

Adhesion failure mechanism of asphalt-aggregate interface under an extreme saline environment: A molecular dynamics study

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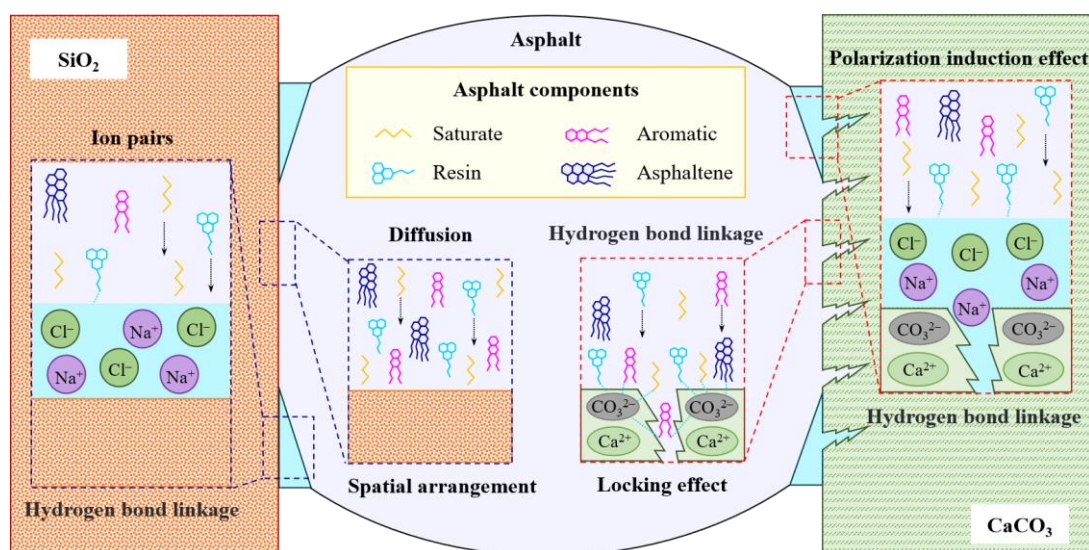
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Graphical abstract:



ABSTRACT

The extreme saline environment seriously threatens the service life of asphalt pavement. The interface adhesion failure between asphalt and aggregate is fundamental to pavement diseases. Therefore, the interface of asphalt-NaCl solution-mineral was simulated by molecular dynamics to investigate the adhesion failure mechanism between asphalt and aggregate in an extremely saline environment. The results show that the polarization-inducing effects of sodium and chloride ions promote the cross-

25 sectional diffusion of the NaCl solution at the interfaces and contribute to the redistribution and
26 rediffusion of asphalt components, and the formation of hydrogen bonds between water and asphalt
27 components. The NaCl solution prevents the accumulation of saturates, resins, and asphaltenes on the
28 SiO₂ surface, and strips aromatics from the SiO₂ surface due to the interaction. Sodium ions can be
29 attracted to the oxygen atoms on CO₃²⁻ to occupy active sites on the CaCO₃ than asphalt, which makes it
30 easier for chloride ions to penetrate the asphalt molecule and asphalt components to detach from CaCO₃.
31 These behaviors effectively impair the adhesion at the asphalt-mineral interface. The 3 wt% and 20 wt%
32 NaCl solutions have the greatest effect on the adhesion work of the asphalt-SiO₂ and asphalt-CaCO₃,
33 reducing them by 55.93 % and 66.03 %, respectively.

34 **Keywords:** asphalt-aggregate interface; adhesion failure; saline environment; damage mechanism;
35 molecular dynamics

36 **1. Introduction**

37 Asphalt pavement refers to the road surface structure formed by blending and compacting aggregate
38 materials with asphalt as the binder [1]. It is currently the most widely used road surface structure owing
39 to its excellent engineering properties and economic efficiency, such as high durability, low noise, and
40 driving comfort [2]. During service, the water on the road surface penetrates the asphalt mixture under
41 the action of load, resulting in the cohesion failure of the asphalt binder and the adhesion failure between
42 the asphalt binder and aggregate [3, 4]. It leads to water damage to pavement, which is manifested as
43 loosening, pothole, and deformation, directly reducing the service life and threatening the traffic safety
44 of asphalt pavement [5, 6]. As two main components of asphalt mixture, the adhesive force between
45 asphalt binder and aggregate is much weaker than the internal cohesion of asphalt binder [7]. Aggregate
46 is polar and hydrophilic, the asphalt adhering to aggregate surface adhesion is easy to be replaced by
47 polar moisture, forming a three-layer system of asphalt [8]. Therefore, understanding the mechanism of
48 adhesion failure between asphalt and aggregate is crucial to the sustainable development strategy of the

49 pavement industry.

