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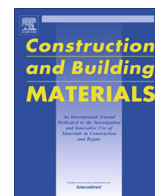To cite this publication, please use the final published version (if applicable).
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Numerical study of sorption of asphalt binders on minerals

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HIGHLIGHTS

- A multiphysics model was developed to simulate the sorption phenomena of asphalt binders onto minerals.
- The predicted profiles and the overall sorption behaviour at different energy conditions has confirmed the benefits of multiphysics model.
- The model can provide a prediction platform of various conversion schemes in hydrocarbon-related processes.

ARTICLE INFO

ABSTRACT

During the production of asphalt mixes, specific functional groups of asphalt binder interact chemically with certain reactive sites on the surface of minerals forming compounds that enhance the material resistance to environmental effects. The thermodynamics of surface phenomena between various combinations of functional groups of minerals and asphalt binders has been studied for quite a long time but it remains extremely difficult to control the desired material properties in practice. In this study, the chemical thermodynamics that determine the sorption phenomena and subsequently the relative affinity of asphalt binders onto mineral particles were analysed numerically and discussed. A two-step sorption configuration is studied in a multi-physics tool including reaction-driven mass transport of free species (i.e., carboxylic acid diluted in binder) onto a reactive surface (i.e., calcium functionalized mineral). Based on this configuration, the mechanism of asphalt-mineral interaction was determined at different surface temperatures and reactivity characteristics (i.e., activation energy and reaction kinetics of adsorption). The sorption model is applicable for various scenarios of asphalt-mineral interactions, especially for functionalized surfaces, in which the reaction-driven distribution of concentrations of asphalt adsorbates on minerals can provide useful information once the energetic parameters are known.

1. Introduction

During the asphalt mix production, at high temperatures liquid asphalt binders and mineral solid particles, such as fillers and aggregates, interact together and this interaction plays critical role in producing durable asphalt materials [1–5]. Specific functionalities, such as carboxylic acids, in asphalt binders interact chemically with the reactive sites on the surface of mineral particles, or minerals, forming compounds that affect the materials' oxidation resistance. The chemical thermodynamics of surface phenomena (i.e., adsorption and desorption) between various combinations of minerals and functional groups in asphalt binders has been studied for quite a long time [1,2] However, it remains extremely difficult to control the desired material properties in practice due to the complex chemical and physical processes that take place between the various functional groups of asphalt constituents.

Adsorption is a surface phenomenon between two phases (i.e., gas, liquid or dissolved solid to a surface) which results in the formation of a thin adhesive film. Adsorption will result in surface changes, in contrast with absorption, which is a volume phenomenon defined as the penetration and dissolution of species into a solid phase. Through the adsorption process, species of a substance, called adsorbates, are attached onto the surface of an adsorbing substrate, called adsorbent, resulting in concentration changes at the interface between the two individual phases. The reverse process is called desorption in which a substance is released from or through a surface. Furthermore, the bonding generated due to adsorption is dependent on the interactions between the various functional groups. Based on the nature of these interactions, adsorption is classified as physical (physisorption), which involves only relatively weak intermolecular forces (i.e., van der

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Waals), and chemical (chemisorption), which involves the formation of strong chemical bonds between the adsorbate species and the surface of adsorbent (i.e., covalent bonds) (Fig. 1) [6].

The interaction between minerals, such as fillers, and asphalt binder depends on the chemistry of individual phases. The surface chemistry of minerals provides the active sites available for interaction with certain functional groups of binders. During the adsorption process, the polar asphalt moieties interact with the active free sites on the surface of minerals with electrostatic, dipole and induced dipole forces [7]. In this way, the desired surface reactions occur, and improvement of the inter-phase interaction can be achieved. However, this can only happen when the functional groups are charged properly. The surface polarity can change to attract the opposite charged, non-uniformly dispersed traces in binders and in this way the desired adhesion can be promoted to form oxygen-resistant compounds [8–10]. Aged binders may be more prone to moisture-induced damage than unaged binders [3], so the full control of sorption and consequently of affinity becomes complicated.

Although asphalt binders are comprised in majority of non-polar hydrocarbons primarily long carbon chains and rings saturated with hydrogen (e.g., alkanes, paraffins, aliphatic compounds), specific functional groups introduce polarity controlling thus the asphalt sorption on minerals [11–15]. Mainly asphaltenes and resins as well as traces of metals represent the polar fractions in asphalt binders and extended studies have been performed on their relative affinity with various types of minerals, showing a certain trend [1,2]. Asphaltenes (molecular weight, M_W: 500–1000 g/mol) mostly comprised of a pericondensed polyaromatic backbone strewn with a few percent of nitrogen, oxygen and sulfur heteroatoms. Paraffinic rings, alkyl linkages, and aliphatic side chains decorate the asphaltenes as well. Of the functional groups in asphalt binders, carboxylic acid and sulfoxide groups have the highest adsorption potential, while ketone and non-basic nitrogen groups had the least [1]. These groups have been the most highly concentrated as adsorbed fractions on minerals however sulfoxide and carboxylic acids are very sensitive to desorption with water (hydrophilic compounds). The general trend of desorption of polar groups from the surface of minerals is sulfoxide > carboxylic acid > non-basic nitrogen ≥ ketone > basic nitrogen > phenol [1].

In addition to asphalt binders and their radicals (reactive functional groups), the contribution of active sites on the surface of minerals is critical to the overall affinity. The active surface sites of minerals serve as free space to attract the polar compounds of an asphalt binder [1,15]. For example, by using asphaltenes, the functional groups that adsorbed on silica surfaces have shown the following affinities: phenylsulfoxide > quinoline > phenol > benzoic acid > benzophenone > benzylbenzoate > pyrene [21]. On the other hand, the use of goethite as adsorbent is ranked as benzoic acid > diphenylsulfoxide > indole [22]. It is important to note that oxidation of asphalt binders causes changes to the functional groups, leading to an increase of oxidized compounds [11,16–18]. Ketones particularly are characterized of low affinity and adsorption of ketones becomes less with increasing the oxidation time. Oxidized groups adsorb to surfaces and thus change the asphalt binder sorption on minerals as well [1].

Most of the reactions happening when minerals interact with binder are known by a previously established research [2]. Certain nitrogen heteroatom groups (i.e., pyridines, pyrrolic, quinoline) in asphalt binders tend to hydrogen bond with the dry (polar) surfaces of minerals. However, the overall performance of nitrogen functional groups is linked with the type of acids involved in sorption process. Sodium (Na) and potassium (K) soap-type elements in asphalt binders (i.e., monovalent cation salts), formed from a reaction with carboxylic acids, are much more water-soluble than calcium elements (i.e., divalent salts) and as a consequence their formed hydrogen bonds on the surface of minerals are quickly broken in the presence of water [2,12]. Soap elements can be used as moisture promoters at various interfaces as well. For this reason, the treatment of asphalt binders with acids including insoluble salts of relatively hydrophobic surfaces (e.g., magnesium and calcium elements) is widely used to form insoluble compounds adsorbed on surfaces. A well-known example is the use of calcium hydroxide, which will be discussed later. Moreover, minerals composed with iron and aluminium can promote high affinity with asphalt binders because they assist on forming strong acid sites. Recently, a variety of nanomaterials have been incorporated in asphalt binders as well to promote affinity, increase oxidative aging resistance and enhance the asphalt durability [23,24]. Exemplary nanoparticles are nanoclay, layered silica, metal oxides, and carbon nanotubes [25–29], while surface functionalized particles, such as (3-aminopropyl)triethoxysilane, are able to form covalent bonds with asphalt binders [30,31].

