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Comprehensive review on the transport and reaction of oxygen and moisture towards coupled oxidative ageing and moisture damage of bitumen

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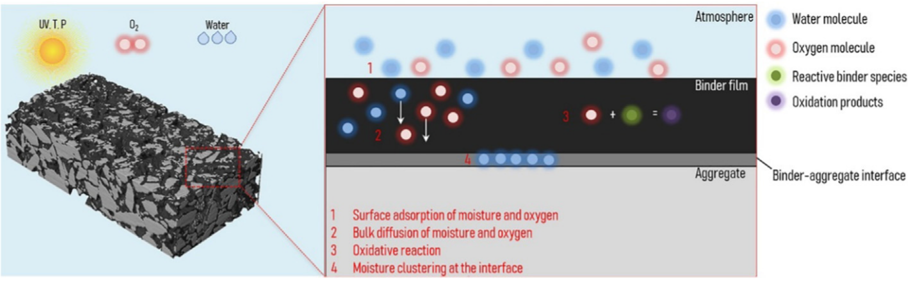
HIGHLIGHTS

- Oxygen-moisture kinetics control the oxidative ageing and moisture damage of bitumen.
- The transport and reaction processes of moisture and oxygen in bitumen are reviewed.
- Moisture-oxygen strongly affect the physicochemical and mechanical bitumen properties.
- The possibilities for coupling the effects of moisture and oxygen are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxidative ageing and moisture damage are key factors in bitumen degradation and asphalt pavement deterioration. The effects of oxygen and moisture on bitumen are governed by their transport and reaction processes. This paper provides an overview of theories and concepts developed to describe the kinetics, thermodynamics and mechanisms of transport and reaction of moisture and oxygen within bitumen. The moisture- and oxygen-induced changes of the physicochemical and mechanical properties of bitumen are also discussed. The aim is to summarize literature findings and conclusions and discuss the possibilities of establishing coupled moisture-oxygen models to be used for long-term pavement performance predictions.

1. Introduction

Bitumen, which is the residue from the distillation of crude oil, has been used widely to construct asphalt pavements for quite a long time. However, the durability of asphalt pavements can be significantly compromised by environmental factors that can cause or accelerate distresses such as raveling, rutting, cracking etc. Many studies have focused on the mechanisms and factors resulting in pavement damage [1–3]. Specifically, it is considered that moisture transport and oxidative ageing play a fundamental role in the raveling and cracking of asphalt pavements [4,5]. The ubiquitous presence of oxygen and moisture in ambient environment demonstrates the need for research of the moisture and oxygen damage related mechanisms and their effect on bitumen properties and pavement performance. Quantifying the transport and reaction processes of moisture and oxygen in bitumen can enable the prediction of bitumen properties, and in turn of pavement performance. Moreover, the selection of materials with lower diffusion coefficients of oxygen and moisture, can decrease the damage rate, thus an extension of the service life of a pavement can be achieved [6,7].

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Water/vapor transport in bituminous mixtures involves convective flow in the void network of the mixtures and diffusion into the bitumen and aggregates as indicated in Fig. 1. Water flow in the voids can be quantified using permeability, which is determined using Darcy's law or Fick's law for different mixture types, where the mixture type, void content, void distribution and traffic pressure are dominant factors [8,9]. Water in the voids can then diffuse through the bitumen bulk and interact with the bitumen to cause a reduction in cohesion (cohesive strength). The bitumen properties such as the chemical composition and the ageing level govern the diffusion behavior. With time, moisture can further reach the bitumen-aggregate interface, compromise the adhesive bond (strength) and result in bitumen stripping [10]. Overall, the concentration gradient required for the diffusion in the bitumen and at the interface is provided by the water/vapor flow in the voids, leading to cohesive failure within bitumen and adhesion failure at the interface. As the concentration of moisture increases, the failure mode can change from cohesive to adhesive failure [11]. The transport of moisture/water can be regarded as one of the fundamental contributing factors to moisture damage [12]. This paper discusses the moisture diffusion behavior within bitumen at the micro-scale, including the following consecutive steps: (i) moisture adsorption on the surface, (ii) diffusion into the bitumen film and, (iii) the clustering at the bitumen-aggregate interface. Many attempts have been made to formulate the mathematical descriptions about the sorption and transport process in various solid and liquid matrices such as metals, polymers and petroleum, involving the transport kinetics and thermodynamic equilibrium state as a function of temperature, pressure, species etc. In most of the cases, Fick's law is used and puts forward continuum and phenomenological equations governing the diffusion process. However, the diffusion of moisture in bitumen can show non-Fickian behavior possibly because of the clustering of water molecules and the bonding interaction between water molecules and functional groups of bitumen [13]. Moreover, there is still no standard or universally accepted method to measure the diffusion coefficient of bitumen. More efforts are still needed to better describe diffusion of moisture in bitumen.

In addition to moisture diffusion, oxygen (that exists in atmospheric air and hence in the voids of bituminous mixtures) diffuses into the bitumen and provides an oxygen source for oxidative reaction in bitumen. As a result, the active bitumen components can react with oxygen and lead to bitumen hardening and embrittlement. Several studies have been performed about the chemical, physicochemical and mechanical characterization of bitumen after oxidation [14–17]. The chemical composition of bitumen varies widely with the crude oil source, and the test data from different types of bitumen may show dissimilar properties and characteristics. The oxidative reaction in bitumen is primarily dependent on the bitumen microstructure and chemistry, but also on temperature, pressure and UV light [18]. The fraction of polar and strongly-associating groups coming from oxidative reaction in bitumen changes with ageing time, followed by molecular agglomeration and structural rearrangement. The oxidative reaction keeps consuming the diffused oxygen in bitumen, leading to further diffusion of oxygen. Terminal state can be reached when there are no more reactants in bitumen and no concentration gradient of oxygen [19]. Coupling of the oxygen diffusion and reaction processes in bitumen can demonstrate the dynamic oxygen concentration and reaction kinetics, which can be used in lifetime prediction [20–22]. Disturbed microstructure and increased polarity of bitumen may impede further diffusion of oxygen by denser molecule distribution and cause a non-Fickian diffusion process.

Moisture and oxygen are two mutually affected factors for pavement deterioration, which cause continuous degradation of bitumen. It seems reasonable that moisture transport can be influenced by the oxidative ageing action. The oxidation of bitumen produces functional groups with high polarity. As a result, more water/moisture molecules may interact and bond to the molecular chains and cluster around them, making it thus more complicate to explain the moisture diffusion phenomenon [23]. What's more, as bitumen is suggested to have a colloidal structure where the

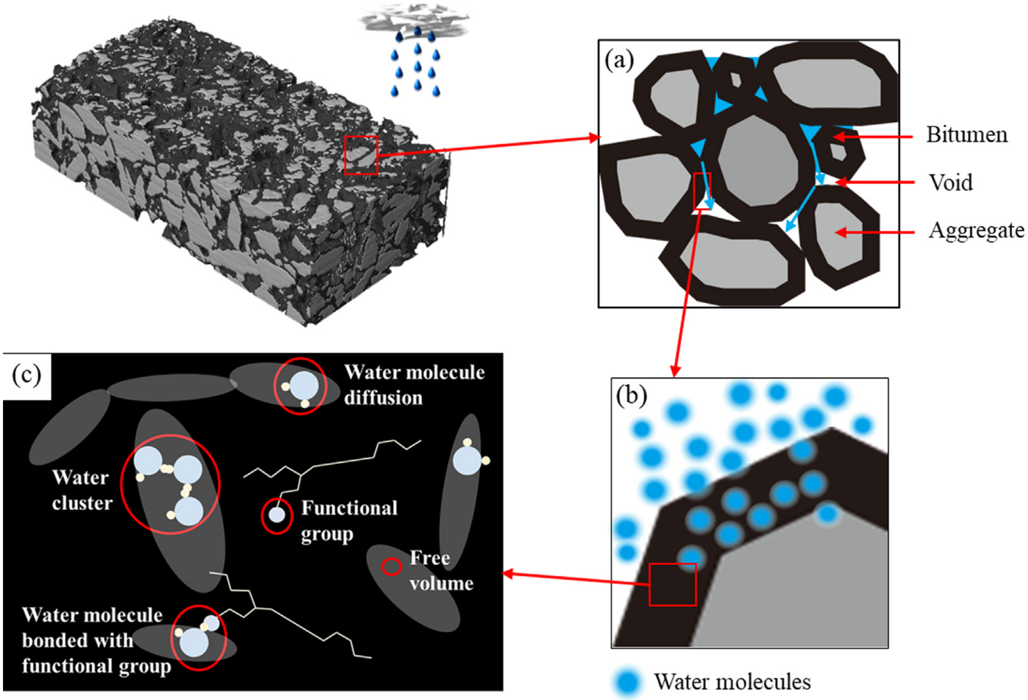

Fig. 1. Water transport in asphalt pavement: (a) convective water flow; (b) water diffusion within bitumen; (c) water diffusion mechanisms.

asphaltenes act as the micelles surrounded by resins, ageing can disturb this spatial structure and change its physicochemical properties, which is essentially related to the diffusion path and diffusion rate of moisture [24]. Studies about the effect of moisture on the ageing process turn to be ambiguous. Some results show little indication that moisture can influence the rheological properties of aged bitumen during ageing [25]. On the other hand, there are also findings that water can disrupt the colloidal structure of bitumen and increase the ageing extent [26]. Water may even intervene in the oxygen reaction kinetics via working with UV light and bitumen [27,28]. Moisture and oxygen should be considered as two inseparable species and they both can affect the microstructural stability and chemical composition of bitumen [26,29]. As such, also the transport behavior of moisture may be affected by oxygen through changes in the microstructure and chemistry and vice versa.

This paper, focusing on bitumen, discusses the transport and reaction processes and mechanisms of moisture damage and oxidative ageing, with the aim to explore and explain the coupled moisture- and ageing-induced damage evolution in bitumen and bituminous mixtures. In view of the limited papers on diffusion and coupled moisture-oxygen phenomena in bitumen, literature studies from other areas, specifically from polymers and petroleum, are included to better discuss this topic. The development of theories and models about the sorption and diffusion kinetics are introduced, for which detailed testing procedures and parameter determination methodologies are explained. Oxidative reaction kinetics and analysis are shown and the integration of the diffusion and reaction processes is elaborated. In order to present, quantify and explain the transport and reaction phenomena, the changes in the physical, chemical, morphological and mechanical parameters of bitumen and bituminous mixtures are also considered in this review. After individually introducing the moisture and oxygen behavior, the issues and challenges to develop advanced models on coupled moisture and oxygen diffusion–reaction in bitumen and upscale to bituminous mixture level are discussed. This review mainly considers the physical and chemical models and mechanisms of transport and reaction of oxygen and moisture in bitumen; more comprehensive reviews about the oxidative ageing properties [14], laboratory ageing tests [15], and mechanisms and characterization of moisture damage [30,31] are recommended to the readers to further understand ageing and moisture damage of bitumen and bituminous mixtures.

2. Transport and sorption models and mechanisms

2.1. Definition of transport and sorption

Mass can be transported by molecular motion (diffusion) and bulk motion of fluid (advection). In this paper, the terms diffusion behavior and transport directly refer to diffusion transport phenomena, unless explicitly stated otherwise. Diffusion is defined as the movement of a chemical species from a region of high concentration to a region of low concentration. Diffusion behavior can be interpreted as the kinetic transport process characterized by the diffusion coefficient. The thermodynamic equilibrium state resulting from diffusion can be evaluated by sorption or solubility. In most cases, diffusion and transport are cited indicating the kinetic molecular motion, whereas sorption denotes the equilibrium state [32]. Sorption includes both surface adsorption and bulk absorption. Adsorption is used to describe the process in which gas molecules are attached to sites on an internal or external surface and absorption shows the dissolution of gases in the bulk [33].

In bitumen, we mainly focus on the diffusion process of oxygen and moisture considering their significant effects on bitumen properties and pavement performance. Moisture is the presence of water in trace amount. In this paper, water and moisture are used interchangeably. Water molecules are dipolar with hydrogen bonding. The polar attribute results in the strong interactions of water and other polar groups in bitumen. Absorbed water may show three different states: single free water molecule, aggregated water molecules and water molecules bonded with polar groups of bitumen (Fig. 1). The clustering of moisture contains both mutual agglomerates between water molecules and water-polar group interactions [13,34]. In the case of mixtures, water can cluster at the interface between the bitumen film and the aggregates. The cluster phenomenon in this paper indicates the interaction of water molecules with polar groups in the bulk of bitumen, if without clarification. Limited literature has been published to discuss the diffusion behavior and mechanisms in bitumen. Therefore, it is essential to introduce the basic theories about transport and sorption in order to better understand the diffusion mechanism of moisture and oxygen in bitumen.

2.2. Sorption equilibrium

2.2.1. Surface adsorption

Adsorption and desorption processes are divided into two categories including physical adsorption and chemisorption. Physical adsorption resembles the condensation of gases to liquids and is dependent on the physical force of attraction between the solid absorbent and the adsorbate gas [35]. Physical adsorption is rapid and reversible and the adsorption heat should be in the range of the condensation heat. Chemical adsorption results from the reaction of vapor and surface species [36]. Compared with physical adsorption, chemisorption is distinguishable by the higher adsorption heat, suggesting the generation of chemical bonds. At high temperature, it is possible that chemisorption is observed with high activation energy whereas the physical adsorption is small because of low adsorption energy.

Many theories relatable to adsorption isotherms have been developed based on kinetic motion or energy. The isotherm model proposed by Langmuir separates the kinetic adsorption process from adsorption and desorption and concerns the vapor attached to the surface as monolayer [37]. When the adsorption and desorption rates are equal and the adsorption is at dynamic equilibrium, one can get the isotherm equation:

$$c = C'_H bp/(1 + bp) \tag{1}$$

where c is the adsorbed gas concentration, C'_H is the Langmuir capacity factor, p is the gas partial pressure and b is the Langmuir affinity constant. Langmuir fits the Type I (Fig. 2) isotherm curve introduced by Brunauer [38], while most adsorption processes reveal multilayer adsorption which is later illustrated by the Brunauer–Emmett–Teller (BET) model. The BET model extends Langmuir's approach to multilayer adsorption, which is very common in cases of physical adsorption [39,40]. Other isotherm models (Freundlich, Redlich–Peterson, Dubinin–Radushkevich, Guggenheim–Anderson–de Boer and Radke–Prausnitz isotherm) have been formulated to describe more complex conditions, such as polar adsorbate, micropore solids, etc. [41].