50 Serious water damage diseases generally occur in these areas, including coastal areas, saline areas,
51 and high-freezing areas [9, 10]. Salt spray and tides, which often occur in coastal areas, can carry salt
52 from seawater into asphalt pavements [11]. With a total area of 5 million hectares of saline soils in the
53 humid southeastern coastal region, rainwater can carry large amounts of salt solution onto asphalt
54 pavements [12]. In frozen areas, ice melts salt and salt storage asphalt binder is used as the traditional
55 means of snow and ice melting on asphalt pavements [13]. Seawater, saline-alkali soil, snowmelt salt,
56 and salt storage asphalt binder all contain high levels of NaCl that have a certain harm to the service life
57 of asphalt pavement [14]. The effects of dynamic water, temperature, freeze-thaw cycles, wet and dry
58 cycles, loading, and UV irradiation on the performance of asphalt mixtures in chloride salt environments
59 have been studied by scholars. The results show that dynamic water accelerates the erosion of chlorinated
60 salt on asphalt mixtures, and it is related to the concentration and temperature of the salt solution [15].
61 The destruction of asphalt mixture voids can be caused by crystallization pressure and freezing expansion
62 pressure of salt solution under the coupled action of sea spray and freeze-thaw cycles [16]. Loading and
63 dynamic water have the greatest effect on pavement performance, followed by chloride concentration
64 and temperature, and UV radiation had a lesser effect [17]. The resistance to salt damage of the asphalt
65 mixture is also depend on the adhesion between asphalt binder and aggregate, which rely on the
66 physicochemical interaction on the interfaces [18]. Xu et al. [19] found that the adhesion work of asphalt
67 binder with aggregate decreased significantly with the addition of salt through contact angle tests and
68 boiling water tests. Zhang et al. [20] conducted an atomic force microscopy (AFM) test and a four-
69 component test on asphalt binders in a NaCl environment. The results showed that the NaCl solution
70 altered the chemical composition content of the asphalt binder and weakened the adhesion of the asphalt
71 binder to aggregate. Yang et al. [21] compared the asphalt-aggregate adhesion property after salt erosion
72 through the surface free energy. They found that the salt solution increased the polarity component and

73 decreased the dispersion component, which reduces the asphalt-aggregate adhesion work. However,
74 laboratory characterizations can only reflect changes in performance after erosion, making it challenging
75 to visualize the evolution mechanism for the chemical components and adhesion of the asphalt-aggregate
76 interface in a salt environment.

77 Molecular dynamics (MD) simulation is a computational method that simulates the behavior of
78 molecules at the microscopic level based on the principles of Newtonian mechanics [22]. In the field of
79 materials science, MD simulations have been applied to study the mechanical characteristics and
80 chemical reactions of materials [23, 24]. It can be used to simulate interfacial adhesion failures and
81 quantify the mechanisms at the molecular scale. Long et al [25] combined AFM tests and MD simulations
82 to find that chloride ions lead to the formation of a gradient zone with weak adhesion on the asphalt
83 surface, and assist water molecules to penetrate the softened asphalt film to reach the asphalt-aggregate
84 interface, thereby eroding its interfacial adhesion. However, the impact of sodium chloride on the
85 interfacial adhesion based on the molecular scale is less well studied. And NaCl concentration in the
86 environment varies with different regions (offshore and offshore) and atmospheric humidity. The law and
87 mechanism of adhesion failure at the interface in extreme NaCl concentration are still unclear. In addition,
88 it can be found from the relevant research that the conclusions based on adhesion properties are often
89 relatively dispersive. The reason is that the chemical composition, structural morphology, and mechanical
90 properties at the interface need to be further refined.