Overall, the fundamental forces that occur through the asphalt sorption onto minerals depends on the chemistry of involved phases. Despite the above reported evidence from literature, no reports are available on the fundamentals of chemical thermodynamics of sorption phenomena between asphalt binders and minerals. To what extent the surface reactions depend on the asphalt functional groups and the processing conditions is not discussed. This research contributes to establish a framework on the binding mechanism of a solid–liquid system like asphalt-mineral. It is important to point out that kinetics and thermodynamic parameters contribute differently and should be analysed to control the affinity. On the one hand, thermodynamics describe the spontaneity of the asphalt-mineral interaction but reveal nothing about the time it will take. On the other hand, reaction kinetics define how fast the reaction proceeds. The parameters of these two categories
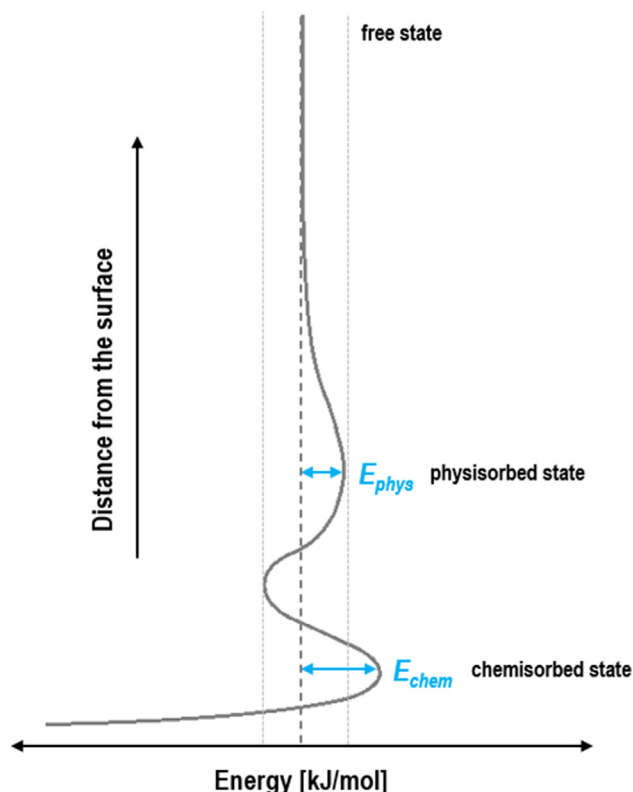

Fig. 1. Schematic of energy diagram for the case of chemisorption and physisorption governed by depth E_{chem} and E_{phys}, respectively.

are discussed in the following section based on the relevant mathematical models.

2. Theoretical considerations

2.1. Thermodynamics of sorption

Thermodynamics describe spontaneous processes occurring on their own without external interventions between two energy tendencies. The conversion of potential energy into work and heat is described by a parameter known as enthalpy. Similarly, the spontaneous increase of the randomness (chaos) of a system is described by another parameter named entropy. From the thermodynamics point of view, adsorption of an adsorbate (radicals of asphalt binder) on an adsorbent (active sites on mineral surface) can be related to these parameters via the Gibbs free energy (ΔG) [32] which describes the energy difference between energy states as

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where T is the absolute temperature [K], ΔS is the change in entropy [J mol^{-1} K^{-1}], and ΔH is the change in enthalpy [kJ mol^{-1}]. Enthalpy is the total heat released or absorbed through the adsorption to realise the adsorption between two oppositely charged radicals.

The change of Gibbs free energy of (isotherm) adsorption reaction [kJ mol^{-1}] is defined as

$$\Delta G = -RTln(K_{eq}) \tag{2}$$

where R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and K_{eq} represents the equilibrium adsorption constants of the isotherm fits. For negative and positive values of Gibbs free energy, the process can and cannot occur in a spontaneously way, respectively, hence the adsorption reactions with negative ΔG are thermodynamically favourable. When the system is at this state of minimum energy, the adsorption process is in equilibrium and described in the form identical to the integrated classic van't Hoff equation [33] as

$$ln(K_{eq}) = -\frac{\Delta G}{RT} \tag{3}$$

or

$$K_{eq} = \exp\left(-\frac{\Delta G}{RT}\right) \tag{4}$$

When the interaction between the involved phases is chemical (chemisorption), the binding energy of the adsorbate is subjected to an equal loss of free energy of the prior state which ranges from 80 to 450 kJ mol^{-1}. The losses of free energy in case of physisorption are usually from 10 to 80 kJ mol^{-1} including electrostatic interactions. The order of magnitude of energy difference between chemical and physical interactions is a function of the distance from the surface of adsorbent (see Fig. 1). However, the knowledge of magnitude of adsorption and desorption thermodynamic parameters is not sufficient to define a process like the interaction of minerals with asphalt functionalities. Hence, the reaction kinetics are used for further interpretation of sorption phenomena.

2.2. Surface kinetics

Surface bonding formed by certain reaction pathways and the production of new compounds on the surface of minerals with asphalt binders is a complex process and thus the single-sorption process of binder on minerals does not predict the actual behaviour [2]. From a reaction kinetics point of view, when a set of j reactions involve i species, the chemical reactions of adsorption and desorption are expressed based on the mass action law as

$$aA + bB + \cdots \underset{k_{des,j}}{\overset{k_{ads,j}}{\rightleftarrows}} xX + yY + \cdots \tag{5}$$
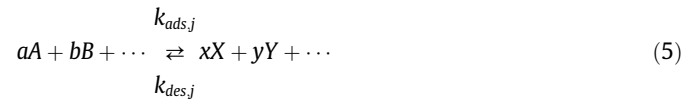
where $k_{ads,j}$ and $k_{des,j}$ denote the forward and reverse rate constants, respectively.

The reaction rates r_j [mol/(m^3·s)] of the above set corresponding to its chemistry is described as

$$r_j = k_{ads,j} \prod_{t \in react} c_i^{-v_{ij}} - k_{des,j} \prod_{t \in prod} c_i^{v_{ij}} \tag{6}$$

where c_i [mol/m^3] denotes the concentration of species i. The stoichiometric coefficients are denoted v_{ij} and defined as being negative and positive for reactants and products, respectively. A reaction seldom involves more than two species colliding in a reacting step in reality, so a kinetics expression is usually of order 2 or less.

The enthalpy and the entropy of adsorption is related to stoichiometric coefficients and defined as

$$H_j = \sum_{i=1}^{Q_p} v_{ij}h_i - \sum_{i=1}^{Q_r} (-v_{ij})h_i \tag{7}$$

$$S_j = \sum_{i=1}^{Q_p} v_{ij}s_i - \sum_{i=1}^{Q_r} (-v_{ij})s_i \tag{8}$$

where h_i and s_i are the molar enthalpy and entropy of involved radicals, respectively.

