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EXPERIMENTAL AND COMPUTATIONAL INVESTIGATION OF GAS DIFFUSION IN BITUMEN

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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

1   INTRODUCTION

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

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

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

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

29   EXPERIMENTAL METHOD

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

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

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

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

48   For the sample, the tube with an internal diameter of about 35 mm, was filled with 20 grams of
49   bitumen (PEN 70/100). Then the dripping bitumen formed a 20 mm thick flat layer on top of the wad
50   of quartz wool under influence of gravity, Figure 1 (b). As both oxygen and nitrogen are diatomic
51   molecules and their van der Waals radii are very similar (N_2; 150×10^{-12} m, O_2; 140×10^{-12} m), the
52   diffusion coefficient of nitrogen can be used to simulate oxygen diffusion, but without any
53   aging effects.

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

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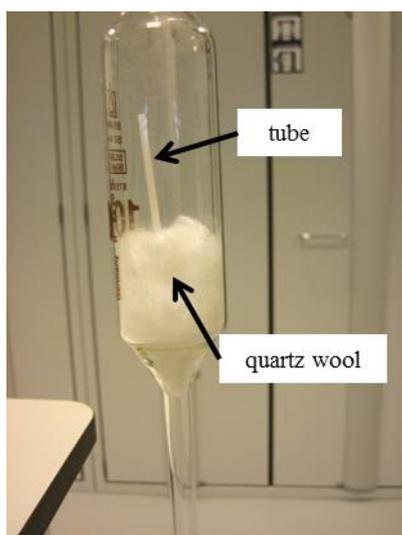
(a) Small tube balances pressure change   (b) Bituminous material filling

<div align="center">
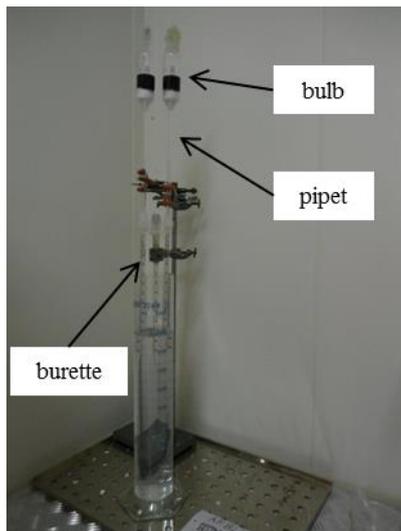
(c) Measuring instrument   (d) Temperature controlled environment

</div>

69   **Figure 1   Experimental setup**

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

72   **Results and Discussion**
73   The resulting absorbed nitrogen from the recordings at different temperatures are presented in Figure
74   2. The increasing rate of absorption over time was larger at the beginning and decreased later. It can
75   be seen that the absorbed nitrogen at 60 °C is more than at 20 °C. This shows that gas absorption at
76   this elevated temperature is faster than at lower temperatures.
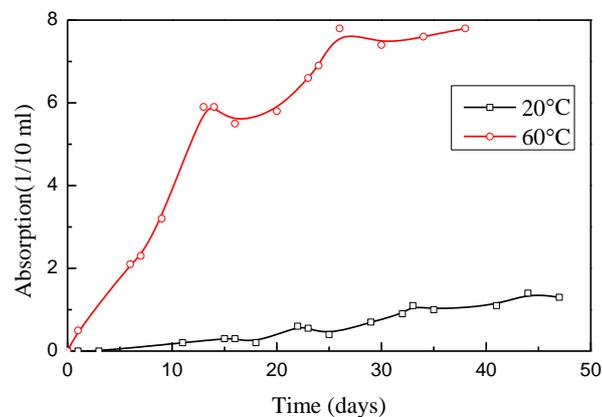
77

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

79   **SOLUTION OF THE GAS DIFFUSION EQUATION**

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

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

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

85
$$x = 0 \quad \frac{\partial c}{\partial x} = 0$$
$$x = a \quad c = c_0$$
(2)

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

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

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

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

91
$$x = 0 \quad \frac{\partial \bar{c}}{\partial x} = 0$$
$$x = a \quad \bar{c} = \frac{c_0}{p}$$
(5)

92   where p is the Laplace transform variable.