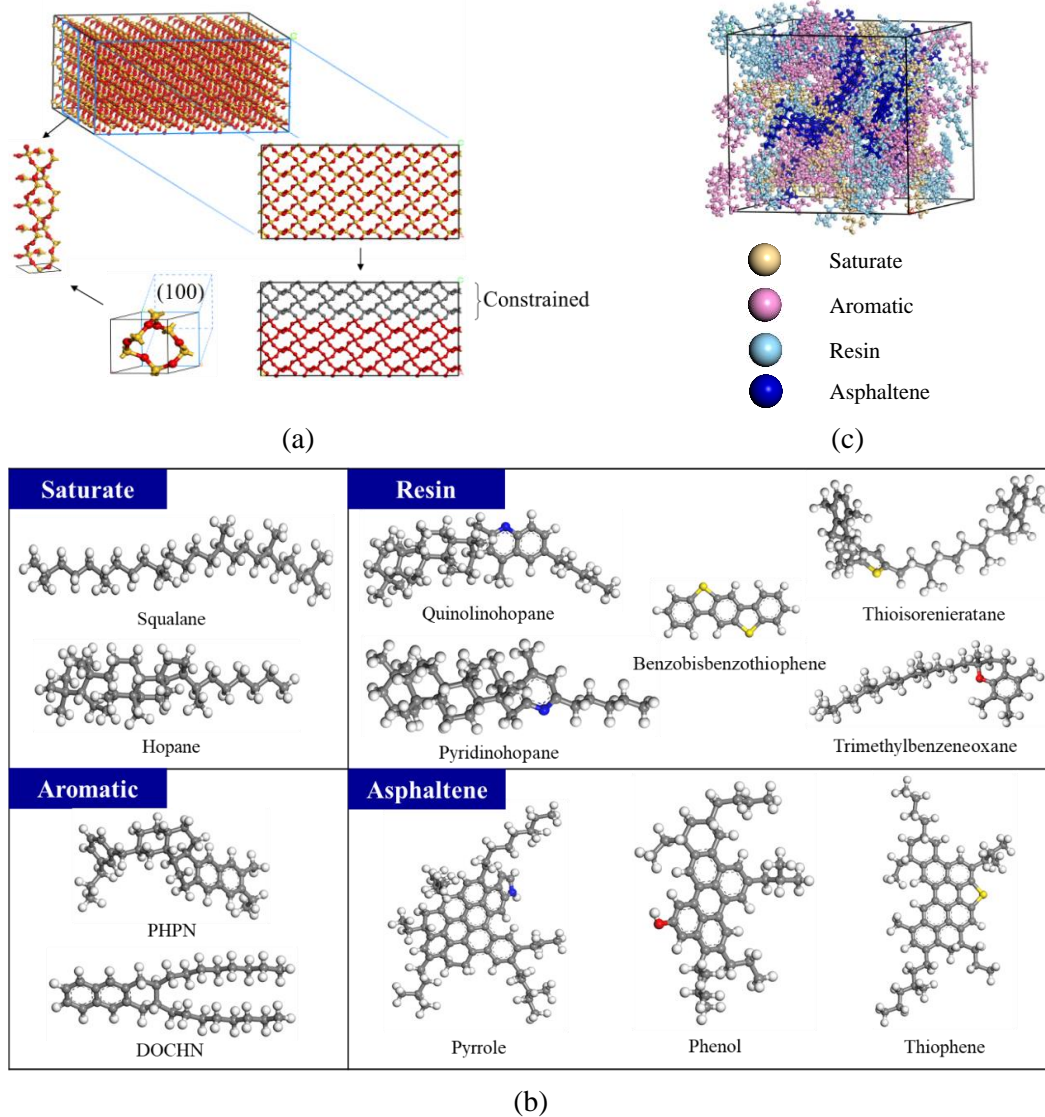
91 Herein, the impact of extreme concentrations of NaCl solution on the adhesion of asphalt binder to
92 the mineral interface and the damage mechanisms are investigated in this study. Common minerals in the
93 aggregate are quartz and calcite, which are the most abundant components of the acidic and basic
94 minerals respectively [26, 27]. MD simulations of the interface of asphalt binder on silica and calcium
95 carbonate substrates were undertaken in an environment with extreme concentrations of NaCl. The
96 characterizations contain the diffusion behavior of the NaCl solution at the interface, the spatial

97 arrangement of asphalt components, and the changes in the interfacial adhesion work.

98 **2. Simulation models and methods from molecular dynamics**

99 ***2.1. Mineral model***

100 Natural rock minerals are polycrystalline and have a local periodicity [28]. The geometric structure
101 of minerals is usually represented by a box with parallel sides [29]. Quartz and calcite were selected and
102 the effect of NaCl solution on their adhesion to asphalt binder was investigated by MD simulation. Table
103 1 showed the structures and the detailed parameters of the minerals from the Cambridge Structural
104 Databas. The qualitative analysis of interfacial adhesion is not significantly affected by different Miller
105 planes [30]. According to the previous papers and the principle of the most stable energy and the
106 minimum lattice mismatch, the most suitable Miller planes were selected to present sufficient
107 coordination sites for asphalt adhesion [26]. Taking SiO₂ as an example, the construction of the supercell
108 model was illustrated in Fig. 1a. The unit cell was cut along the Miller index surface (1,0,0) and then
109 constructed into a supercell with a thickness of 20.65 Å, which met the requirement of greater than the
110 cutoff radius of 15.5 Å. Next, a vacuum layer was placed on top of the supercell to form a mineral block
111 with three-dimensional periodic boundary conditions. The movement of the mineral was avoided by
112 constraining the bottom of the supercell within half the thickness of the mineral slab, which satisfied a
113 balance between computational efficiency and accuracy. And the mineral surface was allowed to relax
114 sufficiently to adsorb with the asphalt molecules. Similarly, the Miller index surface (0,1,8) with a
115 thickness of 22.02 Å was chosen to be constructed into a CaCO₃ supercell, also following the principle
116 that the mineral thickness was greater than the cutoff radius.

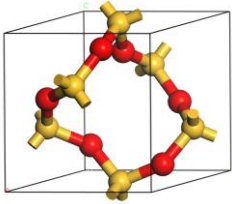
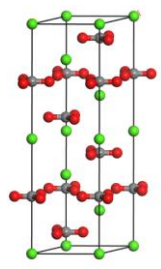


117

118 Fig. 1. Molecular models for interface system (gray atom is carbon, white atom is hydrogen, red atom is
 119 oxygen, yellow atom is sulfur, and blue atom is nitrogen); (a) construction of supercell model for SiO₂
 120 mineral; (b) 12-component of asphalt model; (c) molecular model of asphalt binder.