The heat source of reaction [W/m^3] is computed from the heat of each reaction j as

$$Q_j = -vH_jr_j \tag{9}$$

In the case adsorption and desorption reactions are in equilibrium, the kinetics are expressed [33] as

$$K_{eq} = \frac{k_{des}}{k_{ads}} \tag{10}$$

or

$$K_{eq} = \frac{c_X^x c_Y^y \cdots}{c_A^a c_B^b \cdots} \tag{11}$$
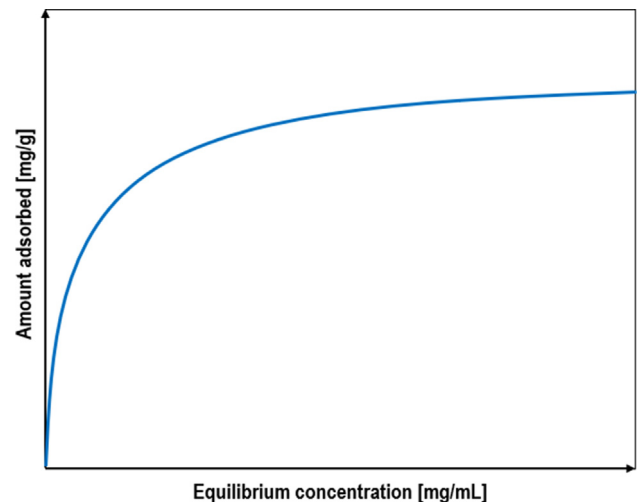

Fig. 2. A typical monolayer sorption plot illustrating the amount of adsorbed species (radicals) on a mineral as a function of species concentration.

2.3. Modelling approach

Radicals from both asphalt binder and sorbents interact chemically together forming new compounds. The relative affinity is quantified by the amount of a set of compounds, such as asphaltenes, adsorbed per surface area of sorbent [mg/m^2]. Regarding the asphaltenes as the primary group of reactive species in asphalt binders, the simple adsorption isotherms of asphaltene solutions (e.g., asphaltenes in aromatic solvents/solution) have been studied and the relative affinity of various substrates was shown to be limited under 4 mg/m^2 [19,20]. A typical plot of a model set of species at varying concentrations relative to the amount of adsorbed species is shown in Fig. 2, and such plots are used to determine the sorption isotherms and affinities. The following discussion and the case model of this study will highlight the sorption performance of an asphalt binder, or a solvent with diluted species, which is able to adhere onto sorbents (e.g., minerals).

As discussed earlier, the effect of various functional groups of asphalt binders have been extensively studied by having minerals as sorbents. In this study, the surface interaction of diluted species (i.e., carboxylic acids) in a solvent (i.e., asphalt binder) is modelled. The presence of carboxylic acids (COOH) in asphalt binder plays significant role on generating hydrogen bonds with the hydroxyl groups (SiOH) on mineral surfaces. Nevertheless, the hydrogen bonds are prone to be disrupted by water, and thus, among others, hydrated lime (Ca(OH)$_2$) is added in asphalt binder to converse the carboxylic acids to water insoluble compounds at surfaces [12]. Calcium hydroxide dissociate to species in asphalt binder producing calcium ions (Ca^{++}), able to interact with the carboxylic acid. With this interaction, insoluble calcium salts are formed leaving
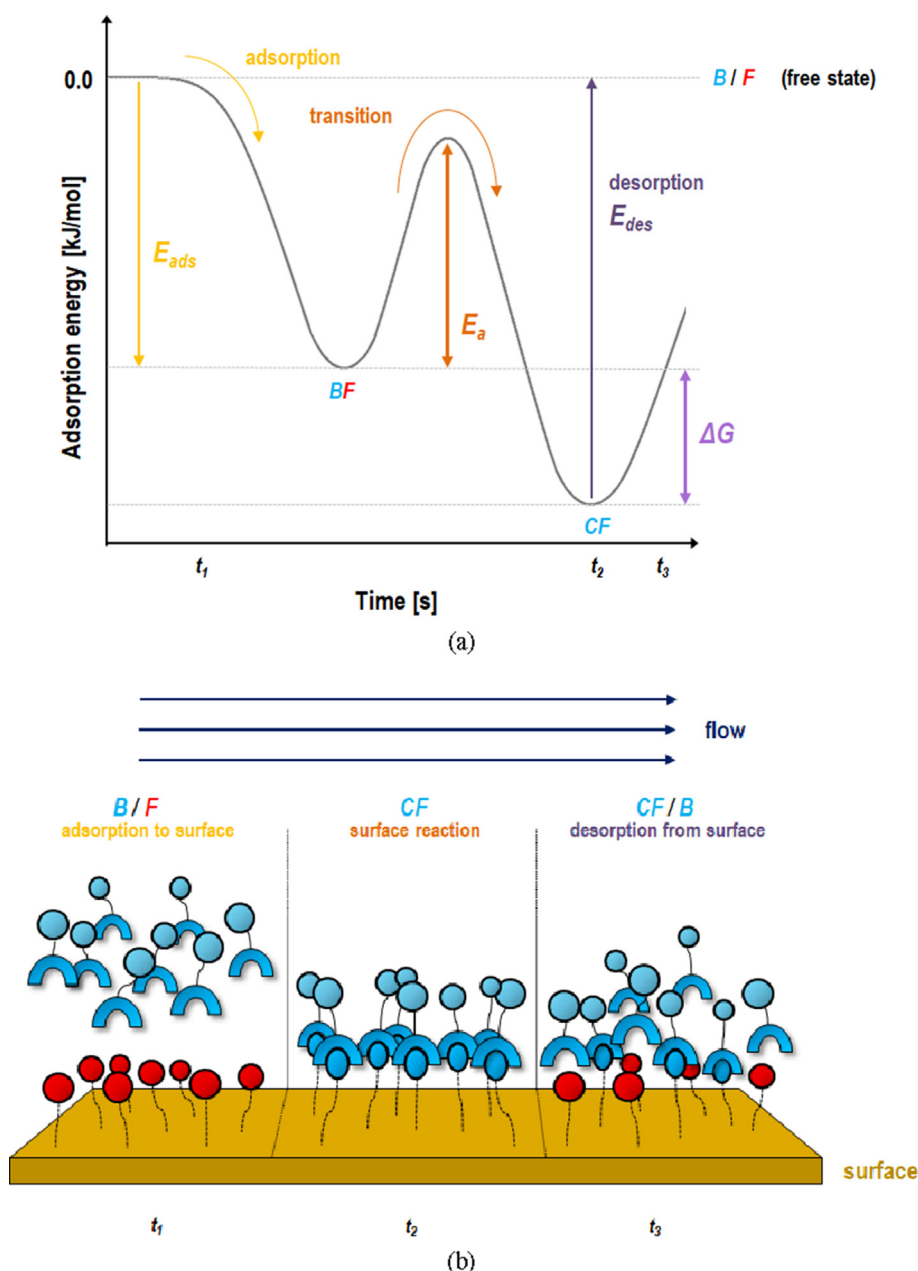

