary.

The differential diffusion equation can be solved with the Laplace transform method. The Laplace transform of the diffusion equation and the boundary conditions can be rewritten as:

$$D\frac{\partial^2 \overline{c}}{\partial x^2} = p\overline{c} \qquad (4)$$

$$\begin{aligned} x = 0 \quad & \frac{\partial \overline{c}}{\partial x} = 0 \\ x = a \quad & \overline{c} = \frac{c_0}{p} \end{aligned} \qquad (5)$$

where $p$ is the Laplace transform variable.

The solution of equation (4) satisfying the boundary conditions (5) in Laplace space can now be written as:

$$\overline{c}\left(x, p\right) = \frac{c_0}{p}\frac{\cosh\left(\sqrt{\frac{p}{D}}x\right)}{\cosh\left(\sqrt{\frac{p}{D}}a\right)} \qquad (6)$$

The solution of equation (1) satisfying boundary condition (2) is found by applying the inverse Laplace transform for equation (6):

$$c = \frac{1}{2\pi i}\int_{e-i\infty}^{e+i\infty} e^{pt}\overline{c}dp \qquad (7)$$

The singularities of the integrand, the so-called poles, are at $p = 0$ and at $\cosh\left(\sqrt{\frac{p}{D}}a\right) = 0$. The latter results to :

$$p_n = -\frac{D}{a^2}\left(n + \frac{1}{2}\right)^2 \pi^2, n = 0, 1, 2... \qquad (8)$$

A real value for $c$ must be chosen such that the path of integration in the p-plane takes a course which leaves the pole of the integrand at the left side. The line integral can be evaluated by transforming it into a closed contour and applying the theorem of Residues hence:

$$c = \mathrm{Res}\left(p = 0\right) + \sum_{n=0}^{\infty}\mathrm{Res}\left(p = p_n\right) \qquad (9)$$

It can be shown that :

$$\mathrm{Res}\left(p=0\right)=c_0$$

$$\mathrm{Res}\left(p=p_n\right)=\frac{2c_0\left(-1\right)^{n+1}}{\left(n+\frac{1}{2}\right)\pi}\cos\left((\mathrm{n}+\frac{1}{2})\pi\frac{x}{a}\right)e^{-\frac{D}{a^2}\left(n+\frac{1}{2}\right)^2\pi^2 t} \tag{10}$$

and therefore :

$$c=c_0+\sum_{n=0}^{\infty}\frac{2c_0\left(-1\right)^{n+1}}{\left(n+\frac{1}{2}\right)\pi}e^{-\frac{D}{a^2}\left(n+\frac{1}{2}\right)^2\pi^2 t}\cos\left((\mathrm{n}+\frac{1}{2})\pi\frac{x}{a}\right) \tag{11}$$

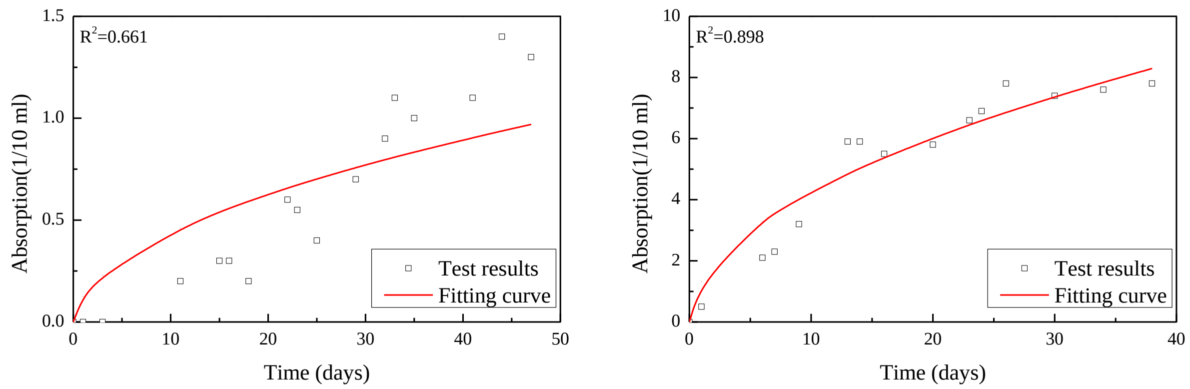
Applying the initial condition (3), the solution (11) will change into :

$$c=-\sum_{n=0}^{\infty}\frac{2c_0\left(-1\right)^{n+1}}{\left(n+\frac{1}{2}\right)\pi}\cos\left((\mathrm{n}+\frac{1}{2})\pi\frac{x}{a}\right)\left(1-e^{-\frac{D}{a^2}\left(n+\frac{1}{2}\right)^2\pi^2 t}\right) \tag{12}$$