2.2.2. Bulk absorption

There are two parameters that control gas sorption and transport including gas solubility and diffusion coefficient. Solubility here thermodynamically refers to the saturated amount of gas dissolved in a solid. When the partial pressure is quite low and the solute state is similar to ideal gas, the ideal gas law, namely the Henry's law, can be used to describe solubility. Henry's law states that the saturated amount of gas in a solid is proportional to the

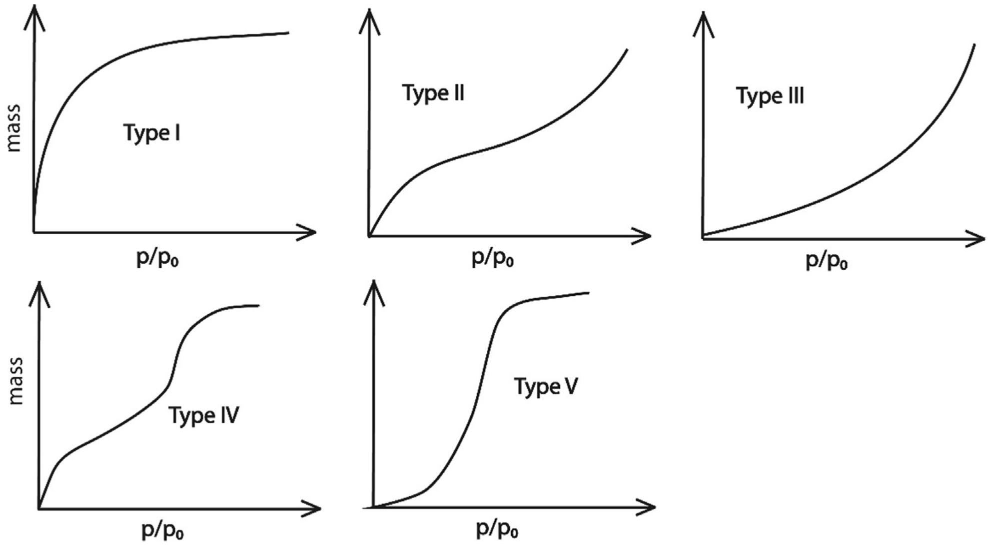

Fig. 2. Isotherm adsorption types (p/p_0 is the relative pressure of adsorbate and mass is the adsorbed amount of adsorbate) [38].

partial pressure of the gas. The mass transfer between different phases is mainly described by partition coefficients such as Henry's constant k_D:

$$c = k_D P \tag{2}$$

where c is the absorption concentration of a gas in solid and P is the partial pressure of a gas.

It should be emphasized that Henry's law describes a strict equilibrium state of no flux through gas–solid interface. As long as there is a concentration gradient, Henry's law is violated and net flux occurs [42]. The Henry's law applies only to the solutes of infinite dilution without considering the effect of interaction between solute and solvent. The Flory-Huggins theory can be used to indicate the interaction between solute (such as water vapor) and solvent (such as polymer or bitumen) using water activity α_1, a function of the volume fraction $\phi_1$of the solute and the Flory-Huggins interaction parameter χ [34]:

$$\alpha_1 = \phi_1 exp\left((1-\phi_1) + \chi(1-\phi_1)^2\right) \tag{3}$$

This theory considers that water molecules can interact not only with the polar groups in the solid phase but with themselves through hydrogen bonding. Three molecule states are possible dependent on the composition of solid absorbents and water activity: single water molecule (without interaction with other water molecules or the solid phase), aggregated water molecule (water clustering with each other) and bonded water molecules (bonding between the water and the solid phase due to its hydrophilicity). When at lower water activity, the water molecules diffuse into the solid and interact with the solid molecules through Van de Waals and hydrogen forces. As the water activity increases, water molecules begin to cluster via hydrogen force.

Zimm and Lundberg [43] introduced a cluster integral parameter to illustrate the cluster tendency of water molecules in a polymer:

$$G_{11}/\upsilon_1 = -(1-\phi_1)\left[\partial\left(\frac{\alpha_1}{\phi_1}\right)/\partial\alpha_1\right]_{P,T} - 1 \tag{4}$$

where G_{11} is the cluster integral, υ_1 the partial molar volume of diffusing species, α_1 the water activity and ϕ_1 the water volume fraction. When $G_{11}/\upsilon_1 < -1$, gas or vapor molecules are more likely to stay isolated. When $G_{11}/\upsilon_1 > -1$, the molecules start to cluster and thus exert more complex effect on the whole sorption and diffusion process.

Brown [44] later combined the Flory-Huggins theory and the cluster theory to analyze the randomly distributed water molecules and restricted water molecules at the same time with the cluster number N_c:

$$N_c = 1 + K_1\phi_1 - K_1\phi_1^2 \tag{5}$$

where K_1 is constant and $\phi_1$the water volume fraction.

2.2.3. Coupled adsorption and absorption

Several mechanisms can contribute to sorption behavior including adsorption, absorption and clustering. A dual-mode sorption model of a gas in a polymer matrix has been proposed including surface sorption and bulk absorption. Combining the Langmuir-type adsorption and the Henry's law for absorption leads to the equilibrium concentration that can quantitatively be shown as [45]:

$$c = k_D p + C'_H bp/(1 + bp) \tag{6}$$

where c is the gas concentration, $C'_H$is the Langmuir capacity factor, k_D is the Henry's parameter, p is the gas partial pressure and b is the Langmuir affinity constant.

Moreover, the isotherm sorption of water can show a triple-mode sorption involving concentration in Henry's mode, Langmuir mode and clustering mode as described in the equation below:

$$\begin{aligned} c &= c_{Henry} + c_L + c_{cluster} \\ &= k_D p + C'_H bp/(1 + bp) + K'_c (k_D p_{sat})^n p^n / n \end{aligned} \tag{7}$$

where c is the gas concentration, c_{Henry} is the concentration from Henry's mode, c_L is the concentration from Langmuir mode, $c_{cluster}$ is the concentration from clustering mode, K'_c is the constant for clustering, p_{sat} is the saturated pressure and n is the mean number of water molecules per cluster [46].

2.2.4. Factors affecting sorption

Sorption isotherms vary with different gas–solid systems, pressure and temperature. Adsorption isotherms at different temperatures are determined by heat sorption. The constant factor (such as the Langmuir constant factor) in an isotherm equation can be a function of temperature and heat sorption via the Arrhenius equation. The sorption heat thus dictates whether the adsorbed gas content increases or decreases with temperature [47].

The saturated bulk absorption content or solubility of gas in the solid phase usually decreases with higher temperature and increases with pressure (Fig. 3) [48]. The temperature-dependent behavior of solubility can be described by the Arrhenius relationship:

$$S = S_0 exp(-\Delta H/RT) \tag{8}$$

where S is the solubility (mol/m-3), ΔH is the heat dissolution, R is the universal gas constant (8.314 J/K mol), T is the temperature (K) and $S_0$is the pre-exponential coefficient. Compared with the relationship between the sorption fraction and the partial pressure of diffusing species, a decrease in solubility with increasing temperature is not applicable in all cases. It depends on the dissolving process which can be endothermic or exothermic. In a wide range of temperatures, the solid matrix may go through structural or chemical changes, which also add to complexity of the relationship between sorption and temperature. Pace et al. [45] proposed that the Langmuir capacity factor, C'_H has different equations for different temperatures:

$$C'_H = \begin{cases} C_0 exp(-\Delta H_h/RT) \; T > T_g \\ C_0 exp(-\Delta H_h/RT_g) \; T < T_g \end{cases} \tag{9}$$

where ΔH_h is the enthalpy of hole formation (increase of microvoids during transition from glassy state to rubbery state), C_0 is the pre-exponential constant, T_g is the glass transition temperature. Moreover, different gases have varying solubility and the existence of other gas species in a system can affect the solubility of the target gas. Svreck et al. [49] showed that carbon dioxide was the most soluble and nitrogen was the least soluble in bitumen among the carbon dioxide, methane, and nitrogen gases. Including nitrogen in carbon dioxide can affect the solubility of carbon dioxide itself as shown in Fig. 3 [50]. The solubility is also related to the number of polar groups of materials. Particularly, water solubility has a complex relationship with the concentration and the position of polar groups. For example, water solubility has been found to increase with temperature in epoxy and nanoparticle-incorporated epoxy composites. This behaviour can be related to the higher contribution of bound water and the capability of water to be retained in a hydrothermally plasticized polymer [51].

2.3. Transport kinetics of sorption

2.3.1. Surface adsorption kinetics

Kinetics determine the evolution of surface adsorption with time. Pseudo-first-order (PFO) and pseudo-second-order (PSO) models are commonly used to predict the adsorption process. The PFO model developed by Lagergren, suggests a rate equation following the first order mechanism [52]:

$$dq/dt = k_1(q_e - q) \tag{10}$$

where q and q_e are the adsorbate (grams of solute per gram of sorbent) at time t and at equilibrium state respectively, $k_1$is the rate constant of first-order sorption, which is a linear function of the initial concentration of the solute.

On the other hand, the PSO model assumes the dq/dt is proportional to the available sites on the absorbent and the adsorption rate is a function of the number of active sites. The kinetics law is shown as

$$dq/dt = k_2(q_e - q)^2 \tag{11}$$

The effective adsorption kinetics can also be interpreted by considering adsorption rate and desorption rate [53]. The rate equation is

$$dq/dt = k_a c_0 (1 - \theta) - k_d \theta \tag{12}$$

where θ is the site fraction covered by adsorbate, c_0 is the molar concentration of the solute (the concentration is considered to be constant with time), k_a and k_d are the adsorption and desorption rate constants, respectively.

From equation (12) it can be derived (similar to the from PFO model):

$$ln(1 - \theta/\theta_e) = -k_1 t \tag{13}$$

where $\theta/\theta_e = q/q_e$, and $k_1 = k_a c_0 + k_d$, θ_e is the equilibrium coverage fraction.

It can be noted that PSO can fit better than PFO for the sorption of lower initial concentration of solute [53].

2.3.2. Bulk diffusion kinetics

Diffusion is the process when diffusing species move from a region of higher concentration to a region of lower concentration through random Brownian motion. The diffusion process is tradi-

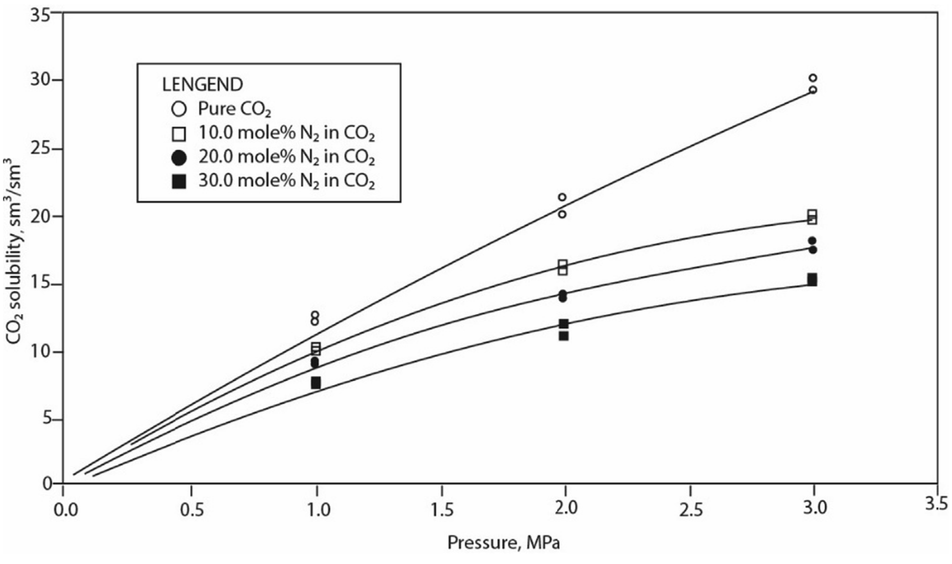

Fig. 3. The solubility of pure and impure carbon dioxide in Aberfeldy heavy crude oil at 23 °C [50].

tionally described by means of the Fick's law [54]. The Fick's first law relates the diffusion flux to the concentration gradient under steady state:

$$J = -D\nabla c \tag{14}$$

where J is the flux diffusing through per unit area per unit time, D is the diffusion coefficient and c is the concentration of diffusing species. The Fick's second law, as described in Eq. (15), shows how diffusion causes the concentration change with time.

$$\partial c/\partial t = \nabla \cdot (D\nabla c) \tag{15}$$

When the diffusion coefficient is independent of concentration, Fick's second law becomes:

$$\partial c/\partial t = D\nabla^2 c \tag{16}$$

An analytical solution of Fick's law can be obtained by applying appropriate boundary conditions. When the concentration of gas at time zero is 0, the gas concentration at the thin film surface is constant and the gas concentration at bottom is zero, the one-dimensional mathematical solution of Fick's equation leads to:

$$M_t/M_\infty = 1 - \frac{8}{\pi^2}\sum\nolimits_{n=0}^{\infty}\frac{1}{(2n+1)^2}exp\left(\frac{-(2n+1)^2 D\pi^2}{4h^2}t\right) \tag{17}$$

where M_t is the weight change at time t, M_∞ is the weight change at equilibrium state, h is the film thickness and D is the diffusion coefficient [55].

The thin film method can be used to determine the diffusion coefficient. Samples are required to have a thin thickness or monodisperse spherical particles [56]. The thin film sample is regarded as having the same constant boundary conditions at the upper and bottom surface of the film by virtue of rapidly establishing sorption equilibrium. When considering the boundary condition at instantaneous equilibrium, the solution leads to [54]:

$$M_t/M_\infty = \frac{4}{h}\sqrt{Dt/\pi} \tag{18}$$

In polymers, Frisch [57] considered three different cases for the diffusion process based on the dependency of mass change on time, as described in the Eq. (19):

$$M_t/M_\infty = Kt^n \tag{19}$$

where K and n are constants.

- Case I (Fickian diffusion, n = 0.5), when the rate of diffusion is much less than that of relaxation due to mechanical, structural modes of polymer-gas system. Sorption equilibrium can be rapidly established, showing no dependence on swelling kinetics. Mostly the polymer is in a rubbery state when the diffusion exhibits instantaneous response.
- Case II (n = 1) and super case II (n > 1), in which diffusion is quite rapid comparing with relaxation time. Slow relaxation allows no time for structure adjustment and results in swelling and other structure change.
- Case III, when diffusion and relaxation are comparable and non-Fickian or anomalous diffusion can occur.