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

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

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

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

99   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

100   latter results to :

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

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

105   $$c = \text{Res}(p = 0) + \sum_{n=0}^{\infty} \text{Res}(p = p_n)$$ (9)

106   It can be shown that :

$$\text{Res}(p = 0) = c_0$$

107

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

108   and therefore :

109

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

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

111

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

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

114

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

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

(a) 20 ℃   (b) 60 ℃
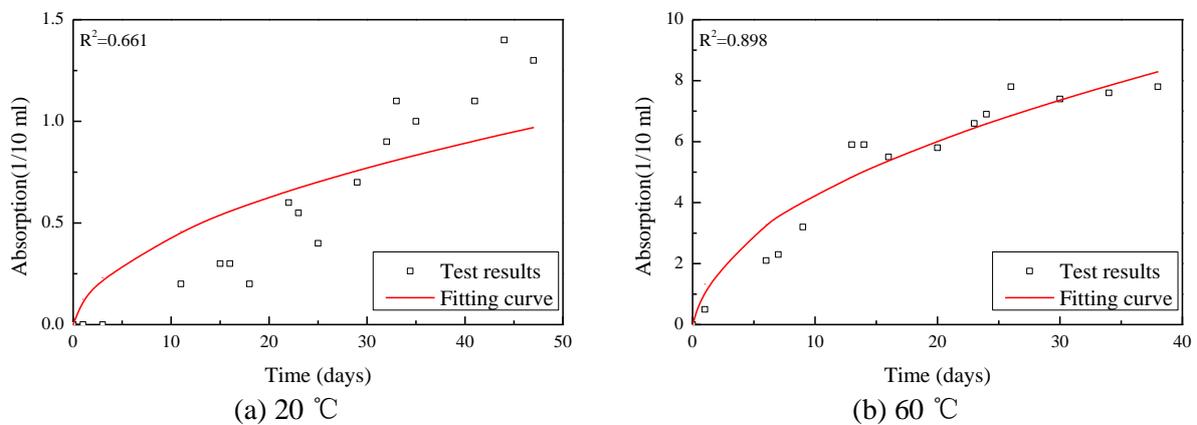
121   **Figure 3   Absorbance curve fitting**

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

124   4.463×10^{-14} m^2/s at 20 ℃ and 60 ℃, respectively. These values are similar to those of van Oort
125   (around 7.2×10^{-16} m^2/s at 50 ℃). In summary, the gas diffusion coefficient of bitumen increases
126   when the temperature increases. The coefficient at 60 ℃ is about 100 times of that at 20 ℃.

MODEL VALIDATION

127

Simulation

128
129   Simulations of gas diffusion in 3D thin bituminous films were performed for a 50 days' time period
130   which is similar to the duration of the experiments. As the samples in the experiments absorbed gas
131   from top and bottom, the geometry of the bituminous film is modelled as a block with a thickness of
132   10 mm, length of 2 mm and a width of 2 mm. The bituminous film was assumed to be an isotropic
133   material. The diffusion coefficients were obtained based on the measurements performed in the
134   previous section. The input values of the diffusion coefficients were 5.108×10^{-16} m^2/s and 4.463×10^{-14} m^2/s at 20 ℃ and 60 ℃, respectively.
135

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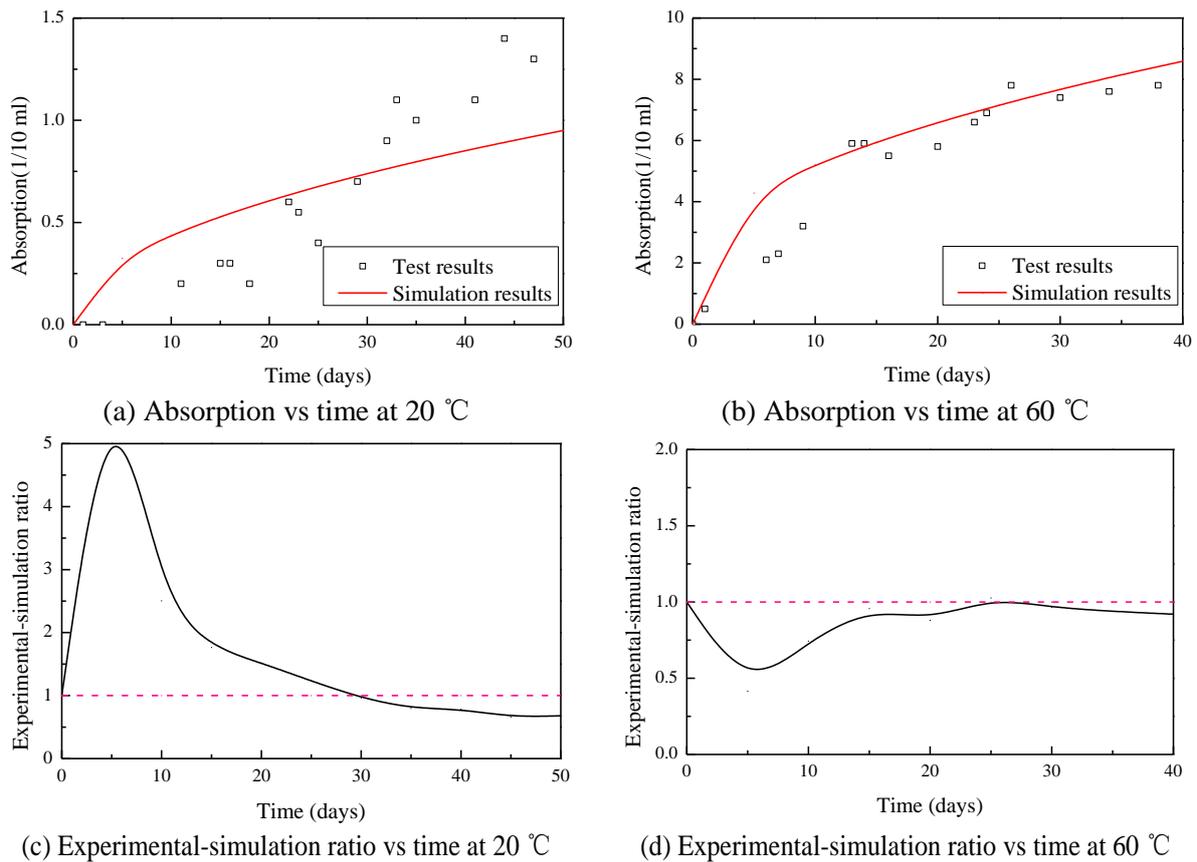140   boundaries, Figure 4.