Fig. 3. Schematic of (a) energy diagram illustrating the two-step interaction between radicals of asphalt binder and active sites of a functionalized surface and (b) adsorption–desorption and mass transfer processes during the mineral-asphalt binder interaction.
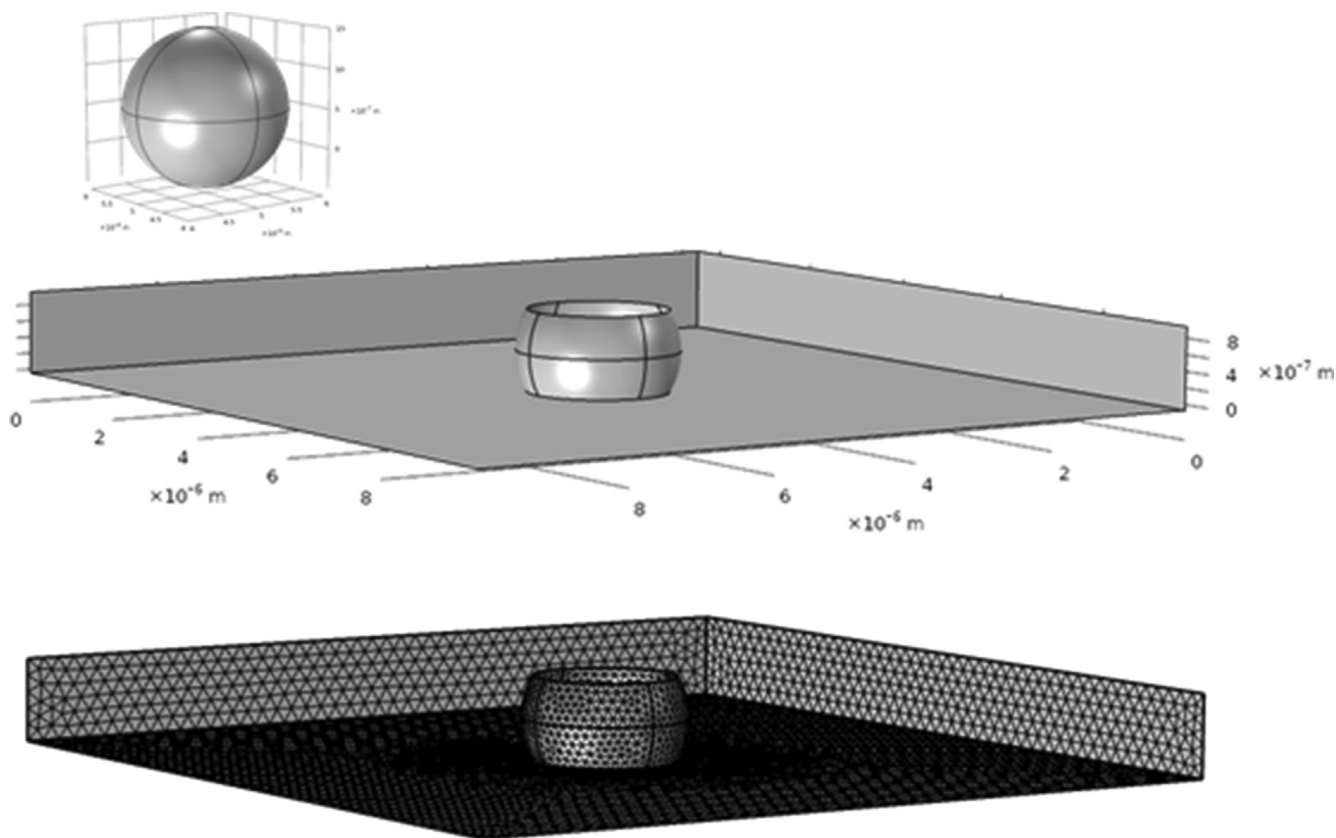
Fig. 4. Three-dimensional geometry (top) and mesh (bottom) of studied domain representing a functionalized particle in asphalt binder.

hydroxyl groups free to adhere with the nitrogen groups in asphalt binder [1,2] and possible prevent the adsorption of water-sensitive acids at free state.

From the literature, the reactions of some specific functional groups in asphalt binder, particularly carboxylic acids, with a mineral surface has been recognized as the major sorption configuration when binder interacts with hydrated lime. Numerous competitive sub-processes may be involved in the current prediction frame to determine the overall concentration profile of reactants and reaction products. By increasing the number of components involved in the reaction, the number of sub-processes will increase as well. To restraint the scope of this study, a two-step sorption model is proposed including the production of insoluble calcium salts on the surface after adsorption of acids.

In Fig. 3, a schematic energy diagram illustrates first the adsorption of free species of carboxylic acids (B), diluted in a binder, onto the mineral surface (F) with limited coverage (certain amount of active free sites, Γ_m). According to the sorption thermodynamics, certain quantities of energy are needed in the system to have a free species attracted and bonded on a surface (E_{ads}). Immediately afterwards, the attached species of acids on the surface (BF) create new compounds (CF) with the calcium ions. Here, the ions are considered not dissolved in binder but attached on the surface.

For the analysis of the above phenomena between asphalt binder and minerals, and particularly hydrated lime, the radicals diluted in asphalt binder (COOH or B) are adsorbed (surface reaction rate, k_{ads}) and desorbed (surface reaction rate, k_{des}) by the active surface of a particle. The adsorbed carboxylic acids (BF) interact with calcium ions (Ca^{++}) on the surface of a mineral under an irreversible reaction and insoluble calcium salts (CF) are formed (reaction rate, k_1). The exact two step reaction pathway is described as

Table 1
Model parameters used in the finite element analyses.

Parameters	Values at 25 °C
Gibbs free energy, ΔG [kJ/mol]	30
activation energy of adsorption, E_{ads} [kJ/mol]	50
activation energy of desorption, E_{des} [kJ/mol]	80
reaction rate of adsorption, K_{ads} [mol/(m²s)]	4E-8
reaction rate of desorption, K_{des} [mol/(m²s)]	1E-3
initial concentration of B, c_B [mol/m³]	1E-6
initial concentration of BF, c_{BF} [mol/m³]	0.01E-5
surface coverage, Γ_M [mol/m²]	10E-6

$$B + F \underset{k_{des}}{\overset{k_{ads}}{\rightleftarrows}} BF(ads) \overset{k_1}{\rightarrow} CF(ads) \qquad (12)$$

The rate of adsorption depends on the concentration of radicals (i.e., carboxyl acids) in a binder and the rate in which these molecules strike the active sites on the surface of minerals. Active site is a term used to describe radicals and also the surfaces of minerals implying a process wherein a surface reaction is promoted by certain species on the reactive surface.

According to the Langmuir isotherm theory [34], a monolayer of adsorbed species is formed on the energetically uniform surface sites ready to be covered by molecules. Theoretically, the adsorbed asphalt species by these sites (i.e., carboxylic acids – B) do not interact with each other, but only with the polar species on the surface (i.e., calcium ions – F) to form the new compound (i.e., CF). Thus, the rate of adsorption [mol/(m²·s)] is expressed as

$$r_{ads} = k_{ads}c_B(1 - \theta) \qquad (14)$$

with

$$k_{ads} = K_{ads}(T)\exp\left(-\frac{E_{a,ads}}{RT}\right)$$

where c_B is the bulk concentration of reactive species in asphalt binder [mol/m³], $E_{a,ads}$ is the energy to have a free species attracted on a surface [kJ/mol] and K_{ads} is the adsorption reaction factor. The fraction (i.e., surface concentration) of active sites occupied by adsorbed asphalt species (θ) is described as

$$\theta = \frac{\sigma_i c_{f,B}}{\Gamma_f} \tag{15}$$

where $c_{f,B}$ is the surface concentration of B on filler [mol/m²], Γ_f is the total surface concentration of active sites [mol/m²], in other words the density of surface sites, and σ_i is the site occupancy number for each molecule and accounts for the situation in which a large molecule covers more than one surface site. The latter is considered in this study, thus molecules do not cover more than one site.