Boundary conditions are fundamental for solving the kinetic equations of diffusion process. Numerical analysis of diffusion kinetics requires explicit boundary conditions, particularly the ones that constrain the concentration variation at the gas/solid or liquid/solid interface. The most commonly-applied boundary conditions involve constant Dirichlet boundary, time-dependent Dirichlet type, constant Robin boundary and time-dependent Robin boundary. The Dirichlet boundary condition that defines the concentration as constant is the simplest and most used one [58]. It is applicable for most tests with constant concentration or negligible concentration change. For example, in order to measure the diffusion coefficient of water, test samples can be either immersed in the water bath or conditioned in a confined chamber with specific relative humidity ranging from 0% to 100%. In the first case, Dirichlet boundary conditions can be applied; however, in the second case the boundary conditions can be more complicated when the mass of surface adsorption is comparable with the mass of bulk diffusion or when an isotherm sorption test is conducted. In environmental conditions, the partial pressure of moisture and oxygen varies with days and years, thus the interface concentration can be recognized as a function of temperature, pressure and time etc. Etminan et al. took into consideration a complicated boundary condition including gas solubility, diffusion and surface resistance to analyze the diffusion kinetics of CO_2 in bitumen using pressure decay method [42]:

$$-D\left.\frac{\partial C_g}{\partial z}\right|_{z=0} = k\left(C_{g-int}(t) - C_g(z=0,t)\right) \tag{20}$$

where C_{g-int} is the gas concentration above the gas-bitumen interface, $C_g(z=0,t)$ is the concentration below the interface, k is the mass transfer coefficient. In this case, C_{g-int} decreases as pressure reduces due to gas dissolution. When an interfacial resistance is present against gas diffusion, a discontinuity of gas concentration can be formed across the interface, so $C_g(z=0,t)$ is different from C_{g-int}. The film resistance cause higher gas concentration at the interface than the saturation concentration at early time of diffusion.

2.4. Transport mechanisms

Theories have been developed to analyze the diffusion process from molecular level to macro level. From a molecular perspective, the diffusion is no more than the thermodynamic molecular motion, thus can be inferred from the aspects of molecular dynamics. Diffusion requires spatial space for molecules to move from one site to another, based on which, free volume theory has been proposed and applied in many studies in literature.

2.4.1. Molecular dynamics theory

The diffusion coefficient can be determined through the kinetic process of molecular motion. For the diffusion in liquids, the hydrodynamic theory and Eyring activated-state theory can be used to calculate the diffusion coefficient by relating it to some thermodynamic and physical parameters [32]. Taking into consideration the molecular motion of diffusing gas and solid, as well as the prevailing intermolecular forces, Flory developed an equation for the diffusion coefficient of a dilute suspension of spherical colloid particles as:

$$D = kT/\xi \tag{21}$$

where k is the Boltzmann's constant, ξ is the dilute solution limit, and T is the temperature..

Similarly, the Stokes-Einstein equation is used for diffusion of large particles in solvents:

$$D = kT/6\pi R\mu \tag{22}$$

where R is the mean molecular radius and μ is the molecular viscosity.

As for the diffusion in polymers, the diffusion coefficient is regarded as proportional to the inverse square-root of molecular weight M based on the bead-spring chain model and hydrodynamic interaction between beads models [59]:

$$D\ 1/\sqrt{M} \tag{23}$$

2.4.2. Free volume theory

Holes or vacancies are required for all types of molecular motion beyond simple vibrational and rotational states. Molecules with more freedom of motion compared with solids can be shifted over a distance of macroscopic scale through holes or interstitial space, known as free volume. In polymers, the diffusion coefficient of a gas is correlated to the fractional free volume of the polymer. By calculating the molecular mobility and jumping units, Vrentas and Duda [60] derived the diffusion coefficient as follows:

$$D = \frac{D_1 \omega_1 \omega_2}{RT} \left(\frac{\partial \mu_1}{\partial \omega_1} \right)_{T,P} \tag{24}$$

where ω_1 and ω_2 are the mass friction of diffusing gas and polymer respectively, μ_1 is the chemical potential of the diffusing species, D_1 is the self-diffusion coefficient (diffusion of a species in itself) of diffusing species. For glassy polymers, diffusion mainly appears due to pre-existing micro pores. As for rubbery polymers, micro pores are generated by fluctuation of polymer chains. Rubbery polymers above the glass transition temperature respond instantaneously to the imposed stress due to diffusion [61]. This elastic response usually corresponds to a Fickian diffusion behavior [62]. When a polymer is cooled below the glass transition temperature, the free volume will change and the free volume (void space) in the glassy polymer is in the range of 0.2% to 10% [63]. Given that polymer relaxation is time-dependent, the free volume is correlated to time and thus a non-Fickian behavior is observed from tests. Based on the estimation of the fractional free volume at various environmental conditions, free volume is used to predict the diffusion coefficient of water vapor through glassy polymer films [64] (Fig. 4). Correlation between diffusion coefficient and free volume in film samples is found to be step-wise, which can be used to predict the diffusion coefficient at any given material variable.

Compared with molecular dynamics, the free volume theory can be applied on experimental data obtained by test measurements. As for more sophisticated cases, molecular simulations can be used to simulate the diffusion process based on thermodynamic theories and solubility concepts by means of the Grand Canonical Monte Carlo method [65].

The diffusion coefficient is a physical constant dependent on molecule weight, molecule size and other properties of diffusing gases, as well as solid types, temperature and pressure [66]. Some primary conclusions can be reached according to the molecular models and the free volume theory. The Arrhenius equation can describe the positively exponential dependence of diffusion coefficient on temperature. The diffusivity or diffusion coefficient of the gas at a state of infinite dilution is almost independent of the concentration and increases with temperature, while at high concentration, the diffusivity is strongly concentration-dependent. The diffusion coefficient is known to decrease with the increase of the hydrophilicity of solid matrices due to the immobilization of water molecules at polar sites. However, the moisture-induced plasticization may facilitate diffusion. These contradictory factors denote a complicated water sorption behavior in solid phases with polar groups [67,68].

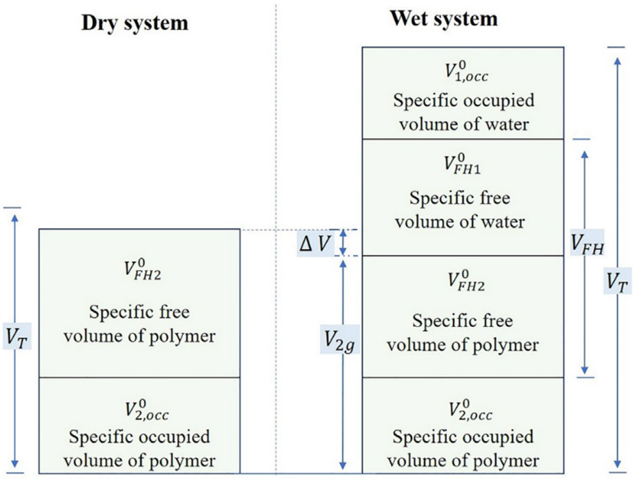

Fig. 4. Schematic diagram of free volume before (left) and after (right) addition of moisture of an amorphous polymer [64].

For bitumen, it will be more challenging to determine the required parameters in the expressions for diffusion coefficient due to its complex chemical composition. Nevertheless, these theories can help to understand the mechanisms of oxygen and moisture diffusion in bitumen and the construction of correlation between diffusion behavior and physicochemical and mechanical parameters.

2.5. Coupled sorption and diffusion

The kinetic process and equilibrium state are the two main elements involved in the sorption and diffusion process. Equilibrium sorption is dominated by solubility and surface adsorption, as described for example by Henry's law and Langmuir adsorption. These dual- and triple- mode sorption processes can be coupled with diffusion. When sorption is coupled with gas transport (diffusion and advection), sorption equilibrium provides the boundary and final conditions, and is not directly involved in the partial differential equations of kinetic diffusion or diffusion–reaction models, as shown in Eq. (25) [69]:

$$\begin{aligned} \partial C/\partial t &= \partial(C_H + C_L + C_P)/\partial t \\ &= \nabla \cdot (D \nabla C) - dC_H/dt - dC_p/dt - k_a S C + k_s (C'_H - S) \end{aligned} \tag{25}$$

where C is the gas concentration, C_H is the mass concentration absorbed according to Henry's mode, $C_L$is the concentration in Langmuir mode, C_P is the concentration of clustering, k_a and k_s are absorption and desorption rates, S is the concentration of empty Langmuir sites, and C'_H is the Langmuir capacity constant.

2.6. Deviation from common theories

For the ideal Fick's diffusion to be valid, the structural and physicochemical material variations caused by the diffusion process must be negligible and diffusion should occur in the micropores, which in most cases is not representative. Many diffusion phenomena are of non-Fickian nature; hence the mass change is initially proportional to the square root of time (fitting for Fick's law) and subsequently deviates from the mass-time curve according to Fick's law. Various explanations have been proposed to describe the abnormal diffusion behavior such as the formation of hydrogen, the structure heterogeneity, the variation in free volume, relaxation phenomena, material degradation, glass transition temperature depression and structure weakness [70,71]. In addition, the diffusion coefficient and boundary conditions can be time-dependent or concentration-dependent.

In particular, some authors attempt to explain the moisture diffusion process using a two-phase mode, namely the free phase and the bonded phase [72]. According to the two-phase mode, a fraction of the diffusing gas is immobilized at some fixed sorption sites and the remaining fraction can freely diffuse through the bulk. By adding the two parameters and showing the probability of conversion between the free phase and the combined phase, the diffusion process can be better modeled. Pereira et al. [73] further eliminated the restriction that immobilized species cannot diffuse and regarded it as partially mobile.

Continuum mechanics can be also employed to model the diffusion process. Linear viscoelastic models construct the relationship between diffusion and time-dependent stress response [74]. The diffusion-relaxation model can used to interpret the abnormal sorption under the molecular relaxation theory combining continuum mechanics and thermodynamics [75]. Starkova et al. analyzed the abnormal sorption to be related to the delayed free volume change [51]. The total sorption weight $w_{BH}(t)$ is divided into two parts with one $w_F(t)$ following the Fick's mode and the other one $w_R(t)$ a delayed response as shown in Fig. 5:

$$w_R(t) = w_{\infty R}(t)[1 - exp(-t/\tau_R)] \tag{26}$$

where $w_{\infty R}(t)$ is the equilibrium weight specified by relaxation and τ_R the first-order relaxation time.

3. Transport and sorption of oxygen and moisture in bitumen

3.1. Transport of oxygen in bitumen

Polymers are composed of thousands similar monomers covalently linked to form bonded chains. In contrast with polymers, the units of bitumen are much more diverse. Compared to polymers, the homogenized molecular weight is relatively smaller and the molecular weight distribution is wider. The asphaltene fraction with higher molecular weight and the agglomerates of molecules through polar associations cause the polymeric characteristics of bitumen. Nevertheless, the bitumen polymeric characteristics can be weakened or disappear with increasing temperature. Specific research about the transport of oxygen in bitumen can be conducted combining developed theories from the polymers area and the unique characteristics owned by bitumen. Most studies adopt the Fick's law and the Arrhenius equation to deal with the diffusion process in bitumen and bituminous mixtures [76,77]. The diffusion coefficient of oxygen in bitumen ranges in the magnitude of 10^{-11} to 10^{-15} m^2/s for different types of bitumen with different testing methods and conditions (Table 1).

The mass of absorbed oxygen cannot be easily detected by most mass balances, therefore few research studies have used the gravimetric method to determine the diffusion coefficient. The pressure-decay method is mainly used to determine the diffusion coefficient of nitrogen, which involves placing a bituminous film is into a pipet that is filled with nitrogen. After sealing the pipet, the pressure change is monitored and then used to calculate the diffusion coefficient via Fick's law [78]. Instead of the direct measurement of the oxygen diffusion coefficient, the diffusion of nitrogen can be used as an analogy, due to their similar van der Waals forces, in order to eliminate the effect of oxygen reaction and measure purely the diffusion phenomena [79]. The oxygen solubility in petroleum oils is assumed to be twice than that of nitrogen. By interpolating data from Blokker and Van Hoorn [80], Dickinson [81] calculated the oxygen solubility assuming the Henry' law and a linear relationship with temperature:

$$S = 2.0 \times 10^{-5} \times (1 + 0.0215(T - 30)) \tag{27}$$

where S is the solubility in kg/L at the temperature T.

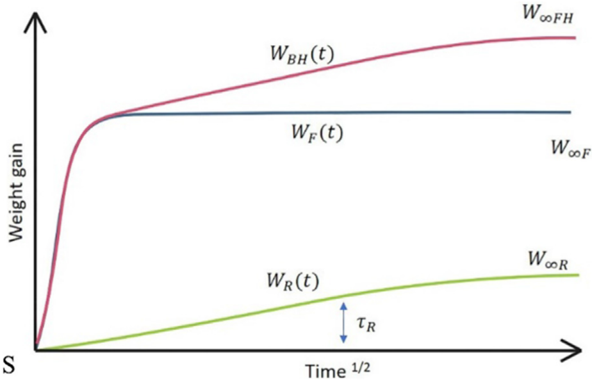

Fig. 5. Graphical illustration of diffusion-relaxation model.

Han et al. [82] have used indirect spectroscopic measurements to determine the oxygen diffusivity. The researchers have deposited bitumen on an premolded aluminum tray with 1.5 mm thickness to get a thin bitumen film. The diffusion coefficient is then measured by comparing the oxygen reaction rate at the surface and bottom of known reaction kinetics using Fourier Transform infrared spectroscopy (FTIR). Oxygen diffusion in bitumen also shows non-Fickian behavior. The abnormal diffusion of oxygen in bitumen can be attributed to the fact that a small amount of gas can dissolve in the fraction with polar groups after the sorption sites are occupied [79].

3.2. Transport of moisture in bitumen

Gravimetric sorption has been used to study moisture diffusion and sorption in bitumen, but the transient diffusion and kinetic adsorption have not been well explained. When using the gravimetric method to determine the diffusion coefficient, the difficulty is to separate the adsorbed species (on the surface of the sample) and absorbed ones (within the bulk of the sample). By analogy with the one-dimensional consolidation of soil, a moisture diffusion model in bitumen is introduced where the percentage of completed consolidation is like the degree of completed adsorption [85]:

$$\omega = \omega_{100}\left(1 - e^{-3Dt/t^2}\right) + \omega_a\left(1 - e^{-\alpha t}\right) \tag{28}$$

where ω_a is the maximum adsorption on the surface of bitumen sample, α is the adsorption constant, ω_{100} is the maximum absorption of bitumen film and D is the diffusion coefficient.