The total quantity of gas absorbed, *M*, can now be computed by integrating over the thickness of the layer and multiplied by the cross-sectional area *A*:

$$M=\sum_{n=0}^{\infty}\frac{2aAc_0}{\left(n+\frac{1}{2}\right)^2\pi^2}\left(1-e^{-\frac{D}{a^2}\left(n+\frac{1}{2}\right)^2\pi^2 t}\right) \tag{13}$$

To determine the gas diffusion coefficient of a bitumen film at different temperatures, Equation (13) was applied and fitted to the time-absorption curve in Figure 3, where $a$=10 mm, and $A$=962.11 mm$^2$ (test sample with a thickness of 20 mm and diameter of 35 mm, absorbed gas from both top and bottom). One mole of an ideal gas will occupy a volume of 22.4 litres at standard temperature and pressure (i.e. 0 ℃ and 101 kPa). Therefore, based on the Ideal Gas Law, the concentrations of free gas at boundary $c_0$ are 41.60 and 36.60 mol/m$^3$ at 20 ℃ and 60 ℃, respectively.




(a) 20 ℃ (b) 60 ℃

**Figure 3 Absorbance curve fitting**

On the basis of the measurement results, Figure 3, and the above presented solution of the boundary value problem, it was found that the gas diffusion coefficients of bitumen were 5.108×10$^{-16}$ m$^2$/s and

$4.463 \times 10^{-14}$ $m^2/s$ at 20 ℃ and 60 ℃, respectively. These values are similar to those of van Oort (around $7.2 \times 10^{-16}$ $m^2/s$ at 50 ℃). In summary, the gas diffusion coefficient of bitumen increases when the temperature increases. The coefficient at 60 ℃ is about 100 times of that at 20 ℃.

# MODEL VALIDATION

## Simulation

Simulations of gas diffusion in 3D thin bituminous films were performed for a 50 days' time period which is similar to the duration of the experiments. As the samples in the experiments absorbed gas from top and bottom, the geometry of the bituminous film is modelled as a block with a thickness of 10 mm, length of 2 mm and a width of 2 mm. The bituminous film was assumed to be an isotropic material. The diffusion coefficients were obtained based on the measurements performed in the previous section. The input values of the diffusion coefficients were $5.108 \times 10^{-16}$ $m^2/s$ and $4.463 \times 10^{-14}$ $m^2/s$ at 20 ℃ and 60 ℃, respectively.

In the CAPA-3D FE system, gas diffusion is assumed to follow equation (1). The initial gas concentration in the bituminous film was assumed to be equal to 0. During the simulations, a constant gas concentration boundary condition (41.60 and 36.60 $mol/m^3$ at 20 and 60 ℃, respectively) was applied on the top boundary, while there was no flow going out of the four sides and the bottom boundaries, Figure 4.