On the other hand, the rate of desorption is expressed as

$$r_{des} = k_{des} c_{f,B} \theta \tag{16}$$

with

$$k_{des} = K_{des}(T)\exp\left(-\frac{E_{a,des}}{RT}\right)$$

where $E_{a,des}$ is the desorption activation energy and K_{des} is the desorption reaction factor.

The performance of transport mechanism of convection is given in the following equation which solves the mass conservation equation for the reactive species B in the binder

$$\frac{\partial c_B}{\partial t} + \nabla \cdot (-D_B \nabla c_B) + \mathbf{u} \cdot \nabla c_B = 0 \tag{17}$$

where c_B denotes the concentration of free species B [mol/m³], D_B is the diffusion coefficient of free species B [m²/s], and $\mathbf{u}$ is the velocity vector [m/s]. The first term on the left side of **Eq. (17)** corresponds to the consumption of species. The second term accounts for the diffusive transport, accounting for the interaction between the dilute reactive species and binder. The third term on the left side of **Eq. (17)** describes the convective transport because of a velocity field $\mathbf{u}$.

The mass flux due to desorption is dependent upon the local concentration of adsorbed surface species and is hence coupled to the equations on the active surfaces. The adsorption and desorp-
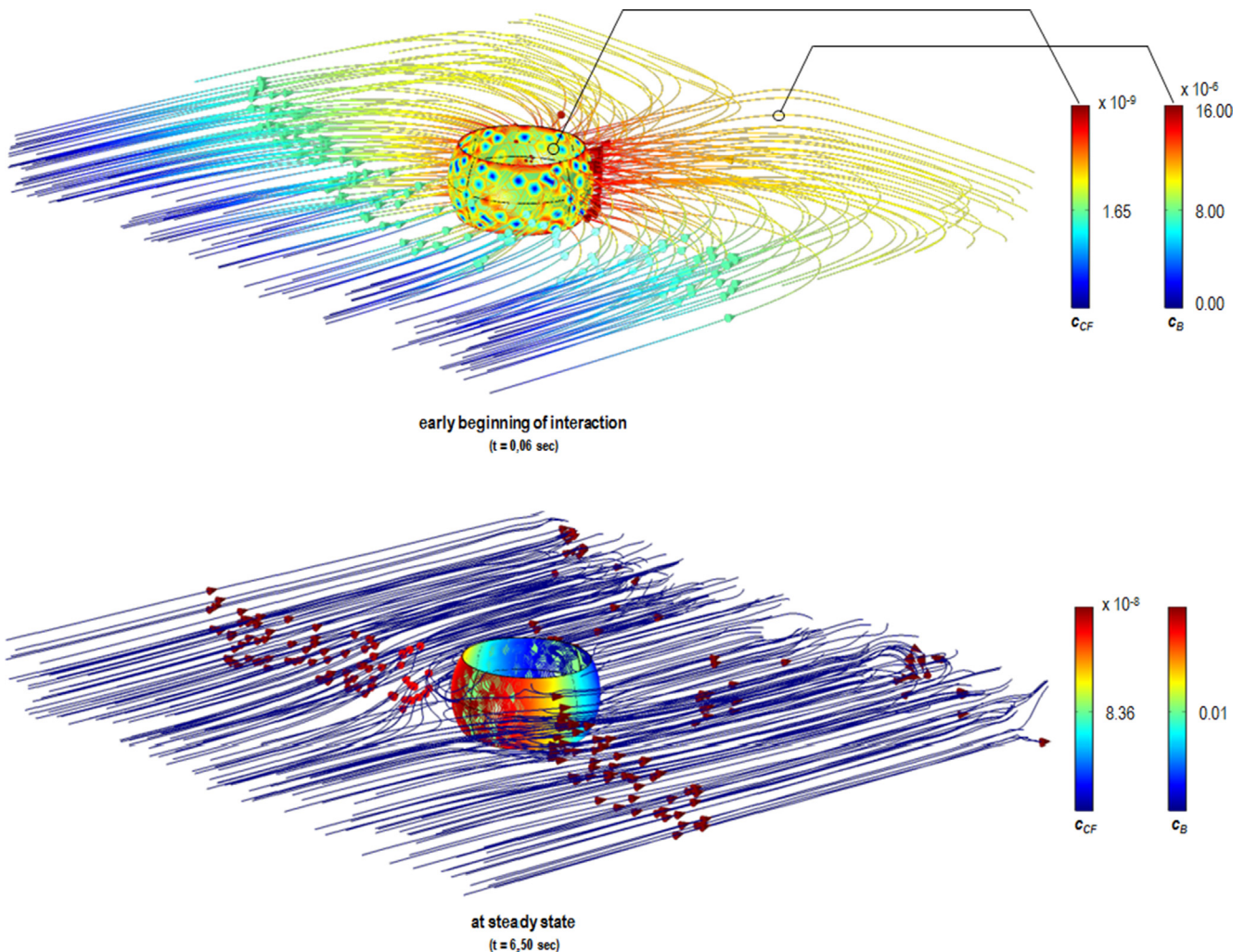

Fig. 5. Simulation results at the early beginning of surface interaction (top) and after reaching the steady state condition, or equilibrium, (bottom) (25 °C). The surface of filler clearly illustrates the generated surface species CF and the asphalt domain the free species of B.
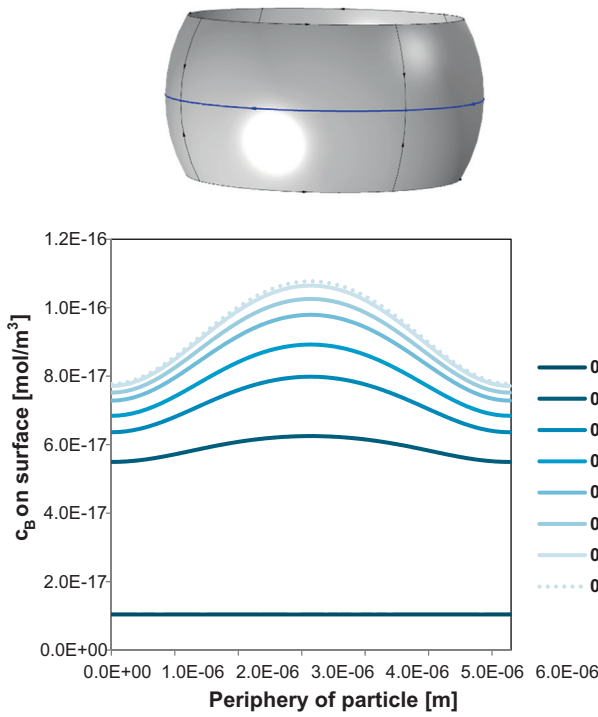
Fig. 6. Species of reactant (B) changes over time along the periphery of the particle at constant temperature.

Table 2
Studied parameters in sensitivity finite element analyses.