FTIR can identify the peak of water and measure the water amount via peak area calculation. Vasconcelos et al. [13] proposed a dual-mode diffusion model for bitumen with Fourier Transform infrared spectroscopy-Attenuated total reflection (FTIR-ATR). The partially mobile fraction of moisture is related to the interaction between water molecules and polar functional groups. Moisture diffusion is then divided into two parts, one with a higher diffusion coefficient and the other with a relatively lower diffusion coefficient. Sorption-desorption cycle process through placing and removing of a water reservoir on the film surface can increase the diffusion coefficient with history effects due to microstructure changes [24]. It can be seen from Table 2 that the value of the diffusion coefficient varies significantly for different experimental tests. This difference could be attributed to the different choice of transport models as described in second chapter or the systematic errors of different test methods shown in Section 3.3. The moisture diffusion process can deviate from Fick's law and show complex sorption phenomenon, due to water clusters, possible reaction, disturbed spatial structure of bitumen, etc. More efforts are indispensable to study the moisture transport in bitumen.

3.3. Test methodologies to determine diffusion coefficients in bituminous materials

The experimental methods to measure the diffusion coefficient in bitumen can be classified into two types, namely direct and indirect methods. Direct methods quantify the gravimetric change

Table 1
The diffusion coefficient of oxygen in bitumen and mastics.

Bitumen type	Method	Temperature (°C)	Diffusion coefficient (m^2/s)	Reference
PEN 40/60	Pressure decay method	50	5×10^{-15}	[83]
PEN 70/100		50	8×10^{-15}	
AAK1	Electrodynamic balance	21	1.00×10^{-11}	[79]
		40	0.15×10^{-11}	
		60	0.42×10^{-11}	
PEN 180/200	Derivation from viscosity through equation (D, T, η)	50	1.83×10^{-10}	[20]
Alon 64-22	Ageing difference between film (1.5 mm) surface and bottom using FTIR, calculated by diffusion-reaction equation	59	1.20×10^{-11}	[82]
		75	4.42×10^{-11}	
		88	2.64×10^{-10}	
Alon 64-22 + 10% filler		59	8.60×10^{-12}	
		75	3.90×10^{-11}	
		88	2.16×10^{-10}	
AAC-1	Ageing for a film (0.4 mm) calculated by diffusion–reaction equation	70	6.0×10^{-11}	[84]
AAK-1		70	1.7×10^{-11}	
Virgin + RAP bitumen	Derivation from shear modulus through equation (c, D, G*)	64	4.88×10^{-11}	[76]
PEN 70/100	Ageing comparison between films of various thicknesses, aged to equilibrium time, Fick' law	50	2.43×10^{-13}	[19]
		100	5.13×10^{-13}	

Table 2
The diffusion coefficient of moisture in bitumen, bituminous mastics and mixtures.*

Bitumen type	Method	Diffusion coefficient (m^2/s)	Reference
AAC-1	FTIR-MIR method, liquid water	1.40×10^{-14}	[86]
AAD-1		2.50×10^{-14}	
AAK-1		3.31×10^{-14}	
AAD-1	Gravimetric method, sorption balance	1.33×10^{-9}	[85]
AAM-1		4.83×10^{-9}	
AAD-1	EIS, thin film on aluminum plate	4.19×10^{-17}	[87]
AAK-1		2.94×10^{-17}	
AAM-1		1.54×10^{-17}	
Bitumen + limestone (<19 mm)	Gravimetric method, evaporation process	3.45–5.67×10^{-10}	[5]
PG 70–22 + diabase (<4.75 mm)	Gravimetric method, climatic chamber	2.54×10^{-10}	[8]
AAB	Dual-phase diffusion coefficients, FTIR-ATR measuring absorbed water amount	1.50×10^{-17}	[24]
AAD		1.62×10^{-17}	
ABD		5.20×10^{-17}	
PEN 40/60 + limestone (<1mm)	Gravimetric method, climatic chamber and desiccator jar environment	2.59×10^{-12}	[88]
PEN 40/60 + granite (<1mm)		2.44×10^{-12}	
PMB + limestone (FAM)	Gravimetric method, climatic chamber	0.72–1.06×10^{-10}	[89]

[*] PMB: polymer modified bitumen; FAM: fine asphalt mixture; EIS: Electrochemical Impedance Spectroscopy.

with time, while the indirect methods mainly measure one or more parameters correlated and altering with the diffusion process such as the volume swelling and the spectroscopy absorbance. Indirect parameters exhibiting the diffusion process include pressure, interface velocity, magnetic field strength or the volume change of the solute [90].

3.3.1. Gravimetric method

Gravimetric techniques (Fig. 6), which directly monitor the mass change with time, have been frequently used to investigate the sorption and diffusion kinetics [79,85,88]. The test sample is placed in the chamber with controlled temperature, partial pressure and concentration of the diffusing species and instantaneous mass change data are collected. Mass change can be measured with a balance of high resolution of 0.1μg [91,92].

3.3.2. Pressure decay method

The pressure-decay method is mostly used in petroleum industry to test the diffusion coefficient of gas in heavy oil and bitumen at high pressure, since the mobility and recovery of bitumen can be improved and the viscosity can be reduced with the injection of these gases. There are two experimental pressure boundaries with different analytical models to get the diffusion coefficient and equilibrium solubility (Fig. 7). The first method involves measuring the pressure decrease in a confined space with gases diffusing into the bulk of the sample and estimating the diffusion coefficient through numerical models. The second method requires that the sample is placed in a cell overlaid by a gas cup and the constant pressure inside the cup is achieved by continuously supplying the depleted gas into the cap [50]. The Fick's second law and the mass balance equation are needed to analyze the mathematical model of diffusion based on the pressure-decay model. The forward problem analysis involves the infinite-acting model, when the gas does not reach the bottom, and finite-acting model when the infinite-acting boundary in not valid [90,95]. An inverse solution methodology involves using the results of actual observation to optimize the parameters characterizing the system [96]. One challenge for the pressure-decay technique is to establish the boundary condition between gas and solvent interface. Research shows that there exists mass transfer resistance at the interface which may affect the analytical results because of different boundaries [97].

3.3.3. Chemical composition method

Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy can be used to study sorption kinetics in situ [75,99–101]. A sample is casted on the ATR crystal prism and then the diffusing gas is loaded above it. Vasconcelos et al. [13] used FTIR-ATR to measure the diffusion coefficient in bitumen by monitoring the spectra change related to water. All stretching bands associated with water at each time point are integrated to get the absorbed water content. The spectra absorbance is proportional to the total instant mass increase within the film. The water reservoir is loaded over the bitumen film and data are collected for 15 days to see the diffusion process. FTIR-ATR cannot only detect the absorption kinetics but the chemical reactions during the diffusion process. The penetration depth of evanescent wave is a function of the angle of incident light, wavelength of light and the refractive indices of the crystal (Fig. 8). For bitumen the penetration thickness is about 0.5-1μm [13]. Thus the overall water

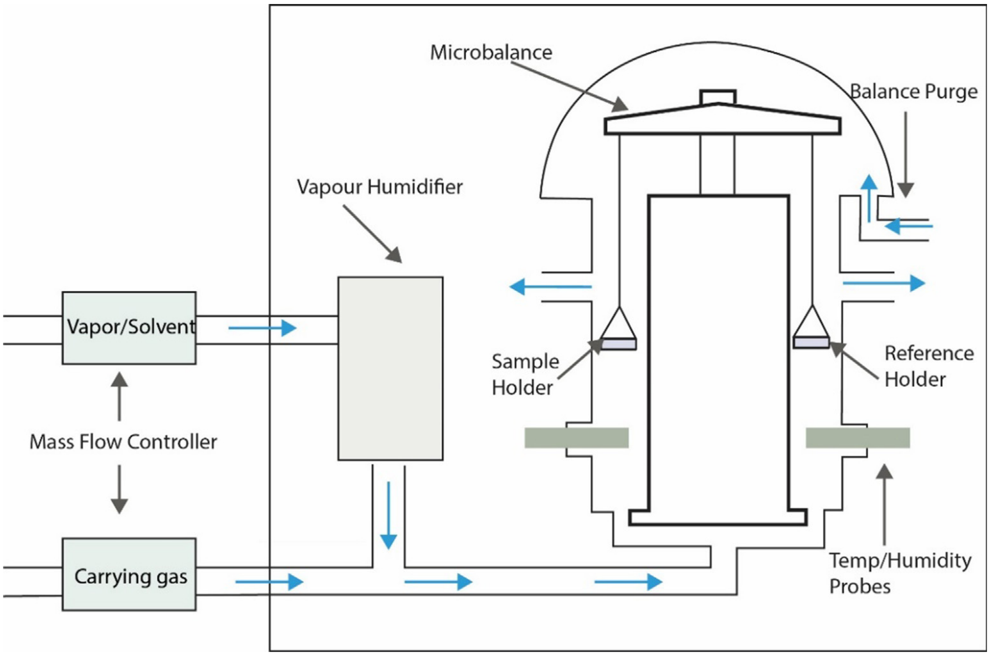

Fig. 6. Schematic of dynamic vapor sorption apparatus [93,94].

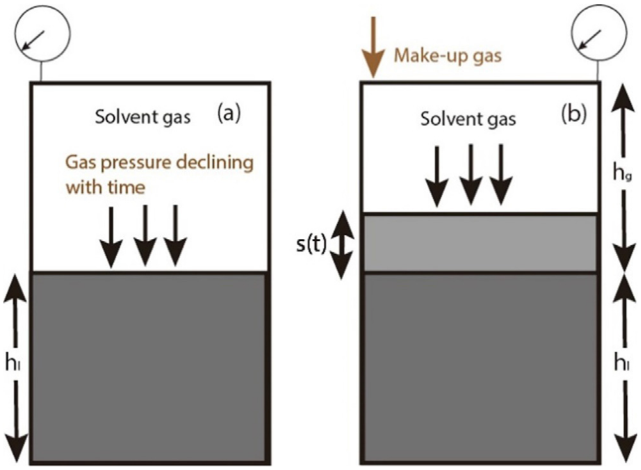

Fig. 7. Schematic of pressure decay cell (a) pressure decay (b) constant pressure with gas make-up (s(t) is the position of the gas-oil interface at time t) [42,98].

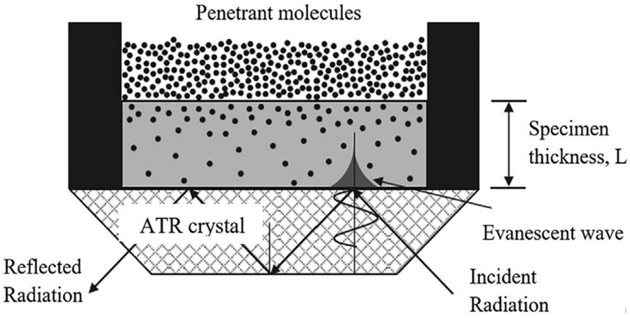

Fig. 8. Schematic diagram of ATR for diffusion experiment [102].

absorption refers to the sample regions within this depth. Since the absorbance of FTIR-ATR is proportional to the mass absorbed, the method fails to reveal the real mass absorption.

Nuclear reaction analysis (NRA) can be used to obtain the concentration of chemical elements along the depth of a solid film. NRA can release d^+ ions to the sample and interact with the deuterium of D_2O diffused into the bulk, thus measuring the moisture content [103]. The moisture content is shown as a function of film depth. Low-field Nuclear Magnetic Resonance (NMR) is utilized for monitoring the diffusion process of organic solvents in heavy oil or bitumen [104]. Solvents such as heptane and kerosene are placed on the top of heavy oil/lake bitumen, then the whole container is sealed. The relaxation spectra of heavy oil or bitumen are distinctly different from those of the solvents, so the concentration of the solvent in the mixing area can be calculated according to the spectra.

3.3.4. Volume change method

Diffusion in most cases will result in volume swelling, which can be used to test the diffusion coefficient. An interferometric equipment is used to measure the swelling process caused by water absorption. The film thickness is measured with the electronic speckle pattern interferometry (Fig. 9). The diffusion coefficient is calculated using the evolution of film thickness in humidity between 50% and 90% [105].

Yang et al. [106] used the pendant drop volume analysis (DPDVA) to study the diffusion coefficient and volume swelling of carbon dioxide, methane, ethane and propane in Lloydminster heavy oil under high pressure. A pendant oil drop inside a pressure cell is formed surrounded by a diffusing gas at specified pressure and temperature. The volume change is captured through digital imaging and the diffusion coefficient is related to the volume change.

Indirect methods can display the continuously evolving diffusion process whereas the specific equilibrium mass absorption is indispensable to the numerical solution of diffusion equations, which can be measured from gravimetric tests or calculated based on solubility models. Different methods are proposed based on the various mechanisms of the diffusion process. Comparing diffusion data from different measurement methods can compensate for their individual insufficiencies, when attention should be placed on the boundary and testing conditions of the individual methods.

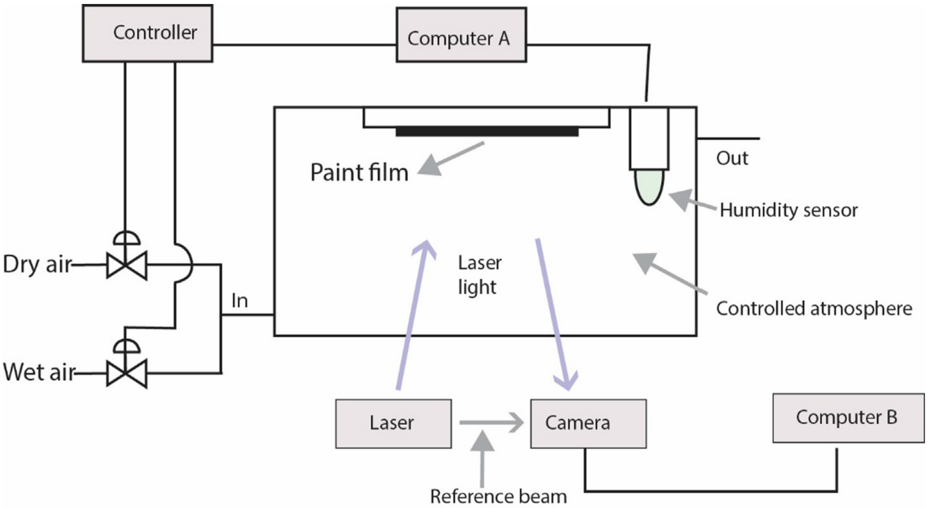

Fig. 9. Set-up to measure the volume change due to diffusion [105].

3.4. Upscaling of oxygen and moisture transport

The addition of fillers (as in the case of bituminous mastics) may change the microstructure, density, relaxation time, glass transition temperature, specific heat and affinity for moisture. In many cases, fillers can profoundly change the sorption path of polymers and bitumen. Fillers can decrease the diffusion coefficient but their actual effect on the sorption process is complicated by the filler type, filler shape etc. For instance, incorporating nano-fillers into epoxy practically depresses the diffusion process and cause a decrease in the diffusion coefficient. However, these effects gradually decline and finally disappear at higher temperature. In this case, the tortuosity resulting from nano-fillers is counterbalanced by the higher activity and mobility of the host polymer [51].