121 **Table 1**

122 Detailed parameters of minerals (yellow and red represent silicon atoms and oxygen atoms, respectively;
 123 green and grey represent calcium atoms and carbon atoms, respectively).

Chemical formula	Unit cell structure	Lattice parameters	Miller planes	Supercell size ($\text{\AA} \times \text{\AA} \times \text{\AA}$)
SiO ₂		a=b=4.913 \AA , c=5.405 \AA ; $\alpha=\beta=90^\circ$, $\gamma=120^\circ$	(1,0,0)	39.30 \times 37.83 \times 20.65
CaCO ₃		a=b=4.990 \AA , c=17.061 \AA ; $\alpha=\beta=90^\circ$, $\gamma=120^\circ$	(0,1,8)	39.92 \times 38.55 \times 22.02

124 **2.2. Asphalt model**

125 The molecule structures of the 12 components from the AAA-1 asphalt model were selected
 126 illustrated in Fig. 1b [31]. Based on the ratio of component molecules in the AAA-1 model shown in
 127 Table 2, an asphalt model with an initial density of 0.1 g/cm³ under three-dimensional cycling conditions
 128 was constructed using the amorphous cell module in Materials Studio software [32]. The geometric
 129 optimization process with 5000 iterations was performed to eliminate unreasonable configurations in the
 130 model so that the energy of each molecule leveled off when the system reached minimum energy. MD
 131 simulations were performed using a constant molecular number, volume, and temperature (NVT)
 132 ensemble at 298 K with a time step of 1 fs for 100 ps [33]. It was then further equilibrated in the
 133 isothermal-isobaric (NPT) ensemble at 298 K and 1.0 atm for 100 ps to obtain a stable structure with a
 134 stable density. The system was maintained near a certain temperature and pressure within the Andersen
 135 barostat and Nose-Hoover-Langevin thermostat. After dynamic equilibrium, the density of the asphalt
 136 model was finally stabilized at 0.997 g/cm³. Herein, a confined layer of asphalt model with a density of

137 0.997 g/cm³ was created by using the amorphous cell module. The width and length of which are set to
 138 the same as the mineral model to enable the construction of asphalt-mineral layers, which were performed
 139 by the geometry optimization and NVT ensemble for 100 ps, and the confined layer of asphalt as shown
 140 in Fig. 1c. The force field of COMPASS was applied to allows accurate calculation and prediction [34].
 141 And the atom-based summation method and Ewald summation method were applied to calculate the
 142 electrostatic interaction and the van der Waals interaction with a cutoff distance of 15.5 Å, respectively
 143 [35].

144 **Table 2**

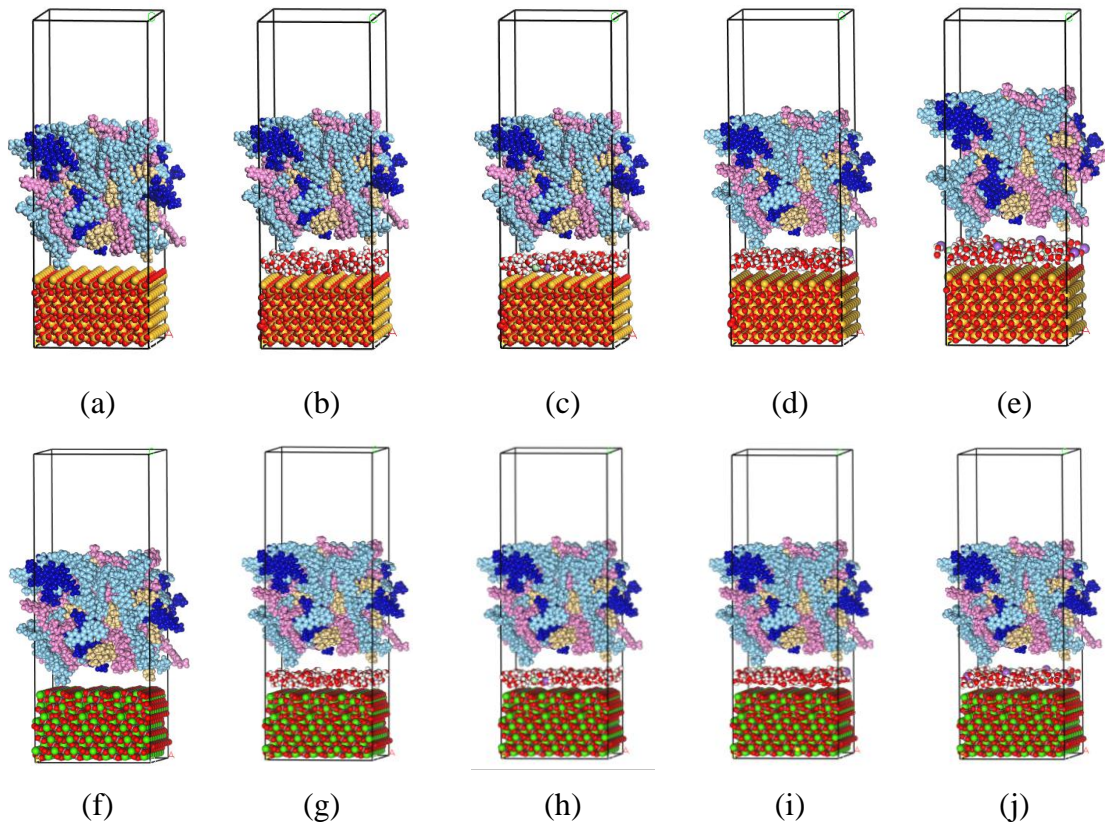
145 Molecular compositions of virgin asphalt models [31].