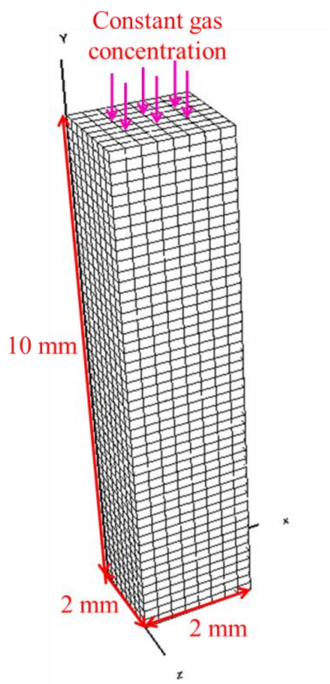
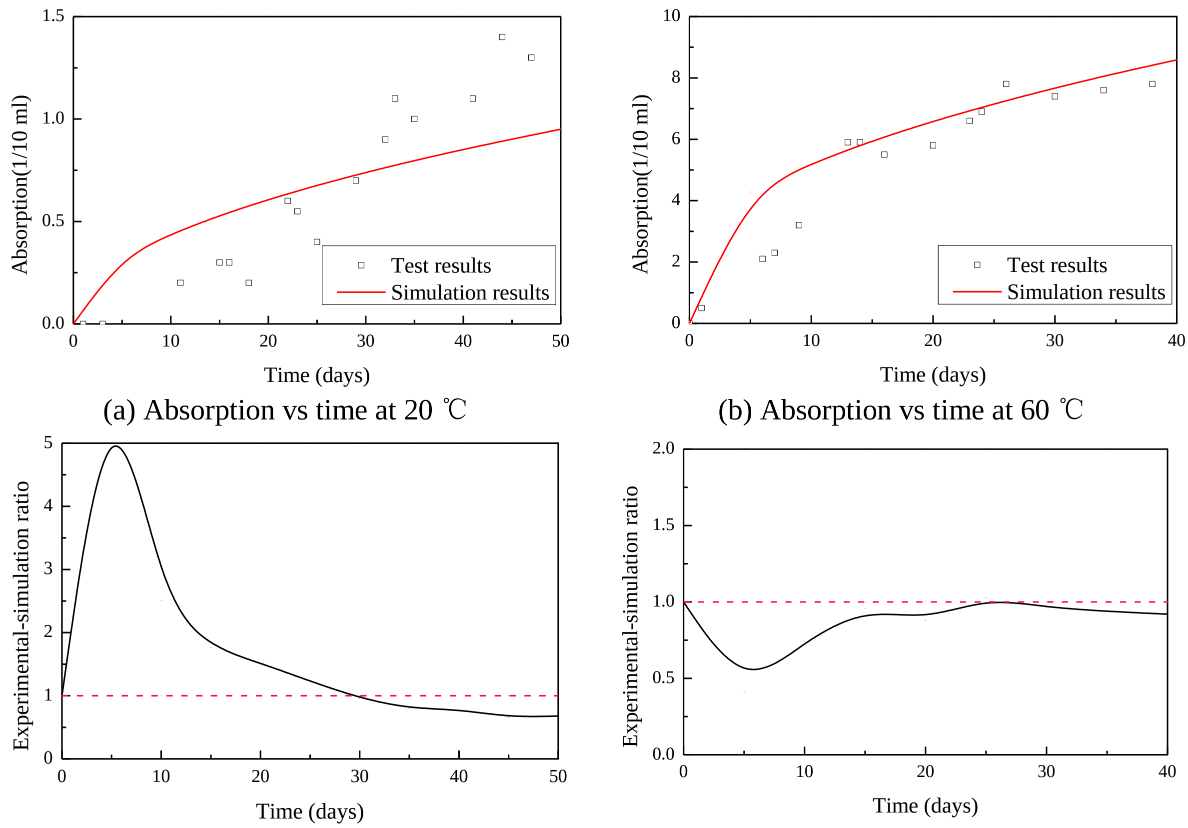



**Figure 4 Geometry and boundary conditions of bitumen film finite element mesh**

## Comparison

For validation of the gas diffusion model in the CAPA-3D FE system, the comparison of the test results and the simulation results are shown in Figure 5. Discounting for some experimental difficulties encountered at the beginning of the test at 20 ℃, Figure 5 shows an overall agreement between the test results and the simulations.