Han et al. [82] compared the oxygen diffusion coefficient of mastics with varying filler fractions. The diffusion coefficient is observed to decrease with the increase of the filler volume fraction. This dependence on volume fraction of filler is in accordance with the Maxwell and Raylegih model (analogy to thermal conductivity) for the matrix containing suspensions of spherical particles:

$$\frac{k_{eff}}{k_0} = 1 + 3\varnothing / \left(\frac{k_1 + 2k_0}{k_1 - k_0} - \varnothing \right) \tag{29}$$

where k_{eff} and k_0 are the diffusion coefficient of mastic and bitumen respectively, k_0 and k_1 are constants, $\varnothing$ is the volume fraction of fillers. Wen et al. [6] developed a two-chamber diffusion apparatus to measure the diffusion coefficient of compacted bituminous mixtures. It appears that the oxygen transport in mixtures is controlled by the air voids phase along with the characteristics of air voids. The diffusion coefficient for the specified mastics and aggregates was constant, while the different mix design method created different void content and distribution, which provided different gas flow path and thus very different diffusion coefficient values for the various bituminous mixtures.

The gravimetric method is mainly used to analyze the transport process of moisture in mastics and bituminous mixtures. Fick's law is mostly used to determine the transport rate. The transport rate is dependent on the type of bitumen, filler and aggregate and the void characteristics of bituminous materials [107]. Mastics with limestone and granite aggregates (or fillers) demonstrate different diffusion rates and equilibrium sorption mass. Bituminous mastics with limestone have higher transport rate, while granite mastics have a high equilibrium sorption amount [88]. It is therefore of importance to study both the transport kinetics and the equilibrium sorption state. Except for Fick's law, the dual-mode model, the Langmuir diffusion model and the time-variable diffusion model are also referred to explain moisture transport behavior in fine bituminous mixtures (a mixture of bitumen, filler and aggregate passing the sieve of 1.18 mm or 2.36 mm) [108,109]. The anisotropy of the diffusion coefficient needs to be considered for the anisotropic distribution of air voids and aggregates [110]. Logically, bituminous mixtures present higher moisture diffusion coefficients than that of the bitumen as shown in Table 2, as bituminous mixtures have more micro-voids for moisture to diffuse. Interconnected voids in bituminous mixtures also provide direct paths for moisture to flow through. This convective flow is incorporated into the overall transport process, therefore much higher diffusion coefficient can be expected.

4. The oxygen- and moisture- reaction in bitumen

4.1. Oxygen-bitumen reaction

4.1.1. Mechanism of oxidation

Bitumen oxidation is the chemical reaction between oxygen and active components in bitumen. Oxidation results in bitumen hardening and brittleness and the deterioration of its relaxation properties, which are manifested in the field by increased propensity of cracking and pavement failures. The reaction process in bitumen is essentially dependent on the process of oxygen diffusion into pavements, namely the reaction kinetics with temperature, the reaction rate, the concentration of reactants and the oxygen interaction with active chemical groups. The main perceivable changes of FTIR data from aged bitumen are the peaks and areas indicating the carbonyl and sulfoxide groups; hence in literature the discussions about oxidation are mainly on these two chemical functional groups. Oxidative reaction is generally divided into a fast reaction and a slow reaction stage. The fast reaction mainly occurs during production and construction. At initial state, the highly reactive hydrocarbons react with oxygen to yield hydroperoxide, which is at least 50 times more active than the slow hydrocarbon reaction. The hydroperoxide is quite unstable and can decompose and react with alkyl or aryl–alkyl sulfides to produce sulfoxides. This decomposition may also accelerate the long-term reaction. The slower oxidative reaction fundamentally imposes the long-term deterioration of bitumen [111] (Fig. 10). The long-term reaction is suggested to be a classic free-radical chain involving oxidation at the benzyl-carbon mainly in the polar

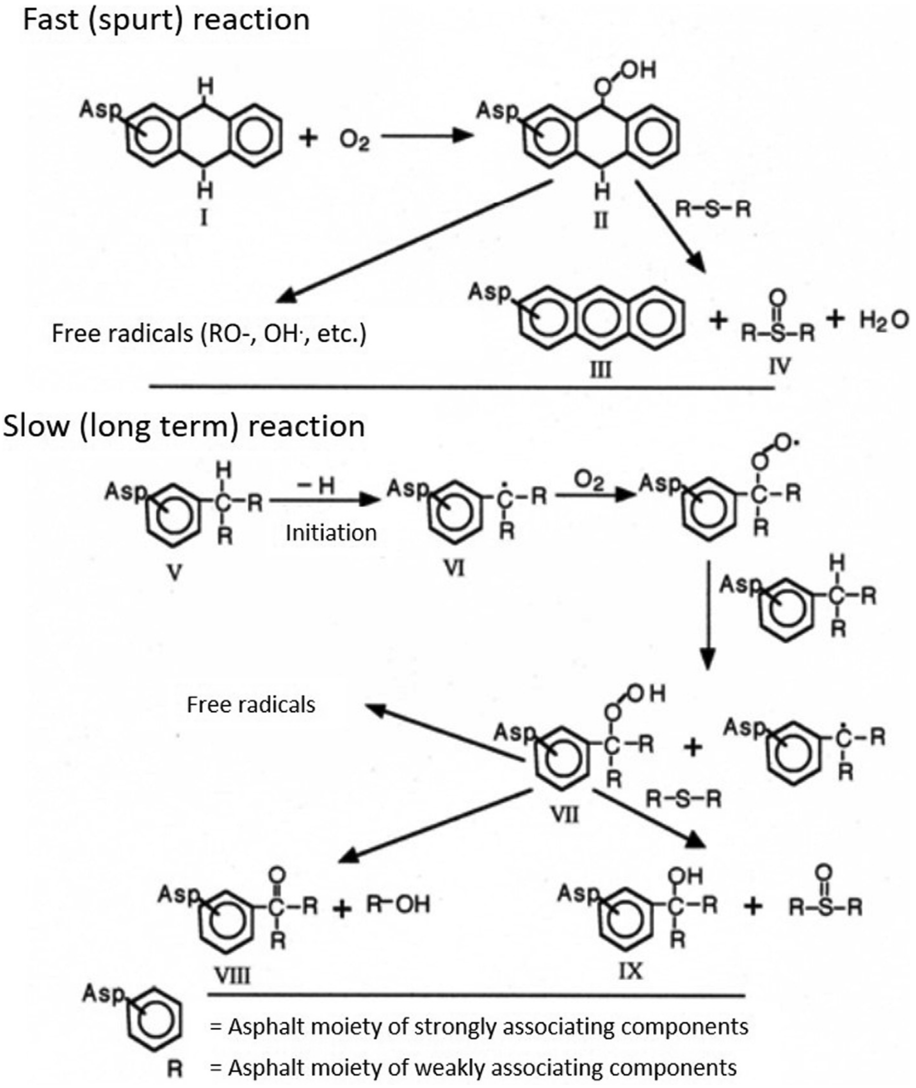

Fig. 10. The oxidation mechanism of bitumen [111].

aromatics fraction. The side chains of those highly condensed aromatic ring systems are likely to be oxidized to form ketone groups [112]. The association forces between polar aromatics fractions are strengthened with the formation of more chemical functional groups to their molecular structure. This leads to the increase of the size of molecular agglomerates in bitumen when exposed to oxidation [113]. More attention is therefore put on the long-term reaction of carbonyl generation. Apart from the reaction exerted by oxygen, other gases like nitric oxides, ozone and soluble oxidants such as HNO_3, H_2SO_4, H_2O_2 can also promote ageing [114]. The oxidative ageing of bitumen is highly dependent on the bitumen structure, compositions and weather conditions [115], which influence the diffusion rate and reaction kinetics.

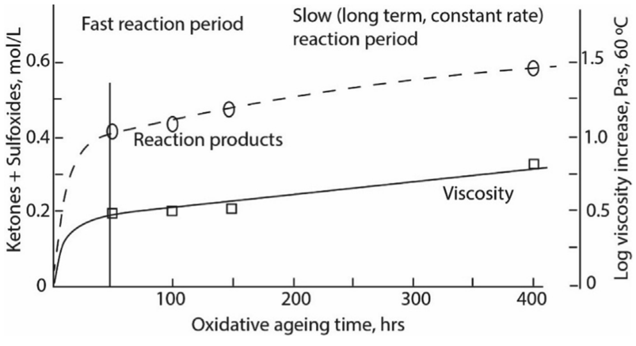

Fig. 11. The kinetics of functional group formation and viscosity change for AAB-1, Pressure Aging Vessel (PAV) aged at 80 °C, 2.03 MPa [120].

4.1.2. Kinetics of oxidation

Various types of bitumen overall exhibit similar kinetics with ketones and sulfoxides formed at different rates as shown in Fig. 11. The oxidation of bitumen can be regarded as the sum of two different reactions. One is fast and usually ends in the short-term as the reactants are rapidly exhausted [14,83,116,117]. The other is slow and keeps a steady reaction rate in the long-term. The oxidative reaction rate is supposed as first order for oxygen and active reactants concentration in bitumen [81]. The formation of sulfoxides goes fast at the beginning and slows down to equilibrium as the reactants are nearly fully depleted while the formation of ketones is much slower and tends to keep constant for a longer time. Petersen proposed an expression relating the viscosity to two concurrent reactions based on the concept that the fast-reaction of sulfoxide is of first order and the slow-reaction of carbonyl is constant [20,118,119]:

$$P = P_s + P_f = P_{f\infty}\left(1 - e^{-k_f t}\right) + P_{s\infty}k_s t \tag{30}$$

where $P_{f\infty}$,$P_{s\infty}$, k_f and k_s are the constant; P is the oxidation products concentration, and $P_{f\infty}$ and $P_{s\infty}$ are the ultimate oxidation product concentrations for fast reaction and slow reaction respectively.

The oxidation kinetics of bitumen is mainly affected by temperature, pressure and UV light [121]. Some bitumen may show different ageing kinetics with temperature. For examples, a slower reaction rate is displayed at lower temperature (60 °C) and a higher reaction rate at higher temperature (130 °C) for some bitumen types. For other bitumen types, the rate keeps constant in relatively small temperature ranges. An explanation is that the colloidal structure of bitumen changes with temperature. Thus the oxidation diffusion rate is correspondingly altered, which in turn leads to inconstant oxidation rate [112] (Fig. 12). In general, the reaction rate can be linked to temperature through the Arrhenius equation [117]. By considering bitumen ageing to be an irreversible first order reaction and relating it to temperature via Arrhenius equation, a kinetic model can be obtained with viscosity in place of product concentration [122]:

$$ln\eta = ln\eta_0 + Atexp(-E_a/RT) \tag{31}$$

where η is the viscosity of aged bitumen, η_0 is the viscosity of original bitumen E_a is the activation energy and A is the pre-exponential constant. It has been determined that activation energy is dependent on pressure and temperature, and varies with bitumen composition [116]. Oxidative reaction at higher temperature or pressure could be misleading since the activation energy could vary from 64 to 109 kJ/mol and reaction order from 0.25 to 0.61 in case of oxygen pressure [123]. In the existence of sunlight, the oxidation can be accelerated within a depth of 10 to 60 μm, in consideration of the penetration depth of UV light, which is similar to the recommended optimum film thickness of bituminous mixtures [124]. As the hardened aged surface of bitumen inhibits the diffusion of oxygen, the bitumen underneath is therefore less aged [125].

4.1.3. Oxidative reaction in polymer modified bitumen

Polymers such as styrene–butadienestyrene (SBS), ethylene vinyl acetate (EVA), polyolefin and rubber have been widely used to improve the mechanical properties and pavement performance of bitumen. Here we mainly focus on SBS modified bitumen. The ultimate ageing kinetics of PMB is determined by the ageing of the base bitumen, the degradation of polymer and the intermolecular associations between each other [126,127]. PMB shows slightly different reaction process compared to pure bitumen and polymers. The activation energy of the base bitumen will increase with ageing evolution. For PMB, it will initially decrease and then increase due to the degradation into smaller molecules and the network structure failure [127]. SBS individually is prone to scission, crosslinking and hardening due to the sensitivity of the double bonds in butadiene [128]. The main products of PMB ageing process are low molecular weight polymers coming from chain scission and reaction products from radical-bitumen reaction [129], while pure polymer shows more cross-linking. SBS decomposition is more sensitive to low molecular weight substrate such as aromatic oil and is restrained by high asphaltene content [127,130]. Compared with base bitumen, PMB has higher activation energy and lower reaction rate, which explain its anti-ageing properties [131], when the SBS copolymer acts as antioxidant to protect the bitumen components from ageing [63]. Both polymeric degradation and bitumen stiffening are responsible for the oxidation ageing of PMB.

4.2. Reaction of moisture in bitumen

There are limited papers dealing with the possible reaction between moisture and bitumen. Some researchers show detectable change of chemical components in bitumen conditioned by moisture [132,133]. Chemical properties are changed after moisture conditioning, including functional groups related to ageing and other components such as aromatic and methylene [134]. In most cases, it has been hypothesized that the oxygen that may exist in moisture reacts with the active components in bitumen. In particular, the effect of moisture on the deterioration of adhesive and cohesive strength is more significant than a possible chemical reaction. It is suggested that a long-term moisture environment can lead to structure failure of bitumen due to the infiltration of moisture molecules into bitumen matrix and the intermolecular associations between water molecules and bitumen components.

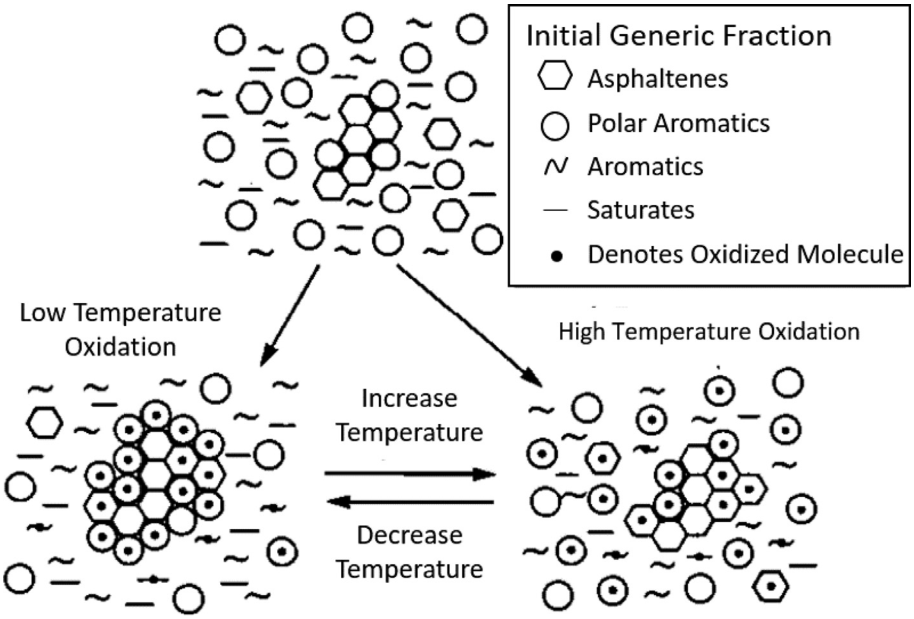

Fig. 12. The Petersen model of bitumen oxidation in terms of temperature, the different kinetics are related to the accessible oxidation sites in specific temperature [112].