Component	Molecular	Chemical formula	Number of molecular	Mass fraction (%)
Saturate	Squalene	C ₃₀ H ₆₂	4	10.71
	Hopane	C ₃₅ H ₆₂	4	
Aromatic	PHPN	C ₃₅ H ₄₄	11	30.72
	DOCHN	C ₃₀ H ₄₆	13	
Resin	Quinolinhopane	C ₄₀ H ₅₉ N	4	41.95
	Thioisorenieratane	C ₄₀ H ₆₀ S	4	
	Benzobisbenzothiophene	C ₁₈ H ₁₀ S ₂	15	
	Pyridinohopane	C ₃₆ H ₅₇ N	4	
	Trimethylbenzeneoxane	C ₂₉ H ₅₀ O	5	
Asphaltene	Phenol	C ₄₂ H ₅₄ O	3	16.62
	Pyrrrole	C ₆₆ H ₈₁ N	2	
	Thiophene	C ₅₁ H ₆₂ S	3	

146 **2.3. MD simulations**

147 The system model of the asphalt-mineral interface was created by combining a mineral block with
 148 an asphalt layer. Then the mirror interactions were avoided by adding a 30 Å vacuum slab above the
 149 asphalt model, which was 2 times the cutoff radius. The asphalt-0% NaCl-mineral interfacial model was
 150 formed by placing 200 water molecules at the interface between asphalt and mineral. This number of

151 water molecules was chosen because it can provide an adequate solvated environment without making
152 the system too large and drastically increasing the computational cost. And so on, different NaCl solutions
153 were formed by adding different numbers of sodium and chloride ions. Coastal pavements are generally
154 exposed to salt spray, which typically has a concentration of 0.7 mg/m^3 or less [36]. With the deposition
155 of salt in the salt spray and splashing of seawater, the concentration of salt environment on the pavement
156 can reach the concentration of seawater, which is 3% [37]. Thus, for asphalt pavements, long-term
157 exposure to seawater concentrations can also be defined as an extreme salt environment. Additionally,
158 the NaCl concentration in seawater is about 3 wt%, and the NaCl concentration often used in the
159 laboratory for salt-erosion acceleration experiments is 10 wt%, and 20 wt% is a more extreme
160 concentration of NaCl solution [14]. Hence, the salt environment was set to 3 wt%, 10 wt%, and 20 wt%
161 NaCl solution. Taking the SiO_2 mineral as an example, the interface systems were illustrated in Fig. 2a
162 to 2e. Based on molar mass and density, the 10 wt % NaCl solution layer contains 200 water molecules,
163 7 sodium ions, 7 chloride ions, and so on for other concentrations of NaCl solutions. After geometry
164 optimization, the interface systems of asphalt-mineral without and with 0%, 3%, 10%, and 20% NaCl
165 solution were subjected to NVT ensemble for 300ps at 298K.



166

167 Fig. 2. Interface system model (purple and green represent sodium and chloride ions, respectively); (a)
 168 asphalt-SiO₂; (b) asphalt-0% NaCl solution-SiO₂; (c) asphalt-3% NaCl solution-SiO₂; (d) asphalt-10%
 169 NaCl solution-SiO₂; (e) asphalt-20% NaCl solution-SiO₂; (f) asphalt-CaCO₃; (g) asphalt-0% NaCl
 170 solution-CaCO₃; (h) asphalt-3% NaCl solution-CaCO₃; (i) asphalt-10% NaCl solution-CaCO₃; (j)
 171 asphalt-20% NaCl solution-CaCO₃.

172 3. Results and conclusions

173 3.1. Verification of asphalt model

174 Density is the fundamental thermodynamic parameter of asphalt binder, and stable density values
 175 of asphalt models can be obtained after molecular dynamics simulations of asphalt models under the NPT
 176 ensemble [38]. After dynamic equilibrium, the density of the asphalt model was stabilized at 0.997 g/cm³,
 177 which was closer to the actual density shown in Table 3. Cohesive energy density (CED) and solubility
 178 parameter (δ) can evaluate the intermolecular attraction and compatibility of asphalt [39]. The CED is
 179 the cohesive energy per unit of volume, the square root of which is the δ . The calculation formulas of the
 180 two are shown in Eq. (1) and (2).

$$CED = \frac{E_{coh}}{V} = -\frac{\langle E_{inter} \rangle}{V} = \frac{\langle E_{intra} \rangle - \langle E_{total} \rangle}{V} \quad (1)$$

$$\delta = \sqrt{CED} \quad (2)$$

181 Where E_{coh} and V represent the cohesion and occupied volume of the asphalt model, E_{inter} represents the
 182 interaction energy, E_{intra} is the intramolecular energy, and E_{total} is the total energy of the system. The
 183 brackets $\langle \dots \rangle$ is an average over the NVT ensemble. The calculated results are shown in Table 3, which
 184 are within the test values. Therefore, these parameters validate the reliability of the asphalt model.