Parameters	Values
Temperature, T [°C]	20, 40, 60, 80, 100
activation energy of adsorption, E_{ads} [kJ/mol]	40, 50, 60, 70
reaction rate of adsorption, K_{ads} [mol/(m²s)]	4E-9, 4E-8, 4E-7

tion of asphalt binder on the surface mineral give rise to a net flux at the corresponding boundaries as

$$N_P = -r_{ads} + r_{des} = -k_{ads}c_B(1-\theta) + k_{des}c_{f,B}\theta \tag{18}$$

where r_{ads} and r_{des} are the adsorption and desorption rates, c_B is the concentration of B, $c_{f,B}$ is the concentration of surface adsorbed species.

The balance equations for the BF and CF species will be

$$\frac{\partial c_{f,B}}{\partial t} = r_{ads} - r_{des} - r_q = k_{ads}c_B(1-\theta) - k_{des}c_{f,B}\theta + k_1 c_{f,B} \tag{19}$$

$$\frac{\partial c_{f,C}}{\partial t} = -k_1 c_{f,B} \tag{20}$$

where

$$k_1 = K_1(T)\exp\left(-\frac{E_{a,1}}{RT}\right)$$

where $E_{a,1}$ is the activation energy of the formation of CF species.

3. Finite element analyses

A finite element mesh built of 190E3 number of domain elements to simulate a sorption case of asphalt-mineral interaction (Fig. 4). A single particle of 1E-6 m radius was set in the middle of a rectangular three-dimensional geometry (10E-6 × 10E-6 × 1 E-6 m³) and part of particle cropped as shown in Fig. 4 (top). Reac-
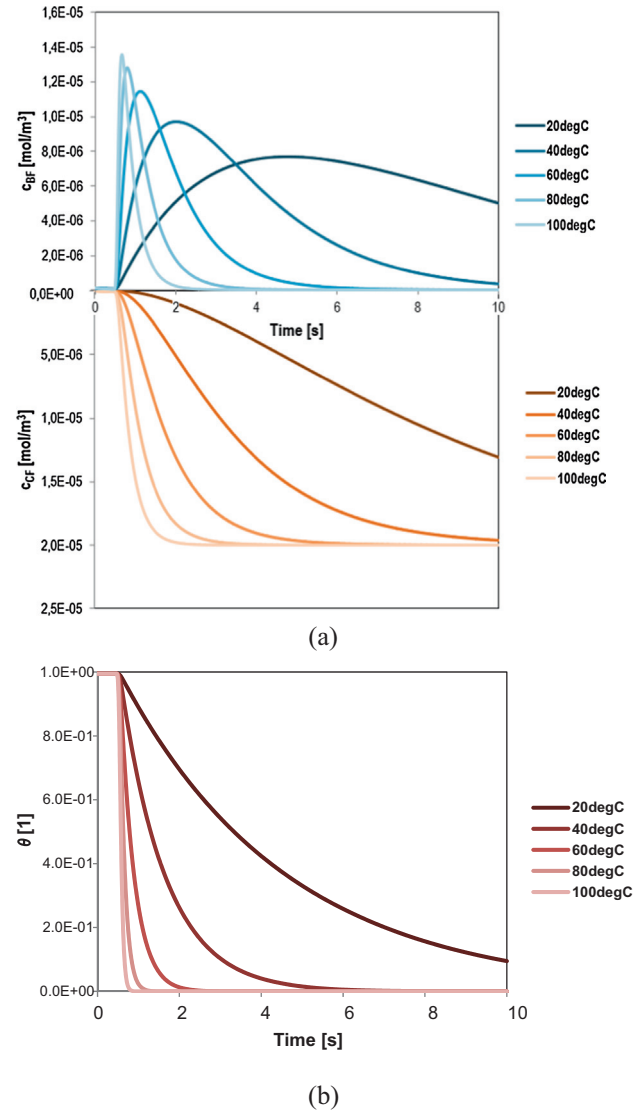

(a)

(b)

Fig. 7. Impact of surface temperatures on surface species changes over time demonstrating the impact of surface temperature on (a) the consumption and production of BF and CF species, respectively, and (b) the fraction of surface free sites.

tions occur at the surface of the particle representative domain where the reactant B is adsorbed onto the surface, consumed and at the same time generates the CF species.

For the current sorption analyses, the values of energetics parameters were obtained from a database generated in (1). Out of all the previously mentioned functionalities that perform differently with different minerals, benzoid acid (M_W = 122.13 g/mol) was considered as the model compound to represent carboxylic acids. At equilibrium state, the negative ΔG and K_{eq} between acid and surface were considered 30 kJ/mol and 4E-5, respectively (25 °C) [1]. According to (1), similar ΔG values of benzoic acids on greywacke and gravel have been determined. By keeping the studied system at equilibrium state, activation energy of adsorption (E_{ads}) of 50 [kJ/-mol] and of desorption (E_{des}) of 80 [kJ/mol] were implemented in the model. Further, 4E-8 and 1E-3 [mol/(m²s)] of reaction rate of adsorption and desorption were used as input, respectively. Regarding the surface coverage, the density of active sites (Γ_M) on mineral surface was considered of 10E-6 mol/m², as in (14). The concentration gradient of species B is considered along one single direction while no gradient exists in the other two directions (initial c_B of 1E-6 mol/m³; initial c_{BF} 0.01E-5 mol/m³) (Table 1).
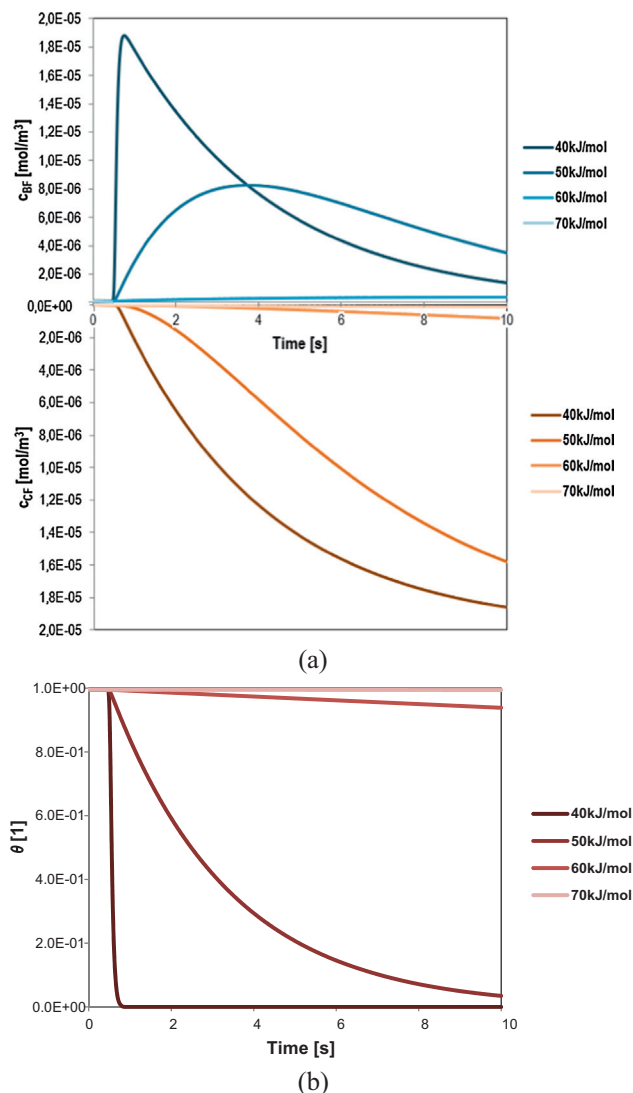
Fig. 8. Impact of activation energy [kJ/mol] on surface species changes over time demonstrating the impact of surface temperature on (a) the consumption and production of BF and CF species, respectively, and (b) the fraction of surface free sites.