4.3. Coupled diffusion and reaction process

Diffusion and reaction are two main contributors in bitumen ageing. Diffusion controls the oxygen distribution of bitumen and thus affects the oxygen reaction rate. Based on the Fick's second law and the reaction kinetics of oxygen, the mass equation can be obtained [135]:

$$\partial C_{O_2}/\partial t = D\nabla^2 C_{O_2} - r_{O_2} \tag{32}$$

where C_{O_2} is the concentration of oxygen, r_{O_2} is the reaction rate of oxygen.

When the oxidative reaction is divided into fast-reaction and slow-reaction, the equation can be written as [20]:

$$\partial C_{O_2}/\partial t = D\left(\partial^2 C_{O_2}/\partial^2 x\right) - k_f\left(P_{f\infty} - P_f\right)C_{O_2} - k_s P_{s\infty} C_{O_2} \tag{33}$$

where$x$ is the depth in the bitumen film, $P_{f\infty}$, P_f, $P_{s\infty}$ are constants.

Oxygen reaction during diffusion process is contributing to the deviation from the classical Fick's law. Reaction changes the original material microstructure and the chemical properties, and also continuously consumes the reactant gases, resulting in a complex concentration gradient change [136,137]. The diffusion process can also be delayed by the hardening of bitumen with ageing [22]. For example, in the case of concurrent diffusion and reaction, the microstructure and chemical components can be a function of the reaction degree and the position and thus have an impact on the diffusion process.

On the other hand, the diffusion coefficient can be hypothesized as a function of the advancement of reaction when reaction affects the diffusion process [138]:

$$D(T, Y) = \widehat{D}(Y) \cdot \exp(-E_a(Y)/RT) \tag{34}$$

where $E_a(Y)$ is the activation energy of transport mechanism. $\widehat{D}(Y)$ and $E_a(Y)$ are functions of product Y, in which $\widehat{D}(Y) = D_0 + D_1 \cdot Y$, $E_a(Y) = E_{a0} + E_{a1} \cdot Y$.

When two diffusive species are involved in the diffusion–reaction system and their diffusion process is mutually influenced, the coupled equation can be [139]:

$$\frac{\partial c_{A/B}(\alpha)}{\partial t} = \frac{\partial}{\partial x}\left(D\left(\alpha, \varepsilon_{A/B}, c_{B/A}\right)\frac{\partial c_{A/B}(\alpha)}{\partial x}\right) - R(\alpha)$$

$$c_{B/A} = c_{B0/A0}(1 - \alpha) \tag{36}$$

where A, B are two species, α is the reaction degree, ε is the volume fraction of A/B, $c_{B0/A0}$ is the initial concentration of A/B.

As stated before, the coupling of sorption and diffusion can be very tricky when dual- or triple- mode of sorption and the non-Fickian diffusion behavior appear in the sorption and diffusion process. If then also the reaction is involved, more parameters have to be determined, in order to analyze the coupled sorption, diffusion and reaction processes. Due to the simultaneous diffusion and reaction of oxygen in bitumen, the diffusion coefficient cannot be exactly determined without being able to separate the diffusion and reaction. The same situation exists in the surface sorption and bulk diffusion. It is difficult to measure separately the surface sorption or the bulk diffusion. Hence, the coupling of sorption, diffusion and reaction is necessary.

5. Moisture and oxygen effects on bitumen properties and their relation to transport processes

Many tests can be used to analyze the bitumen properties under the effect of oxidative ageing and moisture diffusion including Fourier Transform Infrared spectroscopy (FTIR) [140], chromatography [141], differential scanning calorimetry (DSC), X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR) [142], dynamical mechanical analysis (DMA) etc. An overview of the bitumen properties affected by moisture and ageing is given in Table 3. Based on these tests, various parameters and indices have been proposed over the years to characterize the effects of moisture diffusion and oxidative ageing on polymer, bitumen and other organic matrixes. Constructing relations between chemical, physical and mechanical properties helps to get a better understanding of bitumen and its application as construction material. The oxygen- and moisture-induced ageing can be delicately predicted according to their transport behavior [8]. However, the direct identification of diffusion coefficients can be lengthy due to the slow diffusion process with the magnitude to be around 10^{-8} m^2/s to 10^{-12} m^2/s in bitumen and polymers. Research has been done to develop equations providing correlations between diffusion coefficients and chemical, physicochemical and mechanical parameters [50,143].

5.1. Physical and chemical properties

5.1.1. Chemical structure

Corbett [144] developed the widely used SARA classification method, which includes the saturates, aromatics, resins and asphaltenes fractions, based on the method of elution-adsorption liquid chromatography on active alumina with solvents of increasing polarity and aromaticity. Asphaltene is a heterogeneous macromolecular fraction, soluble in toluene but insoluble in alkanes. A small fraction of asphaltenes in bitumen can significantly increase the stiffness and mechanical properties [145]. Oxidative ageing generally results in the decrease of the aromatic content and the increase of the asphaltenes content, therefore it appears that aromatics generate resins and subsequently resins become asphaltenes [146]. The saturates normally remain stable with the ageing process except for in the case of volatile evaporation. Based on the SARA method, parameters relatable to the ageing levels have been proposed to evaluate bitumen properties [147]. The modern colloidal structure of bitumen depicts the asphaltenes as the micelles distributed in the aromatics fraction with resins as a surfactant to prevent the precipitation of asphaltenes [148,149]

Table 3
Summary of bitumen properties affected by oxygen and moisture behavior.

Classification	Methods/ Parameters	Oxygen effect	Moisture effect
Physical and chemical properties	SARA fraction	Increase of asphaltene content and decrease on aromatic content	–
	Chemical composition	Increase of carbonyl and sulfoxide content	Perceivable variation
	Viscosity	Increase with ageing; Decrease with the oxygen diffusion; Diffusion coefficient inversely related to viscosity.	Decrease with moisture infiltration due to plasticization; Diffusion coefficient inversely related to viscosity
Morphological properties	AFM	Number and size change of the image characteristics related to asphaltene and resin	"Nano-bumps" on the characteristic "bee" structures
	SEM	Evolution in the fibril microstructure	–
Mechanical properties	Complex modulus	Increase with ageing	–
	Cohesion	Increase with ageing	Decrease in water
	Adhesion	–	Decrease in water

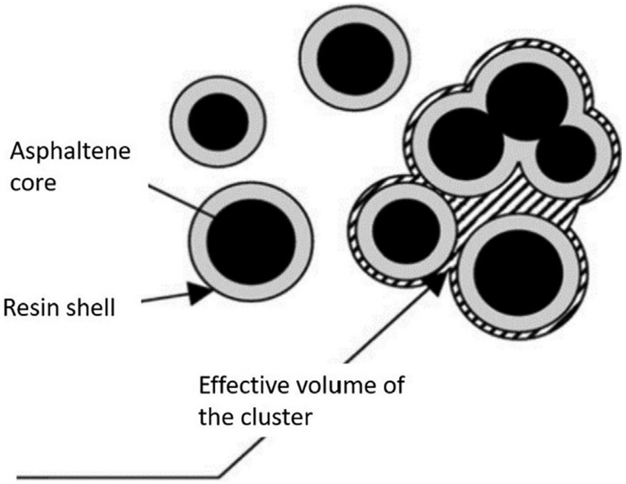

Fig. 13. A simplified view of the colloidal structure of bitumen: the asphaltenes micelles are pictured as spherical to illustrate the concepts of solvation layer (resin shell) and effective volume. The oily dispersion medium is called the maltenes [149].

(Fig. 13). Oxidative ageing has a minor effect on the creep recovery of individual maltenes and asphaltenes and reveals more obvious influence on that of the samples prepared by blending maltenes and asphaltenes. It seems that ageing appears to exert more influence on the microstructure instead of composition evolution [150]. NMR is an effective tool to provide structural information of organic molecules and to identify and quantify the distribution of carbon and hydrogen atoms in different chemical environments [151]. During laboratory oxidation using Rolling Thin Film Oven Test (RTFOT) and Pressure Aging Vessel (PAV), the existence of isomerization and dehydrogenation and the constantly increased extent of compactness and ring condensation with the loss of substituents from aromatic carbons has been reported [142].

Moisture diffusion can also affect the chemical structure of bitumen. The cycled sorption and desorption of moisture in bitumen shows history trace and microstructure change illustrated by different diffusion coefficient at different cycles [24].

Except for the concept of colloidal structure, bitumen can be interpreted as a solution composed of different molecules with different molecular weight [152]. The continuum of polarities and weight of molecules is necessary for the stability. In this case, resins can act as a stabilizer because of the necessary polarity range to keep all fractions in balance. One widely used theory to deal with the solution system is the Hansen solubility theory. The Hansen solubility consists of three elements including dispersive forces (D), hydrogen bonding (H) and polar interactions (N) (Fig. 14). Dispersive forces (D) are weak intermolecular interactions and aged bitumen has lower D value [29]. Polar and hydrogen interactions are responsible for the association and immobility of these molecules. The difference of polar interaction between aged and unaged bitumen is more discernible for field-aged bitumen, possibly due to the appreciable effect of UV on the polarity. Redelius [153] used turbidimetric titrations to get a 3D diagram of Hansen solubility of bitumen, which is more realistic and useful. Different components may be in metastable stage and disturbance such as after oxidative ageing, and blending can lead to spatial rearrangement, which can be predicted by this model. Bitumen is composed of molecules of continuously distributed molecular weight. The polarity, aromaticity and solubility have been frequently used to illustrate bitumen properties which are related to Hansen parameters.

It is shown that samples blended with two compatible polymers have faster moisture diffusion [154]. Bitumen, as a complex substance with diverse chemical compounds, shows complex diffusion. The diffusion behavior in different polymer modified bitumen may be relatable to the solubility. As the solubility is closely linked to the microstructure characteristics, the solubility parameters indicating the colloidal stability of bitumen may be used to study the colloidal structure change due to coupled moisture and ageing effects.

5.1.2. Chemical composition

FTIR [155] is an easy and quick method to quickly determine the chemical components of test samples. Due to the capture of oxygen into bitumen the compounds containing oxygen, especially compounds carrying carbonyl, sulfoxides as well as hydroxyls, increase with ageing. FTIR is widely used to measure the amount of these functional groups [156]. The aliphatic structures are a determining factor for the differentiation of short-term ageing and the content of oxygen compounds is predominant in cases of long-term ageing in terms of FTIR spectra [157]. Many researches use FTIR to illustrate the ageing level instead of viscosity, in view of the correlation between viscosity and functional group generation [117,158].

In contrast, minor chemical changes due to moisture diffusion have been perceived by FTIR. It is described that moisture may act as a solvent to take away some polar components in bitumen, thus changing the chemical composition [125]. Increased surface concentration of polar groups is found from FTIR data when under moisture condition [132,133], but it is not enough to conclude whether the change comes from the oxidative reaction or the reaction between moisture and bitumen. The artifacts or the errors from the experimental methodology may also be a reason for the inconclusive data.

5.1.3. Viscosity

Viscosity is one of the most important criteria to evaluate the fluid properties of bitumen and is significantly dependent on the ageing extent and the ingress rate of gases into bitumen. The vis-

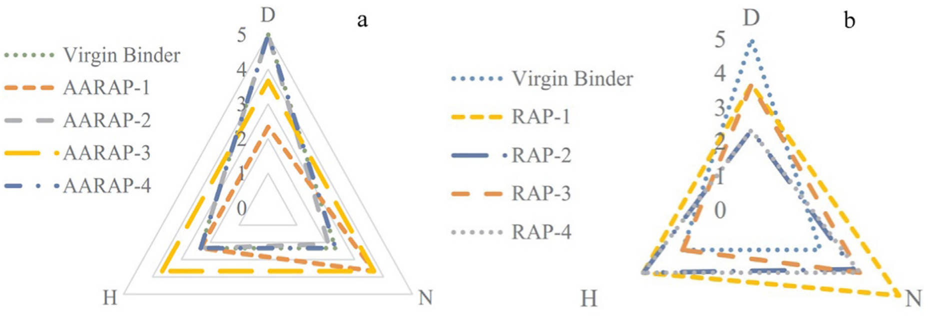

Fig. 14. Strength of intermolecular interactions between virgin bitumen and (a) artificially aged bitumen and (b) field-aged bitumen [29].

cosity can be directly estimated from tests such as DSR and viscometer. Oxidative reaction increases the content of polar groups, which lead to condensed aromatic ring components to agglomerate and evolve into the asphaltenes fraction, thus increasing the viscosity of bitumen. In polymers, gas diffusion can mainly lead to plasticization, followed by weakening of its mechanical properties. Similarly, as oxygen is absorbed, the bitumen structure loosens, making it easier for gases to diffuse. This leads to the plasticization of the bitumen together with the swelling of the samples [79].

Oxygen diffusion in bitumen can be correlated to viscosity. Schmidt proposed an equation for the diffusion coefficient of carbon dioxide in bitumen as [50]:

$$D\eta^{0.16}/T = 2.04 \times 10^{-12} \tag{37}$$

where η is the bitumen viscosity, R is the ideal gas constant and T is the temperature.

By taking the diffusion coefficient of oxygen as 1.5 times higher than that of nitrogen and referring to the Fujita equation, the diffusion coefficient of oxygen can be determined by the following equation [20]:

$$logD = -12.3083 - 0.3351(log\eta) + log(RT) \tag{38}$$

Han et al. [82] also proposed the relationship between diffusion coefficient, viscosity and temperature:

$$D/T = 5.21 \times 10^{-11}(\eta)^{-0.55} \tag{39}$$

The viscosity not only evolves with ageing time and characterizes the ageing properties of bitumen, but changes with moisture diffusion. Bitumen shows lower viscosity in the existence of moisture [159]. It can also be used to determine the sorption parameters of diffusing gas.