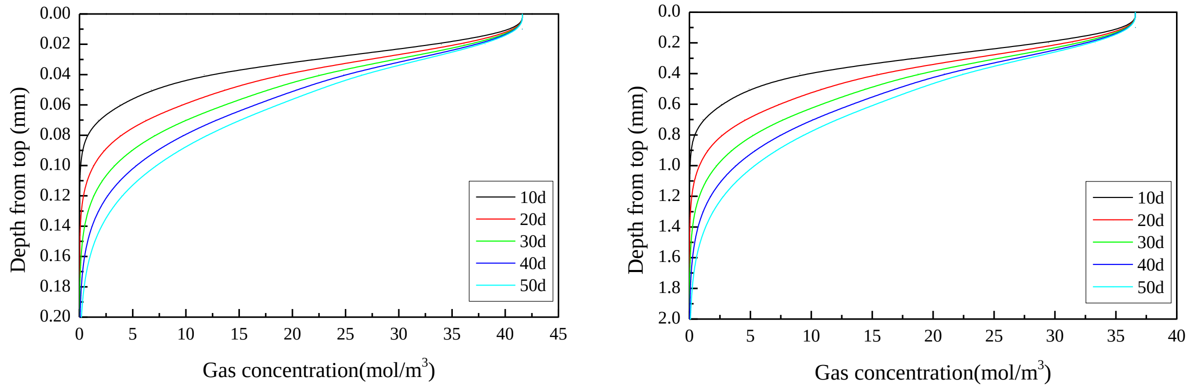



(a) Absorption vs time at 20 ℃ (b) Absorption vs time at 60 ℃

(c) Experimental-simulation ratio vs time at 20 ℃ (d) Experimental-simulation ratio vs time at 60 ℃

**Figure 5. Comparison of test results and CAPA-3D calculated results.**

The gas concentration profiles at different time intervals are shown in Figure 6. Results from the gas diffusion simulations at a given time (days) clearly show that the bitumen film has larger values of gas concentration at 60 ℃ compared to those at 20 ℃. The diffusion rate is increased with increasing temperature. After 50 days of diffusion, the gas diffused into the bitumen only to a depth of 0.2 and 2 mm at 20 and 60 ℃, respectively.




(a) 20 ℃ (b) 60 ℃

**Figure 6 CAPA-3D simulated gas concentration in a bitumen film at different times and temperatures**

## APPLICATION

### Development of 3-D micromechanical mesh

The importance of an accurate representation of the internal structure of an asphalt mix is quite significant in micromechanical finite element modelling since each mixture component has its particular gas diffusion characteristics and, therefore, the geometry of every phase plays an important role in the transport of gas. To address this issue, in this study, a 3-D micromechanical FE mesh was produced from X-ray CT scans by means of ScanIP, a specialized 3-D–based image processing software. In this study, a FE mesh obtained from a porous asphalt mixture was used, Figure 7.

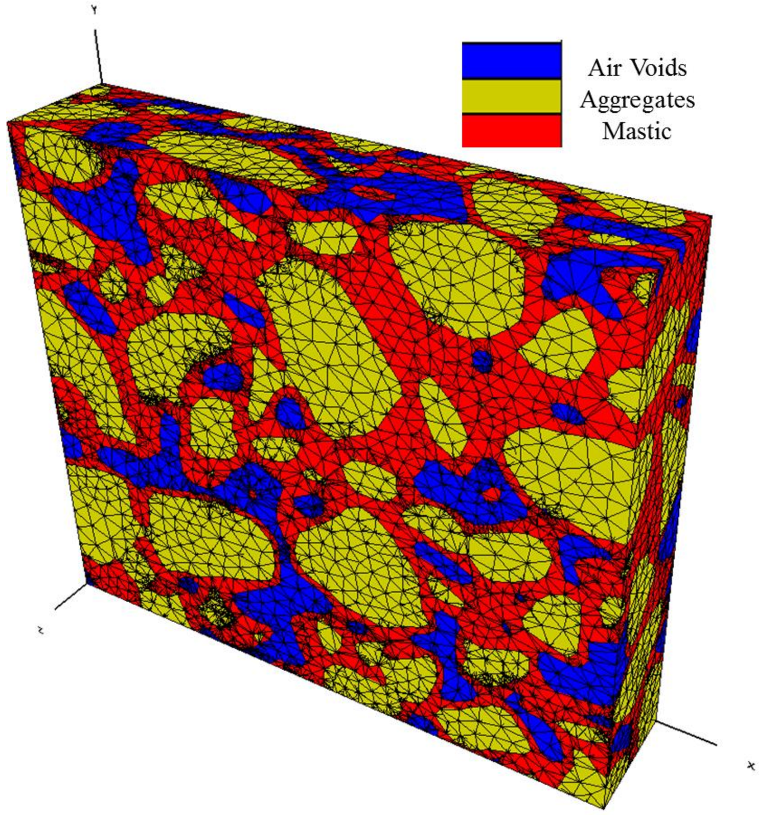



**Figure 7. Volume rendering of FE mesh for PA mixture**

A sample 60 mm in height and 100 mm in diameter was prepared in the laboratory by using a roller compactor, and then used for X-ray CT scanning. The PA mixture had a nominal maximum aggregate size of 10 mm; the particle size distribution and physical properties of the mixture are given in Figure 8. The connectivity of the pores is critical in determining the susceptibility of asphalt mixtures to gas diffusion. For the PA, pore connectivity reached almost 90% of the total volume of the air void phase.