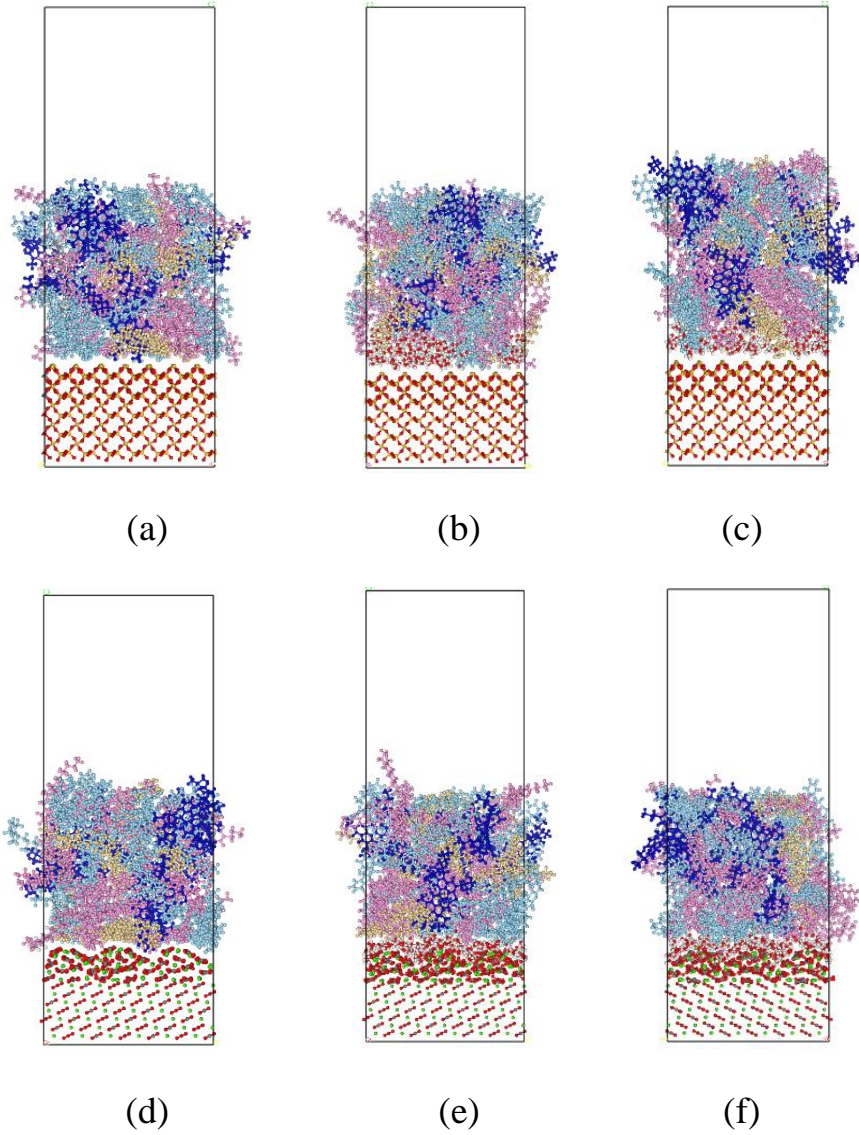
185 **Table 3**

186 Validation parameters of asphalt model.

Parameters	Calculated values	Experiment value
Density (298.15K, g/cm ³)	0.997	1.01–1.04 [40]
CED (10 ⁸ J/m ³)	3.22	3.19–3.32 [41]
δ ((J/cm ³) ^{0.5})	17.95	13.30–22.50 [42]

187 **3.2. Appearance of the interfacial system in the NaCl environment**

188 The asphalt-SiO₂ and asphalt-CaCO₃ systems after MD simulation are compared under dry
 189 conditions and NaCl solution conditions to observe the interfacial adhesion state, as shown in Fig. 3.
 190 After MD simulation, the SiO₂ bound by covalent bonds remains regular and flat, and the asphalt is flatly
 191 distributed on the SiO₂ surface at dry. While water molecules and asphalt interpenetrate to isolate the
 192 asphalt from the SiO₂ at 0% NaCl solution, and the interfacial separation is slightly weakened by 3%
 193 NaCl. An embedded locking phenomenon is observed at the asphalt-CaCO₃ interface, this is because
 194 ionic bonds in CaCO₃ bonded by ionic bonds are more likely to adsorb asphalt molecules. That is
 195 consistent with the Scanning electron microscope results in the previous study [43]. Whereas the presence
 196 of water fills these depressions debonding asphalt from CaCO₃, and the appearance of the asphalt-CaCO₃
 197 interface can be insignificantly affected by 3% NaCl. The interface appearances under different NaCl
 198 concentrations are not discussed, because NaCl concentrations in the same interfacial system do not differ
 199 significantly in appearance.