5.1.4. Other parameters

Other parameters related to the diffusion and reaction of moisture and oxygen in bitumen include the glass transition temperature, crystallinity, density, hydrophilicity etc. These parameters can be mutually affected with a certain correlation. Moisture absorption in bitumen can cause plasticization, lower glass transition temperature (T_g) and a reduction of the mechanical strength. It is noteworthy to mention that during the evolution of microstructure and chemical composition with ageing process, the glass transition temperature shows relatively small changes. In general, crystallinity can reduce the diffusion coefficient compared with the corresponding amorphous polymers [154]. The volume contraction occurs when temperature decreases. The fastest rate ranges from 20 °C to 80 °C, which may be consistent with the crystallization kinetics in bitumen [160]. Therefore, there could be a certain correlation between the diffusion parameters and the crystallinity of bitumen. Moreover, density can reflect the free volume between the molecules of the solid matrix, thus it can also be related to the diffusivity and solubility. Hydrophilicity is also found to be suitable as a predictor of diffusion in polymers. The formation of hydrogen bonds of water in specific chain sites in polymers can affect the diffusion parameters and solubility. Increasing hydrophilicity helps in decreasing the activation energy required for water diffusion and facilitates water molecules to overcome the attractive forces among themselves [23,161].

5.2. Morphological properties

5.2.1. Atomic force microscope

Oxidative ageing and moisture ingression may leave some perceivable change on bitumen surface that can be detected by atomic force microscope (AFM) and scanning electron microscope (SEM). In particular, AFM can be used to explore the surface topography, phase separation along with mechanical properties including viscosity, stiffness, adhesion, and friction [162]. Bitumen displays the obvious "bee" microstructure consisting of hills and valleys at the center of wax crystallite in AFM imaging [163]. The surface microstructure shows some physical and chemical properties connected to the macroscopic properties of bitumen.

During oxidative ageing, number and size changes of the image characteristics related to asphaltenes and resins can be seen in AFM images [164]. The asphaltene micelles can be detected in topographic and phase imaging through AFM, which gradually connect with each other during the ageing process [165]. The AFM images can also be used to calculate the fractal dimension D_f, which indicates the amount of spatial space occupied by the chemical chains of bitumen due to its degree of roughness and irregularity [165]. The fractal dimension exhibits the increased structure compactness with ageing evolution, which in another way, can be reached from the images of fluorescence microscopy, especially for polymer modified bitumen [166].

Pressure, bending or tension originating from water exposure can lead to the spread of material and some weakest points on bitumen surface. AFM images of bitumen exposed to water shows "nano-bumps" on the characteristic "bee" structures on the surface microstructure [132] (Fig. 15). It is hypothesized that nano-bumps are the para phase resins, which absorb water and seep up from underneath the "bee" structure via the pinhole effect.

5.2.2. Scanning electron microscope

SEM produces images of a particular area of samples with a focused beam of electron to get the surface structure at micro meter to nanometer scale. Compared with SEM, environmental SEM allows for the change of environmental conditions such as pressure, temperature and gas composition, suitable for observing viscous bitumen at high vacuum [167]. A typical network of fibrils can be observed related to the bitumen microstructure. A revealed evolution in the fibril microstructure with ageing process demonstrates the relationship between the fibril microstructure and the bitumen properties [168,169]. As bitumen is gradually oxidized, the fibrils are more numerous, organized and densely packed (Fig. 16).

Williams et al. used environmental SEM to study the water penetration in bitumen [170]. The ESEM images clearly show the stripping of bitumen layer from the aggregate surfaces after freeze–thaw cycling and the traces of water penetration into bitumen.

In spite of some promising studies about the application of AFM and SEM in observing the morphology of bitumen under the effect of ageing and moisture ingression, the mechanism of the characteristics of the morphological images is not clear and the quantitative relationship between image parameters and bitumen properties has not been established. The limited knowledge on the correlation between morphology and ageing and moisture damage requires further research toward standard test procedures and evaluation methods.

5.3. Mechanical properties

Master curves are widely used to represent the viscoelastic properties of bitumen over a wide range of temperatures and frequencies. Complex modulus at different temperature with same frequency range can be shifted at a value α_T based, for example, on the WLF equation to get master curve. From the rheological tests and the master curves, the main parameters utilized include the complex shear modulus G*, the phase angle δ (the viscous response lag), the storage shear moludus G' (elastic energy), the loss shear modulus G''(dissipated energy), and the cross-over temperature ($T_{\delta=45^o}$, fatigue cracking) from the frequency/temperature

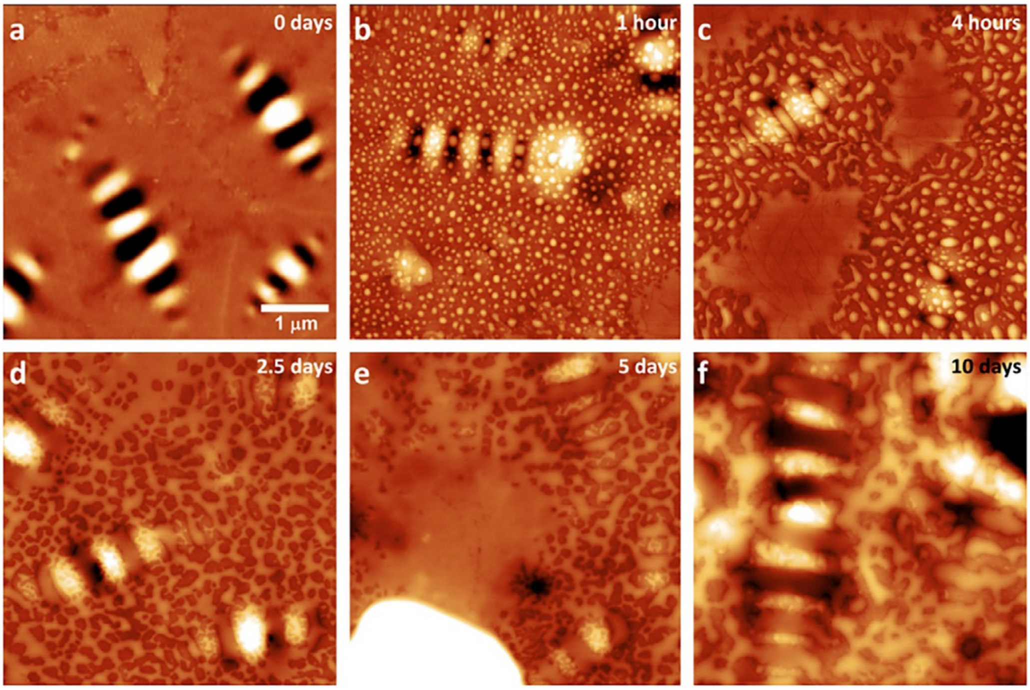

Fig. 15. AFM height images of bitumen samples (a) before and (b–f) after soaking in water at room temperature (22 °C) for one hour to 10 days. Scale bar applies to all images. The false color height scale is 35 nm for (a–c) and 50 nm for (d–f) [132].

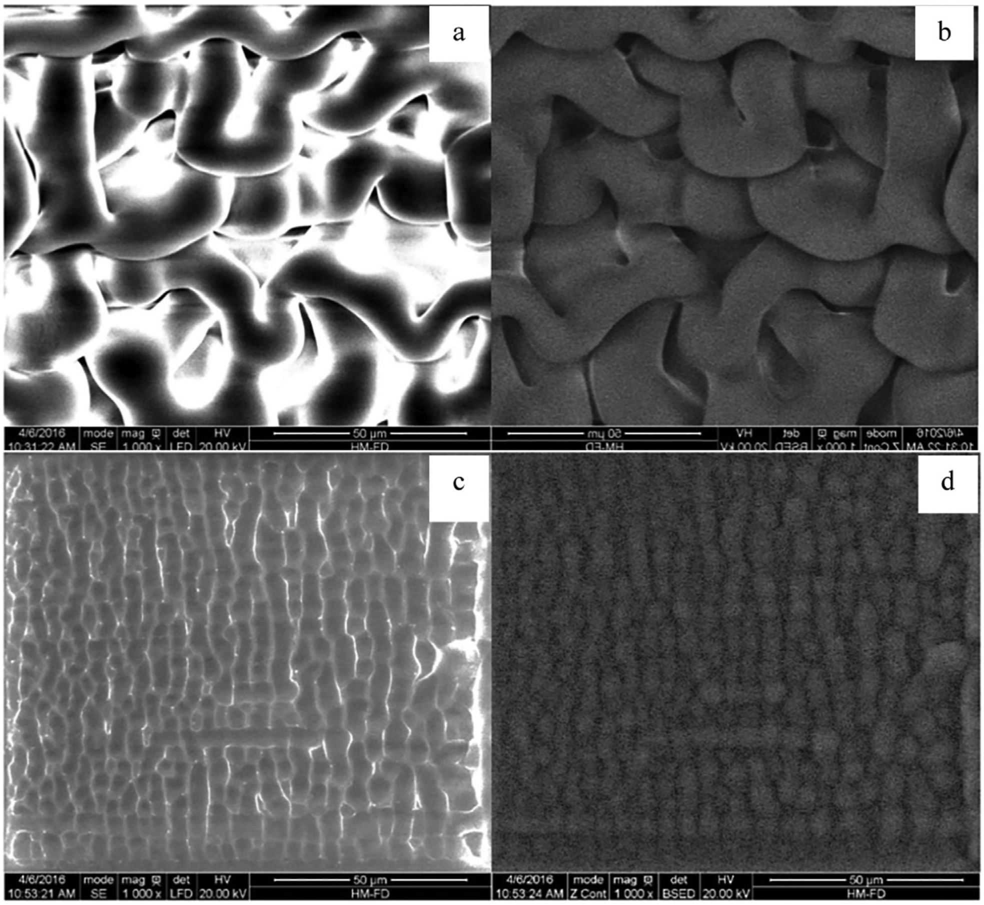

Fig. 16. ESEM images of original with secondary electrons (SE) (a) and backscatter electrons (BSE) (b) modes and oxidized bitumen with SE (c) and BSE (d) modes at 1000x magnification [169].

sweep DSR tests, whereas the creep stiffness S, the relaxation parameter m and the critical temperature ΔT_c can be obtained from the Bending Beam Rheometer (BBR) test [171]. Complex modulus normally increases and phase angle decreases with ageing time due to the higher asphaltenes concentration in bitumen [172]. It is shown that PAV ageing increases the pull-off tensile strength [11]. The cohesion force of bitumen increases with ageing time due to the asphaltenes association. The adhesion increases initially and then decreases, which could be the wettability resulting from the polar products [173]. The Huet model is proved to be more adaptable in modeling the constitutive equation of ageing bitumen, where the values of key parameters is dependent on the reaction progress [19]. A microstructural model of bitumen is proposed considering the micro structural changing with ageing. Different SARA components and their changes with ageing have different contribution to the mechanical properties and they are homogenized considering the micelle structure to get the creep compliance of bitumen [174].

Some compounds in bitumen are found to be soluble in water and are removed away [175], leading to the increase of asphaltene content. As a result, the complex modulus and the fatigue factor increased and the phase angled decreased [176]. Cohesion and adhesion failure are the two main failure modes in bituminous mixtures [11,177]. As the moisture content increases [11] and temperature decreases [178], the failure gradually converts from cohesive to adhesive. Moisture damage can be affected by the air void structure, bitumen type, moisture level and other mixture-related properties simultaneously. Efforts have been made to differentiate the parameters related to mixture damage and study the fundamental binding properties of bitumen. Bitumen cohesion can be measured using the tack test [179] and the cohesion test [180], showing the decrease of tack factor in wet conditions. The surface energy method (SFE), the pull-off test such as pneumatic adhesion tensile test (PATTI), etc. have been developed to evaluate the adhesive bonding of bitumen-aggregates systems [181,182]. The values of SFE and pull-off tests show a strong relationship. The pull-off strength decreases after wet conditioning [183]. A modified DSR test was set to evaluate bitumen-aggregate interaction under water conditioning. The linear viscoelastic complex modulus tested at higher shear stress decreases after wet conditioning [184].

5.4. Mutual relationship of different parameters

Although the individual parameters can describe typical characteristics such as the ageing level and moisture resistance, it is often unsuitable or not fitting for various bitumen types from different sources and with different manufacturing processes due to the molecular heterogeneity and steric complexity. The quantitative comparison between the various bitumen types via similar methods is thus challenging. Using different parameters to estimate the bitumen properties at the same time strengthens the confidence of the conclusions. Building correlations between different parameters gives a more extensive discussion. The bitumen fractions especially the asphaltene content and the molecular weight can be related with the softening point, penetration [160], complex shear modulus and dynamic viscosity, which demonstrate observable changes with ageing and diffusion process. The molecular weight, sulfur content, and density together with the glass transition temperature can be expressed as a function of the complex shear modulus. Elasticity characterized by the complex shear modulus or phase angle may also be related to the extent of polarity based on the turbidimetric titrations, in which the polar interaction between molecules is responsible for the elastic behavior of bitumen [152].

The viscosity can be correlated with other tests and parameters such as molecular weight, aromaticity, solubility, amount of functional groups [185]. The correlation between the logarithm of viscosity and carbonyl area is interpreted as linear for original and polymer modified bitumen [158].

$$ln\eta_{LSV} = HS \times CA + m \tag{40}$$

Through the fitting of the viscosity and the content of the carbonyl group, Herrington revealed a non-linear correlation [20]:

$$log\eta = log\eta_0 + 0.136\left(1 - e^{-5.8419\Delta CA}\right) + 0.0559\Delta CA \tag{41}$$

The molecular weight distribution is also connected to viscosity. The relationship between absolute viscosity and the relative quantity of large molecular size in Gel Permeation Chromatography (GPC) profile can be reached using regression models. This relationship can be applied not only on pure bitumen but also on polymer modified bitumen with a relatively lower coefficient of determination [186].

Storm et al. [187] developed a viscosity model of dilute polydispersed dispersion of hard spheres proposed by Roscoe. Here the bitumen is treated as a complex fluid consisting of a dispersed phase of spherical particles and a two-component solvent in which one acts as an inert continuum and the other is absorbed on the particles. The ultimate viscosity of bitumen is dependent on the viscosity of the non-asphaltenic fraction μ, the solvation constant K and the weight fraction of asphaltenes W_A:

$$\eta/\mu = (1 - KW_A)^{-2.5} \tag{42}$$

RTFOT ageing can multiply the viscosity by 1.5–4 with the asphaltene content increased by 1–4 wt%. It can be approximately estimated that a 2% increase of asphaltenes can double the viscosity. Data analysis from [146] illustrated the linear relationship between viscosity powered by 0.4 and the asphaltene content [149].