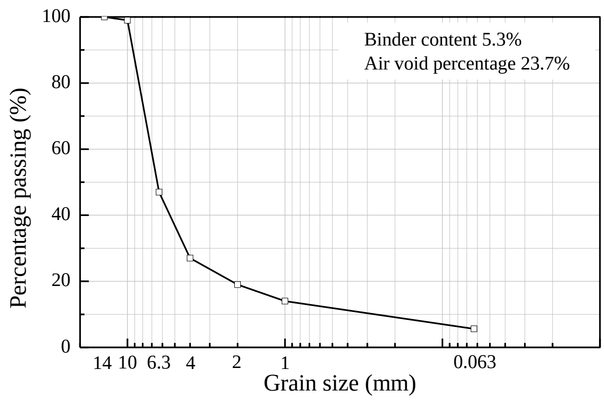



**Figure 8. Aggregate gradation and physical properties of PA mixture**

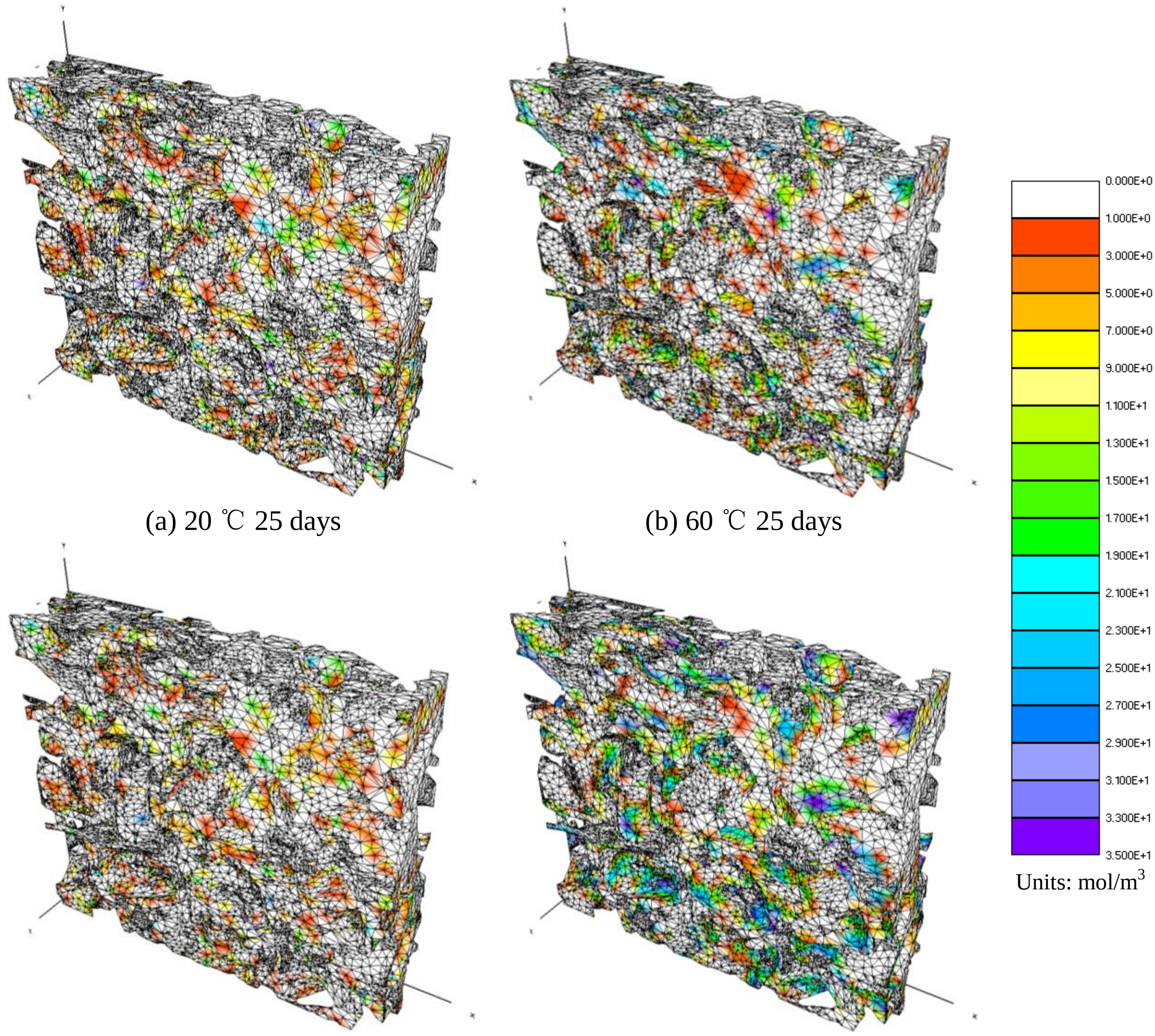
After the segmented data were cropped to the desired dimensions, a robust meshing algorithm was applied to enable the conversion of the 2-D images into FE meshes, which were used for computational analyses via the CAPA-3D FE system. A region with 39.6 mm in height, 39.6 mm in length and 9.85 mm in width of PA mesh was selected for analyses. This area was discretized by using 3-D linear four-node tetrahedral elements and consists of 312,304 elements in total.