Typical output of the model with the above characteristics and of surface reactions are shown in Fig. 5, where the strike of B species and their localized sorption on the active surface sites is demonstrated at the early beginning of interaction and after full coverage on the surface, respectively. Especially, the initial evolution of the concentration profile of B species is shown in Fig. 6, demonstrating the spatial distribution of concentration and concentration variation of B species adsorbed and consumed on the surface across the length of its periphery at the first 0.14 sec of interaction. Different time length of reaction cause different concentration profiles along the particle periphery. Nevertheless, these analyses are limited on one temperature and on a very low concentration of diluted species on a solvent, or binder. In the next subsections, sensitivity analyses were discussed to elucidate the effect of temperature and of reactivity characteristics on sorption performance of the whole system (Table 2).

3.1. Influence of surface temperature

To quantify mechanistically the impact of temperature during the interaction of diluted free species B (1E11 mol/m^3) on the active free sites of a surface (10E-6 mol/m^2), finite element analyses were
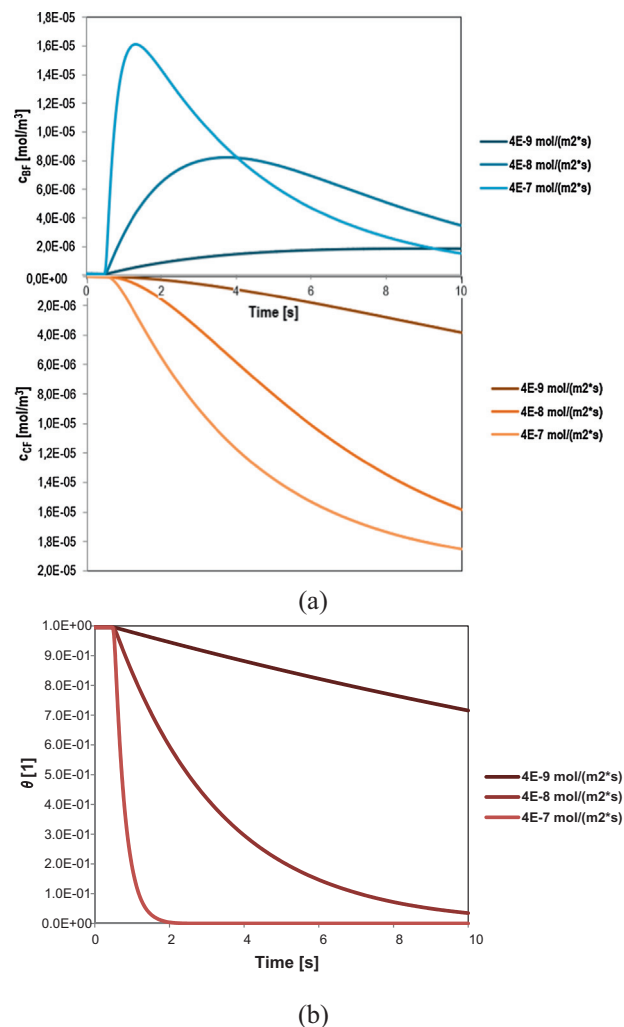

Fig. 9. Impact of adsorption reaction rate [mol/(m^2 s)] on surface species changes over time demonstrating the impact of surface temperature on (a) the consumption and production of BF and CF species, respectively, and (b) the fraction of surface free sites.

conducted at different surface temperatures by keeping the temperature of asphalt domain constant (25 °C). Particularly, the predicted concentrations of BF and CF species on the surface at 20, 40, 60, 80 and 100 °C and their respective evolution due to the sorption reactions are demonstrated in Fig. 7. Fig. 7a (top) and a (bottom) illustrate the concentration changes of B and CF species that were consumed and produced on the surface, respectively, at different surface temperatures over time (i.e., from 0 to 10 sec). Increase of reaction rate is observed with increase of the surface temperature resulting in the fastest consumption of BF species and also the highest surface concentration of CF at 100 °C. As expected from the results obtained from the BF and CF concentration profiles, the surface active free sites are occupied by B species, attached and reacted on surface, and hence the number of active free sites is decreased over time (see Fig. 7b). Further, as temperature increases, the consumption of BF species and the production of CF species on the surface was accelerated and subsequently reduction of fraction of free sites was resulted, reflecting the chemical response of warm minerals when they are in contact with asphalt binders.

3.2. Influence of reactivity

The energetic parameters governing the sorption isotherm phenomena are the adsorption energy (E_{ads}) and reaction rate (k_{ads}) of

the *B/F* configuration, and thus their effects on the extent of surface reaction have been analyses as well. Finite element predictions provided at 25 °C and the influence of activation energy of adsorption (40, 50, 60 and 70 kJ/mol) on the conversion rate of *BF* to *CF* species is analysed and simulation results are shown in Fig. 8**a**. Also, the reduction of active sites on surface due to the conversion of *B* to *CF* species is illustrated in Fig. 8**b**. Lower activation energy values indicate more reactive systems and thus species which are able to initiate a react without high energy demands. On the basis of simulation results, decrease of activation energy leads to a faster reduction of fraction free sites and conversion of new species on the surface (see Fig. 8).

In similar fashion, as expected, increase of reaction rate on the surface (i.e., from 4E to 9 to 4E-7 mol/(m²s)) caused quick sorption and generation of new species (see Fig. 9). The amount of adsorbed *B* species increased faster while the production rate of *CF* species increases on the surface, following the same trend with the activation energy decrease. As seen in both Figs. 8 and 9, adsorption and generation of new specific on the surface of minerals is highly dependent upon the reactivity parameters (i.e., E_{ads} and k_{ads}). The equilibrium concentrations were reached faster in the system with the 40 kJ/mol and 4E-7 mol/(m²s) of activation energy and reaction rate, respectively. Overall, the temperature and the reactivity of individual components strongly influence the surface reaction process between asphalt species and minerals.

4. Summary and future work

Understanding of conversion of functional groups in asphalt binders to useful compounds (e.g., oxidation inhibitors) with minerals, or nature originated particles, is not a well-established modification field in asphalt technology. Here, a fundamental study was presented and insights into the chemical thermodynamics of sorption phenomena of asphalt binders are discussed elucidating the controlling variables. A sorption model extended with surface reactions (two-step sorption model) was developed as well to explain the sorption behaviour of asphalt binders onto minerals. The current analyses could serve in future material studies to restrain the number of selected parameters for investigating the key steps of the sorption phenomena in asphalt mixes. Also, the model is applicable for various scenarios of asphalt-surface interactions in which the reaction-driven distribution of concentrations of asphalt adsorbates can provide useful information once the energetic parameters are known. Finally, the current model can be extended to applications where multiple catalytic processes can compete in various conversion schemes in asphalt- and hydrocarbon-related industries. Some exemplary applications may be the chemical conversion of heavy asphalt fractions (e.g., asphaltenes) to lighter hydrocarbons or reduction of molecular weights of certain groups.