Weigel et al. [188] gave an integrated index through linear combination of the molecular weight and content of saturates, aromatics, resins and asphaltenes and used the rate of the index at original state and aged condition to exhibit the ageing level.

$$\begin{aligned} Y = {} & b_0 + b_1 c_{sat} + b_2 c_{arom} + b_3 c_{res} + b_4 c_{asp} + b_5 M_{n,sat} \\ & + b_6 M_{n,arom} + b_7 M_{n,res} + b_8 M_{n,asp} \end{aligned} \tag{43}$$

where Y can be the softening point, complex modulus, or viscosity, b_{1-8} are the regression coefficients, c is the content in weight percentage, M is the molecular weight (sat, arom, res, asp refer to saturation, aromatics, resin, asphaltene respectively).

Measuring moisture diffusion and oxidative ageing requires a long time. If the parameters and indices that are easy to measure can be linked to direct parameters characterizing diffusion and reaction process, it will save much time and effort to analyze and evaluate these phenomena. Many proposed parameters and indices focus on the evaluation of the physicochemical and mechanical responses upon ageing and diffusion of bitumen, instead of directly relating to the diffusion parameters. It is thus necessary and critical to study this relationship. It can be seen that viscosity can be linked to many other parameters such as physical, chemical and mechanical parameters. It can also be used to determine the diffusion coefficient of oxygen and moisture. Therefore, linking the diffusion coefficient with other physico-chemical parameters is an promising way to predict the transport behavior of moisture and oxygen in bitumen.

5.5. Upscaling of the effect of moisture and ageing

Ageing of bitumen is one of the crucial factors for pavement deterioration. The ageing of bituminous mixtures is also affected by additives, aggregate type, air voids etc. [21]. Upscaling methods, including the generalized self-consistent scheme and the Mori Tanaka scheme, can be used to incorporate the mechanical model of aged bitumen into the ageing model of asphalt mixtures [189]. Direct mechanical models of mixtures are also effective in predicting mixture ageing, where some parameters are a function of the ageing progress. The dynamic modulus model of mixtures changes with the reaction kinetics in mixtures as follows:

$$|E^{*}| = |E^{*}|_{i} + (|E^{*}|_{M} - |E^{*}|_{i}) \times \left(1 - \exp\left(-k_{f}t\right) + k_{c}t \quad (44)$$

where $|E^{*}|$ is the dynamic modulus of bituminous mixtures during ageing, $|E^{*}|_{i}$ is the initial dynamic modulus, $|E^{*}|_{M}$ is the dynamic modulus at the completed ageing stage, k_f and k_c are fast-rate and constant-rate reaction constants, respectively. In bituminous mixtures, the viscoelastic parameters of constitutive models are set as a function of the ageing degree [190]:

$$J_{2}(\omega, h) = \frac{1}{\eta_{1}(h)\omega} + \frac{\eta_{2}(h)\omega}{E_{2}^{2}(h) + \eta_{2}^{2}(h)\omega^{2}} \quad (45)$$

where J_2 is the loss compliance, h ageing rate, η_1, η_2, E_2 are parameters, ω angular frequency.

The performance of bituminous mixtures is well evaluated by the adhesion and cohesion of bitumen when conditioned by water [191]. Mixtures show the same maximum tensile strength ranking with the cohesion ranking of bitumen [182]. In wet conditions, the maximum tensile strength of mixtures can be a function of the combined tack factor of bitumen and the pull-off strength of bitumen-aggregate systems [179]. It has been shown that mixtures prepared with bitumen with higher moisture absorption present higher moisture damage rate [85]. Coupled loading-moisture models have been proposed to model the response of bituminous mixture in wet conditions [192]. The moisture damage of mastic, mastic-aggregate and aggregate can be developed and integrated into a mixture damage model through the homogenization method [193]. Kringos et al. proposed an extra moisture damage parameter d_m included in the Helmholtz free energy function of mixtures to build the constitutive model for bituminous mixtures conditioned by moisture. The moisture damage parameter is a function of moisture damage of the mastic and the mastic-aggregate interface. The mastic-aggregate damage is assumed as a function of moisture content: [194]

$$d_{\theta}^{if} = 1 - \exp\left(-a_{\theta}^{if}\sqrt{\theta}\right) \quad (46)$$

where θ is the normalized moisture concentration, a_{θ}^{if} is the moisture susceptibility parameter and d_{θ}^{if} is the moisture damage at interface.

Caro et al. [195] presented a coupled mechanical model of moisture-induced damage using the cohesive zone modeling technique, where the mechanical properties of mastic and mastic-aggregate interface are moisture dependent. Researchers also developed a three-dimensional elasto-visco-plastic model is used to predict the combined moisture damage and mechanical loading consisting of a generalized Maxwell model in series with and an inelastic component driven by coupled moisture-mechanical damage (Fig. 17) [58].

6. Towards coupling of moisture and ageing in bituminous materials

6.1. Mutual effects of moisture and ageing in bitumen

Some researchers have proved that a mutual influence exist between moisture damage and oxidative ageing. There are intermolecular interactions between water and bitumen and its diffusion process may disturb the colloidal structure of bitumen similar as in the case of increased temperature. The effect of water on the ageing process of bitumen strongly depends on the bitumen type. Gel-type bitumen is more affected than sol-type bitumen probably due to the higher polar compounds and the interactions with bitumen [26]. The increase of concentration of the acid group is higher in the presence of water as well as the asphaltene association [63]. Water soluble films can be formed with ageing [21] since some reaction products are soluble in water, especially the components containing elements such as oxygen, nitrogen, and sulfur [176]. When no moisture is present, these elements increase continuously on the surface of bitumen film with ageing time. In the presence of moisture, they may increase first and then keep constant or even decrease as time progresses due to the dissolution and removal with water flow on the surface [125]. It is shown that PAV ageing with water can accelerate the ageing process, with the average stiffness to be 18.1% higher compared with the standard PAV ageing process. UV light can also accelerate the oxidation process, but it can be delayed when at moist conditions [25]. It is also demonstrated that wet conditions can delay bitumen hardening, since tests show that the cross-over temperature is lower when bitumen is aged in wet environment compared with the samples aged at dry atmosphere [63]. Another research shows the opposite conclusions, namely that bitumen hardens in the presence of water and becomes more rigid due to the solution of oxygen in water [196]. These contradictory observations may be caused by the different experimental conditions, evaluation methods, types of bitumen. Therefore, more studies including more bitumen types, well controlled conditions and evaluations using physico-chemical, microstructural, and mechanical parameters are required.

Limited studies have focused directly on the impact of ageing on the moisture diffusion behavior in bitumen. Moisture infiltration into bitumen weakens the adhesive and cohesive force [197], while ageing has less impact on adhesive failure, especially for the aggregates with higher polarity [198]. The change in polarity, beneficial for adhesion, may be counterbalanced by the hardening of bitumen due to ageing. The correlation between ageing and moisture diffusion into bitumen is still uncertain. The diffusion of penetrant gas into polymers is correlated to the free volume fraction, the rigidity of molecular chains and the intermolecular forces [61]. The diffusion coefficient is inversely correlated to hydrophilicity because of the interaction between water molecules and polar groups in polymers and bitumen can slow down the diffusion process [136]. Oxidation of bitumen shows obvious increase of the carbonyl and the sulfoxide groups [164] and hydrophilicity [199]. From these we can infer that the diffusion coefficient may be reduced when bitumen is aged. On the other side, agglomeration of water molecules in bitumen may occur as ageing products can increase the interaction between bitumen and water, which can damage the structure and impair the mechanical properties.

The interaction between diffusion and reaction of moisture and oxygen is complicated and there is an absence of unequivocal conclusions. One reason is the different evaluation indices and methods used in the studies. Another reason is that the process is significantly affected by bitumen composition and the reaction mechanism. Physical and chemical processes can have a great impact on the final behavior of bitumen. Many mechanisms are interdependent, thus they act and affect with each other. These complex mechanisms and interactions behind ageing and moisture damage are the main contributors to these ambiguous and contradictory conclusions in recent papers. Moisture damage and ageing originate from the diffusion and reaction of moisture and oxygen in bitumen, followed by the microstructural and mechanical damage. Hence it is of critical importance to study the diffusion and reaction behavior through effective tests and modeling methods.

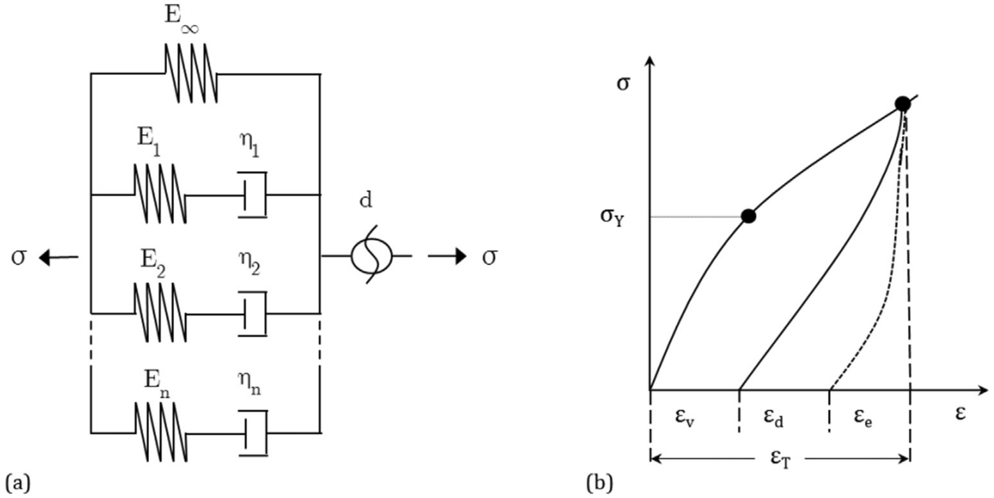

Fig. 17. (a) Schematic of elasto-visco-plastic model with softening due to mechanical-moisture damage. (b) Model response: σ is the stress; σ_Y is the yield stress; $\varepsilon = \varepsilon_d + \varepsilon_v + \varepsilon_e$, where ε is the total strain, ε_d is the strain due to damage, ε_v is the viscous strain and ε_e is the elastic strain [58].

6.2. Upscaling of coupled moisture-oxygen performance

The separate diffusion–reaction model of oxidative ageing and diffusion model of moisture can be applied on pavement performance prediction as moisture damage and in-field ageing performance. In a generic diffusion and reaction process, the reaction rate constant, the diffusion coefficient, and the solubility are related to temperature through the Arrhenius equation. The temperature and other environmental conditions can be obtained from weather station data or environmental models. The environmental conditions, mixture structure and air void distribution can be taken into consideration to develop a 3D pavement performance map. A comprehensive model simultaneously considering ageing kinetics, rheological kinetics, mastic thickness and climatic properties is proposed to predict the long-term pavement performance [200]:

$$ln\eta_{aged} = ln\eta_{t=0} + \left[a_l + b_l\left(t_{ps}\right)^{c_l}\right] \cdot \left[lnA_{ar(s)} + \frac{E_{ar(s)}}{RT_R}\right] \cdot \left[k_l\left(\frac{E_{ac}}{E_{af}}\right)^{m_l}\left(1 - e^{-k_{af}t}\right) + k_{ac}t\right] \tag{47}$$

in which $k_{af} = A_{af}\exp(-E_{af}/RT_a)$, $k_{ac} = A_{ac}\exp(-E_{ac}/RT_a)$, a_l, b_l c_l, k_l and $m_l$are model coefficients, η is the bitumen viscosity, t_{ps} is the primary structure coating thickness, A_{af} and $A_{ac}$are the fast-rate and constant-rate pre-exponential factor respectively, $E_{af}$and $E_{ac}$are the fast-rate and constant-rate aging activation energy respectively, $lnA_{ar(s)}$ and $E_{ar(s)}$ are pre-exponential factor and rheological activation energy of short-term aged bitumen respectively.

Individual evaluation and prediction of moisture and oxidative ageing on pavement performance can lead to opposing conclusions. It is proved that long-term ageing increases the adhesive strength of bitumen-aggregate interface, while aging and moisture together decrease the adhesive strength. Moisture shows the dominant impact on the adhesive strength compared with ageing [11]. If the coupled moisture and oxygen effects on mastics, aggregate and mastic-aggregate interface are modeled respectively, then pavement performance can be predicted by homogenization method or numerical simulation when 3D mixture structure is provided. Das et al. proposed a possibility to capture the coupled effect of ageing and moisture damage on mixture performance from diffusion-controlled ageing model of bitumen and diffusion-controlled moisture damage of mastic [197]. Nobakht presented an integrated ageing-moisture prediction method of dynamic modulus of bituminous mixtures. The master curve of mixtures affected by ageing are considered using a kinetic-based ageing model. The effect of water on dynamic modulus is evaluated by combining adhesive damage model and cohesive damage model through a linear map. The coupled ageing-moisture model is the modification of an ageing model incorporated by an moisture damage factor [201].

7. Conclusion and recommendations

Oxidative ageing and moisture transport in bitumen can significantly affect pavement durability. Considering moisture and oxygen together and their joint effects on the behavior of bitumen makes it possible to predict long-time pavement performance. This paper presents an overview of theories, expressions and applications regarding the sorption transport and reaction process of moisture and oxygen in bitumen. Physical, chemical and mechanical properties are discussed to characterize the effect diffusion and reaction of oxygen and moisture on bituminous materials. Based on this review, the following conclusions can be drawn:

The dual or triple modes including sorption, diffusion and clustering should be taken into consideration when studying the sorption and transport of moisture in bitumen. Coupled diffusion–reaction model of oxygen takes into consideration the oxygen diffusion and reaction concurrently. Published diffusion coefficient of moisture and oxygen in bitumen shows values of various magnitudes. This difference could be attributed to the choice of kinetic transport models and the systematic errors of different test methods.

Chemical structure and composition are chief factors in determining the diffusion and reaction process. Other parameters such as viscosity, solubility and morphology are dependent on the microstructure and composition changes caused by the diffusion and reaction of oxygen and moisture in bitumen. Viscosity as a basic material property is closely related to the microstructure, the chemical composition and the mechanical response. Hence, it can act as an intermediate parameter to connect physicochemical behavior and mechanical properties.

When moisture and oxygen are present together in bitumen, their diffusion and reaction behavior could be affected by each other. This is reflected firstly on their effects on the chemical and mechanical properties, which in return changes the diffusion and reaction processes.

The performance of bituminous mixture is generally dependent on the properties of mastic, aggregate, mastic-aggregate interaction and void characteristics. The coupled kinetics of moisture damage and oxidative ageing can be characterized by the evolution of physico-chemical and mechanical parameters of bitumen. The coupled oxygen-moisture model of bitumen can then be extended to mastics. Pavement performance can be predicted through homogenization model or simulation methods considering mixture structure.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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