**Micromechanical finite element gas diffusion simulations**

Gas diffusion through the asphalt mixture components is considered to be a process that occurs at the molecular level. For PA mixture, gas was set not to diffuse into aggregates, and diffused into air void with a relatively high diffusion coefficient. During the simulations, a constant gas concentration boundary condition (41.60 and 36.60 mol/$m^3$ at 20 and 60 ℃, respectively) was applied on the top, while no flow out of the four sides and bottom boundaries was considered, in order to approximately simulate the condition of asphalt pavement in the field.

By making the simplification that the gas diffusion coefficients of mortar are the same as those of bitumen diffusion coefficients of $5.108\times10^{-16}$ and $4.463\times10^{-14}$ $m^2/s$ at 20 ℃ and 60 ℃ were utilized for the mastic films. The diffusion coefficients of aggregates were set at 0 at both temperatures. The gas diffusion coefficients in a gaseous medium were assumed to be $7.753\times10^{-5}$ and $9.45\times10^{-5}$ $m^2/s$ at 20 ℃ and 60 ℃, respectively, as reported in the study by Marrero et al [20].

The finite element results of the gas concentration in the mortar at different time intervals are shown in Figure 9. Results from the gas diffusion simulations at various days clearly show greater values of gas concentration at 60 ℃ compared with those at 20 ℃. The diffusion rate increases with increasing temperature.




(a) 20 ℃ 25 days (b) 60 ℃ 25 days

(c) 20 ℃ 50 days (d) 60 ℃ 50 days

**Figure 9. Gas concentration in the mortar phase of PA mixture after different days of gas diffusion at different temperatures**

## CONCLUSIONS

Given the strong relation between gas diffusion and aging, knowledge of the gas concentration profile in thin films and asphalt mixtures is of uppermost importance. For this reason, a series of gas absorption experiments were conducted on bitumen films at different temperatures by means of an improved version of van Oort's test set up.

In order to perform diffusion finite element simulations with the CAPA-3D FE system it was necessary to find a methodology to determine the diffusion coefficients used as input. To get the diffusion coefficients a Laplace transform based solution of the diffusion equation was applied. The derived diffusion coefficients were used to simulate absorption versus time at two different temperatures, 20 and 60 degrees Celsius. The measured absorption values from the experimental tests were in good correspondence with the ones coming out of the FEM simulations. The CAPA-3D simulation results clearly confirm the well-known fact that gas diffuses faster in bitumen/mortars at higher temperatures, because both the diffusion coefficients of bitumen and the movement of gas molecules are temperature dependent.

In ongoing research, the same experimental setup will be used to measure gas absorption in the presence of oxygen or air in bitumen, mastics and mortars. This will enable the introduction of oxygen interaction terms into the formulation of the differential equation of gas transport in bituminous binders.