141
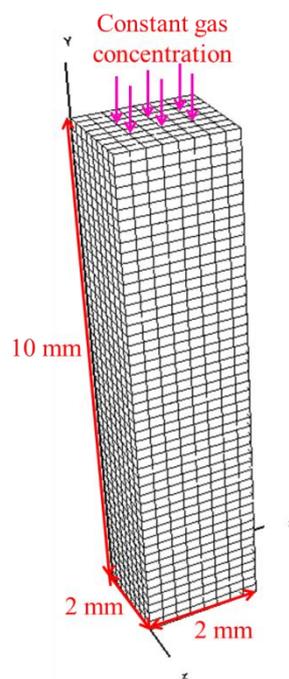
Figure 4   Geometry and boundary conditions of bitumen film finite element mesh

142

Comparison

143
144   For validation of the gas diffusion model in the CAPA-3D FE system, the comparison of the test
145   results and the simulation results are shown in Figure 5. Discounting for some experimental
146   difficulties encountered at the beginning of the test at 20 ℃, Figure 5 shows an overall agreement
147   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 ℃

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

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

(a) 20 ℃

(b) 60 ℃
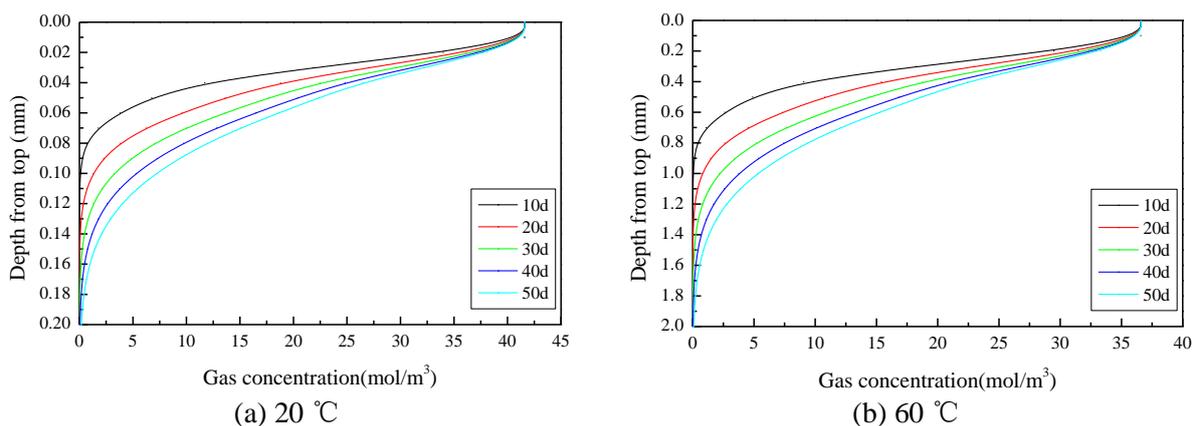
154 **Figure 6   CAPA-3D simulated gas concentration in a bitumen film at different times and**
155 **temperatures**