200

201 Fig. 3. Asphalt-mineral systems after adhesion simulations; (a) asphalt-SiO₂; (b) asphalt-0% NaCl
 202 solution-SiO₂; (c) asphalt-3% NaCl solution-SiO₂; (d) asphalt-CaCO₃; (e) asphalt-0% NaCl solution-
 203 CaCO₃; (f) asphalt-3% NaCl solution-CaCO₃.

204 **3.3. Diffusion and distribution of NaCl solution at the asphalt-mineral interface**

205 **3.3.1. Diffusion coefficient of NaCl solution**

206 The mean square displacement (MSD) function is employed to quantize the motion properties of
 207 molecules and ions and is an important parameter in molecular dynamics analysis, defined as the square
 208 of the displacement of a particle in a fixed period, expressed by Eq. (3) [44].

$$MSD = r^2(t) = \frac{1}{N} \left(\sum_{i=1}^N |r_i(t) - r_i(0)|^2 \right) \quad (3)$$

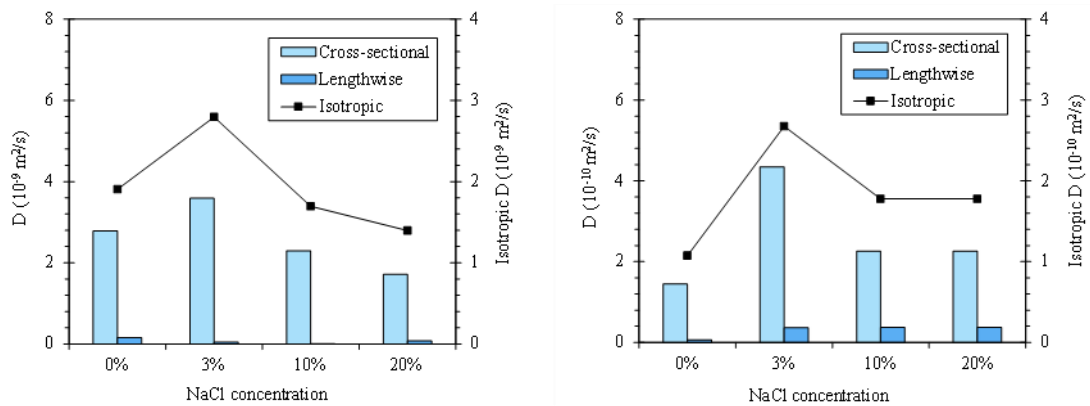
209 where $r_i(0)$ and $r_i(t)$ are the position of molecule or ion i at the initial moment and time t ; N is the number

210 of molecules or ions. To investigate the diffusion law of NaCl solution, the diffusion coefficient (D) from
 211 200 to 300 ps during dynamic equilibrium is calculated using anisotropic displacement curves (including
 212 cross-sectional and lengthwise displacement curves) as well as isotropic displacement curves by Eq. (4)
 213 [45].

$$D = \frac{r^2(t)}{6t} \quad (4)$$

214 where $r(t)$ is the molecular and ionic displacement.

215 Therefore, the D of NaCl solution is calculated by its MSD according to Eq. (4), and the curve of D
 216 with NaCl concentration is depicted in Fig. 4a and 4b. The isotropic D of the NaCl solution in the asphalt-
 217 SiO₂ system is dominated by the cross-sectional diffusion while the lengthwise D is almost zero. The
 218 cross-sectional D can be accelerated by low concentrations of NaCl, while that can be reduced to a lower
 219 D than 0% NaCl solution by high concentrations of NaCl. For the asphalt-CaCO₃ system, NaCl has a
 220 positive impact on the cross-sectional diffusion of the aqueous solution, and there is a peak in its effect
 221 at 3% NaCl. The NaCl accelerates the lengthwise D to a small extent and does not vary with the NaCl
 222 concentration. Therefore, the isotropic D of 3% NaCl solution is the highest, which is 1.47 times and
 223 2.49 times that of 0% NaCl solution in the asphalt-SiO₂ system and asphalt-CaCO₃ system, respectively.
 224 The lengthwise diffusion of NaCl solution into the mineral interior is limited by the poor wettability
 225 between the solution and the minerals [46].