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## REFERENCES

1. Lesueur, D., *The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification.* Advances in Colloid and Interface Science, 2009. **145**(1–2): p. 42-82.
2. Siddiqui, M.N. and M.F. Ali, *Investigation of chemical transformations by NMR and GPC during the laboratory aging of Arabian asphalt.* Fuel, 1999. **78**(12): p. 1407-1416.
3. Saoula, S., et al., *Analysis of the rheological behavior of aging bitumen and predicting the risk of permanent deformation of asphalt.* 2013.
4. Kliewer, J.E., C.A. Bell, and D.A. Sosnovske, *Investigation of the relationship between field performance and laboratory aging properties of asphalt mixtures*, in *Engineering Properties of Asphalt Mixtures and the Relationship to Their Performance*. 1995, ASTM International.
5. Herrington, P.R., *OXIDATION OF BITUMEN IN THE PRESENCE OF A CONSTANT CONCENTRATION OF OXYGEN.* Petroleum Science and Technology, 1998. **16**(9-10): p. 1061-1084.
6. Jin, X., et al., *Fast-Rate–Constant-Rate Oxidation Kinetics Model for Asphalt Binders.* Industrial & Engineering Chemistry Research, 2011. **50**(23): p. 13373-13379.
7. Liu, M., et al., *The kinetics of carbonyl formation in asphalt.* AIChE Journal, 1996. **42**(4): p. 1069-1076.
8. Domke, C.H., R.R. Davison, and C.J. Glover, *Effect of Oxygen Pressure on Asphalt Oxidation Kinetics.* Industrial & Engineering Chemistry Research, 2000. **39**(3): p. 592-598.
9. Juristyarini, P., R. Davison, and C.J. Glover, *Oxidation Hardening Kinetics of the Rheological Function* $G'/(\eta'/G')$ *in Asphalts.* Petroleum Science and Technology, 2011. **29**(19): p. 2027-2036.

10. Anderson, A.P. and K.A. Wright, *Permeability and Absorption Properties of Bituminous Coatings.* Industrial & Engineering Chemistry, 1941. **33**(8): p. 991-995.
11. Beckman, A.O., et al., *Bituminous Coatings.* Industrial & Engineering Chemistry, 1941. **33**(8): p. 984-990.
12. Karlsson, R. and U. Isacsson, *Application of FTIR-ATR to characterization of bitumen rejuvenator diffusion.* Journal of Materials in Civil Engineering, 2003. **15**(2): p. 157-165.
13. Petersen, J.C., et al. *A review of the fundamentals of asphalt oxidation chemical, physicochemical, physical property, and durability relationships*. 2009.
14. Dickinson, E.J., J.H. Nicholas, and S. Boas-Traube, *Physical factors affecting the absorption of oxygen by thin films of bituminous road binders.* Journal of Applied Chemistry, 1958. **8**(10): p. 673-687.
15. Periasamy, R., *THE MEASUREMENT OF OXYGEN TRANSPORT PARAMETERS FOR ASPHALT/AGGREGATE AND ASPHALT/GLASS SYSTEMS USING AN ELECTRODYNAMIC BALANCE.* Fuel Science and Technology International, 1995. **13**(6): p. 699-711.
16. Petersen, J., P. Harnsberger, and R. Robertson, *Factors affecting the kinetics and mechanisms of asphalt oxidation and the relative effects of oxidation products on age hardening.* Preprints of Papers, American Chemical Society, Division of Fuel Chemistry, 1996. **41**(CONF-960807--).
17. Herrington, P.R., *Diffusion and reaction of oxygen in bitumen films.* Fuel, 2012. **94**: p. 86-92.
18. Han, R., X. Jin, and C. Glover, *Oxygen diffusivity in asphalts and mastics.* Petroleum Science and Technology, 2013. **31**(15): p. 1563-1573.
19. Oort, W.P.v., *a study of the ageing of asphaltic bitumen*. 1954, Delft University of Technology.
20. Marrero, T.R. and E.A. Mason, *Gaseous diffusion coefficients.* Journal of Physical and Chemical Reference Data, 1972. **1**(1): p. 3-118.