156 **APPLICATION**

157 **Development of 3-D micromechanical mesh**
158 The importance of an accurate representation of the internal structure of an asphalt mix is quite
159 significant in micromechanical finite element modelling since each mixture component has its
160 particular gas diffusion characteristics and, therefore, the geometry of every phase plays an important

161   role in the transport of gas. To address this issue, in this study, a 3-D micromechanical FE mesh was
162   produced from X-ray CT scans by means of ScanIP, a specialized 3-D–based image processing
163   software. In this study, a FE mesh obtained from a porous asphalt mixture was used, Figure 7.
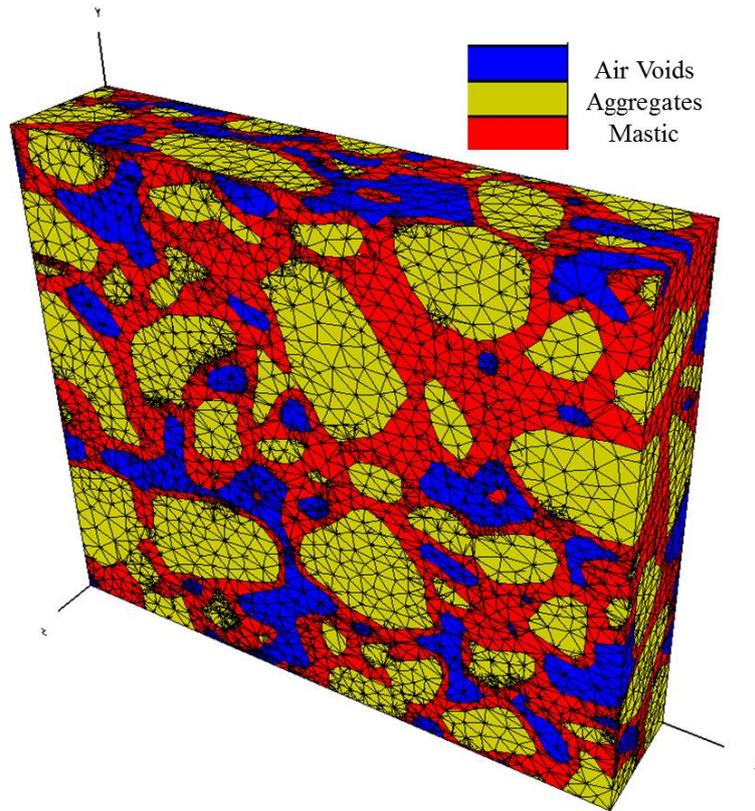

164

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

166   A sample 60 mm in height and 100 mm in diameter was prepared in the laboratory by using a roller
167   compactor, and then used for X-ray CT scanning. The PA mixture had a nominal maximum aggregate
168   size of 10 mm; the particle size distribution and physical properties of the mixture are given in Figure
169   8. The connectivity of the pores is critical in determining the susceptibility of asphalt mixtures to gas
170   diffusion. For the PA, pore connectivity reached almost 90% of the total volume of the air void phase.
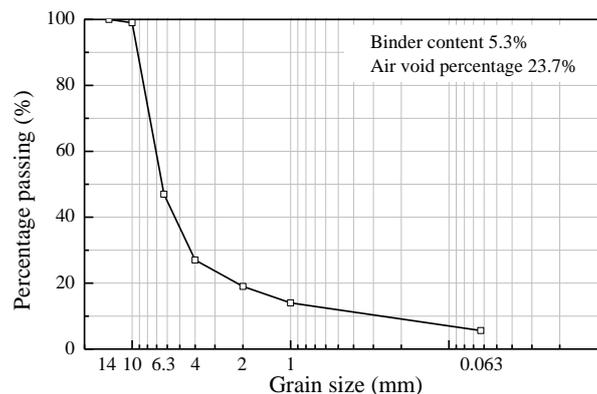
171

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

173   After the segmented data were cropped to the desired dimensions, a robust meshing algorithm was
174   applied to enable the conversion of the 2-D images into FE meshes, which were used for
175   computational analyses via the CAPA-3D FE system. A region with 39.6 mm in height, 39.6 mm in

176 length and 9.85 mm in width of PA mesh was selected for analyses. This area was discretized by
177 using 3-D linear four-node tetrahedral elements and consists of 312,304 elements in total.