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.

References

[1] C.W. Curtis, K. Ensley, J. Epps, Fundamental properties on asphalt aggregate interactions adhesion and adsorption. Strategic Highway Research Program, National Academy of Science, Washington, D.C., 1993.

[2] R.E. Robertson, Chemical properties of asphalts and their relationship to pavement performance. SHRP Report A/UWP-91-510. Strategic Highway Research Program, National Research Council, Washington, D.C, 1991.

[3] D. Williams, D.N. Little, R.L. Lytton, Y.R. Kim, Y. Kim, Fundamental properties of asphalts and modified asphalts. Task K, FHWA Final Report, Volume 2, Contract No. DTFH61-92C-00170, 1998.

[4] R.G. Hicks, Synthesis of Highway Practice 175: Moisture damage in asphalt concrete, TRB, National Research Council, Washington, D.C, 1991.

[4] R.G. Hicks, Synthesis of Highway Practice 175: Moisture damage in asphalt concrete, TRB, National Research Council, Washington, D.C, 1991.

[5] J.C. Petersen, Transportation Research Circular E-C140: A review of the fundamentals of asphalt oxidation: Chemical, physicochemical, physical property, and durability relationships, TRB, National Research Council, Washington, D.C., 2009.

[6] H.-J. Butt, K. Graf, M. Kappl, Physics and chemistry of interfaces, WILEY-VCH Verlag GmbH & Co. KgaA, Weinheim, 2003.

[7] E.K. Ensley, Multilayer adsorption with molecular orientation of asphalt on mineral aggregate and other substrates, J. Appl. Chem. Biotech. 25 (1975) 671–682.

[8] J.C. Petersen, F.A. Barbour, S.M. Dorrence, Catalysis of asphalt oxidation by mineral aggregate surfaces and asphalt components, J. Assoc. Asphalt Paving Technol. 43 (1974) 162–177.

[9] H. Plancher, E.L. Green, J.C. Petersen, Reduction of oxidative hardening of asphalts by treatment with hydrated lime-a mechanic study, J. Assoc. Asphalt Paving Technol. 45 (1976) 1–24.

[10] J.C. Petersen, H. Plancher, P.M. Harnsberger, Lime treatment of asphalt to reduce age hardening and improve flow properties, J. Assoc. Asphalt Paving Technol. 56 (1987) 632–653.

[11] J.C. Petersen, Quantitative functional group analysis of asphalt using differential infrared spectrometry and selective chemical reactions-theory and application, in: Transportation Research Record 1096, TRB, National Research Council, Washington, D.C, 1987, pp. 1–11.

[12] H. Plancher, S. Dorrence, J.C. Petersen, Identification of chemical types in asphalts strongly absorbed at the asphalt-aggregate interface and their relative displacement by water, J. Assoc. Asphalt Paving Technol. 46 (1977) 151–175.

[13] J.C. Petersen, H. Plancher, E.K. Ensley, E.L. Venable, G. Miyake, Chemistry of asphalt-aggregate interaction: Relationship with pavement moisture-damage prediction test, in: Transportation Research Record, 843, TRB, National Research Council, Washington, D.C, 1982, pp. 95–104.

[14] H. Ardebrant, R.J. Pugh, Surface acidity/basicity of road stone aggregates by adsorption from non-aqueous solutions, Colloids Surf. 53 (1991) 101–116.

[15] S. Park, M.C. Jo, J.B. Park, Adsorption and thermal desorption behaviour of asphalt-like functionalities on silica, Adsorpt. Sci. Technol. 18 (2000) 675–684.

[16] J.C. Petersen, F.A. Barbour, S.M. Dorrence, Identification of dicarboxylic anhydrides in oxidized asphalts, Anal. Chem. 47 (1975) 107–111.

[17] J.C. Petersen, H. Plancher, Quantitative determination of carboxylic acids and their salts and anhydrides in asphalts by selective chemical reactions and differential infrared spectrometry, Anal. Chem. 53 (1981) 786–789.

[18] J.C. Petersen, Quantitative method using differential infrared spectrometry for the determination of compound types absorbing in the carboxyl region in asphalts, Anal. Chem. 47 (1975) 112–117.

[19] S. Kokal, T. Tang, L. Schramm, S. Sayegh, Electrokinetic and adsorption properties of asphaltenes, Colloids Surf., A 94 (2–3) (1995) 253–265.

[20] J.J. Adams, Asphaltene adsorption, a literature review, Energy Fuels 28 (2014) 2831–2856.

[21] C.W. Curtis, Y.W. Joen, D.J. Clapp, Adsorption of asphalt functionalities and oxidized asphalts on aggregate surfaces, Fuel Sci. Technol. Int. 7 (9) (1989) 1225–1268.

[22] Y.W. Jeon, S.H. Yi, S.J. Choi, Adsorption of asphaltene functionalities and asphaltene on goethtte, Fuel Sci. Technol. Int. 13 (2) (1995) 195–214.

[23] P.K. Ashish, D. Singh, Use of nanomaterial for asphalt binder and mixtures: a comprehensive review on development, prospect, and challenges, Road Mater. Pavement Design (2019), https://doi.org/10.1080/14680629.2019.1634634.

[24] S. Wu, O. Tahri, State-of-art carbon and graphene family nanomaterials for asphalt modification, Road Mater. Pavement Design (2019), https://doi.org/10.1080/14680629.2019.1642904.

[25] Z. You, J. Mills-Beale, J.M. Foley, S. Roy, G.M. Odegard, Q. Dai, S.W. Goh, Nanoclay modified asphalt materials: preparation and characterization, Constr. Build. Mater. 25 (2011) 1072–1078.

[26] S.N. Amirkhanian, A.N. Amirkhanian, F. Xiao, Influence of carbon nanoparticles on the rheological characteristics of short-term aged asphalt binders, J. Mater. Civ. Eng. 23 (2011).

[27] E. Santagata, O. Baglieri, L. Tsantilis, G. Chiappinelli, Fatigue and healing properties of nano-reinforced bituminous binders, Int. J. Fatigue 80 (2015) 30–39.

[28] E. Santagata, O. Baglieri, L. Tsantilis, D. Dalmazzo, Rheological characterization of bituminous binders modified with carbon nanotubes, Procedia-Soc. Behav. Sci. 53 (2012) 546–555.

[29] P.K. Ashish, D. Singh, S. Bohm, Investigation on influence of nanoclay addition on rheological performance of asphalt binder, Road Mater. Pavement Design 18 (2017) 1007–1026.

[30] S.R. Karnati, D. Oldham, E.H. Fini, L. Zhang, Surface functionalization of silica nanoparticles to enhance aging resistance of asphalt binder, Constr. Build. Mater. 211 (2019) 1065–1072.

[31] S.R. Karnati, D. Oldham, E.H. Fini, L. Zhang, Application of surface-modified silica nanoparticles with dual silane coupling agents in bitumen for performance enhancement, Constr. Build. Mater. 244 (2020) 118324.

[32] J.W. Gibbs, Collected works, Yale University Press, New Haven. Conn, 1928.

[33] D.M. Ruthven, Principles of adsorption and adsorption processes, John Wiley & Sons, Inc, 1984.

[34] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (9) (1918) 1361–1403.