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

185 By making the simplification that the gas diffusion coefficients of mortar are the same as those of
186 bitumen diffusion coefficients of 5.108×10^{-16} and 4.463×10^{-14} m^2/s at 20 ℃ and 60 ℃ were utilized
187 for the mastic films. The diffusion coefficients of aggregates were set at 0 at both temperatures. The
188 gas diffusion coefficients in a gaseous medium were assumed to be 7.753×10^{-5} and 9.45×10^{-5} m^2/s
189 at 20 ℃ and 60 ℃, respectively, as reported in the study by Marrero et al [20].

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

(a) 20 ℃ 25 days   (b) 60 ℃ 25 days

(c) 20 ℃ 50 days   (d) 60 ℃ 50 days
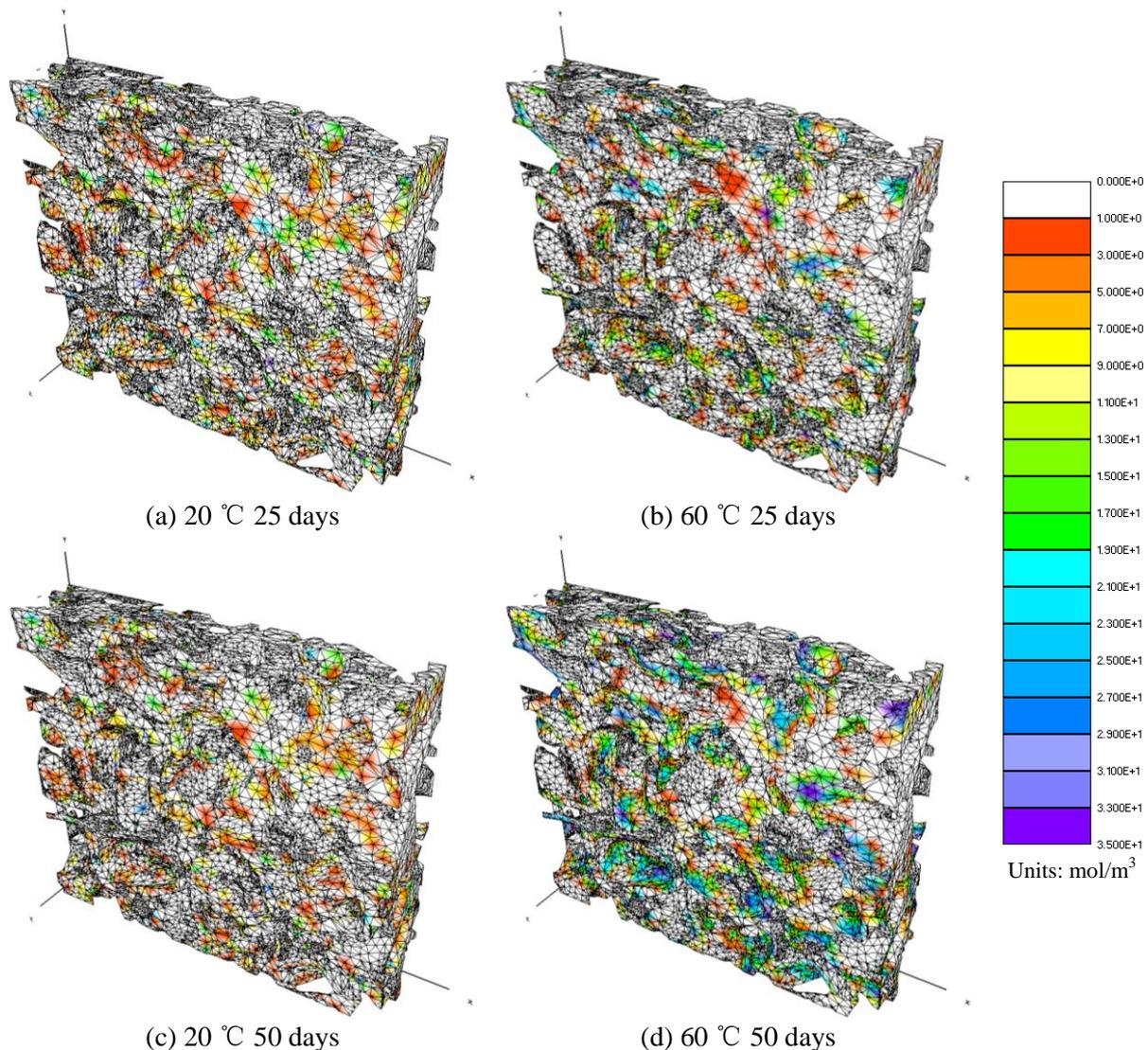
194 **Figure 9. Gas concentration in the mortar phase of PA mixture after different days of gas**
195 **diffusion at different temperatures**

196 ## CONCLUSIONS

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

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

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

214 ## ACKNOWLEDGMENTS

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