226

227 Fig. 4. Diffusion coefficient of NaCl solution; (a) asphalt-SiO₂; (b) asphalt-CaCO₃.

228 3.3.2. Performance parameters of NaCl solution

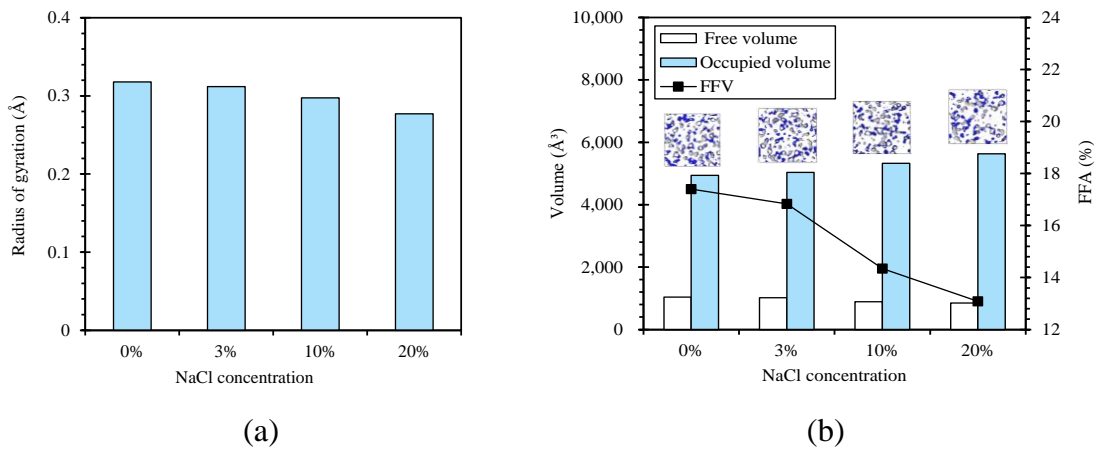
229 To further explore the diffusion behavior of NaCl solution at the interface, the performance
 230 parameters of NaCl solution are studied, including the radius of gyration (R_g) and fractional free volume
 231 (FFV) of NaCl solution. The R_g characterizes the stiffness of the NaCl solution, which affects the
 232 diffusion, and is calculated as in Eq. (5) [47].

$$R_g^2 = \frac{\sum m_i r_i^2}{\sum m_i} \quad (5)$$

233 where m_i and r_i are the mass and the radius of atom i , respectively. The FFV was employed to quantify
 234 the volume percentage of the NaCl solution that is not occupied by molecules [48]. It is calculated by Eq.
 235 (6).

$$FFV = \frac{V_{free}}{V_{free} + V_{occupied}} \times 100\% \quad (6)$$

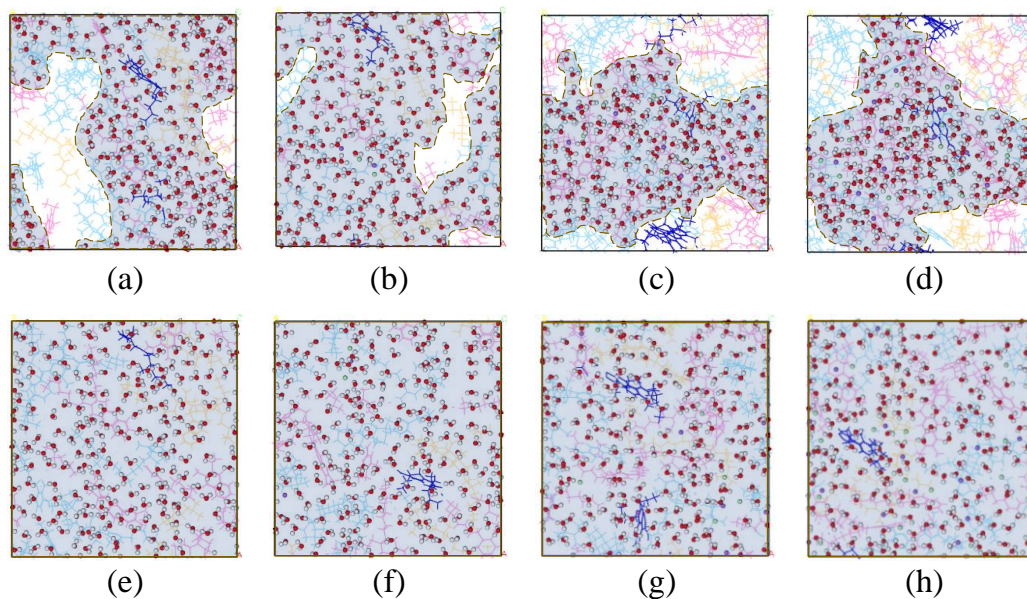
236 where V_{free} and $V_{occupied}$ are the free volume and occupied volume, respectively. The results are illustrated
 237 in Fig. 5a and 5b. The R_g decreases with increasing NaCl concentration. NaCl exists in solution as the
 238 contact ion pairs and the solvent ion pairs, and the motion of atoms in solution is limited. That also leads
 239 to a decrease in the free volume of the atoms, and although the increase in atoms causes an increase in
 240 the occupied volume, the FFV still decreases. These are the reasons for the decrease in the D of the NaCl
 241 solution.



242 (a) (b)
 243 Fig. 5. Performance parameters of NaCl solution; (a) and (b) radius of gyration and volume performance
 244 parameters.

245 3.3.3. Distribution of NaCl solution

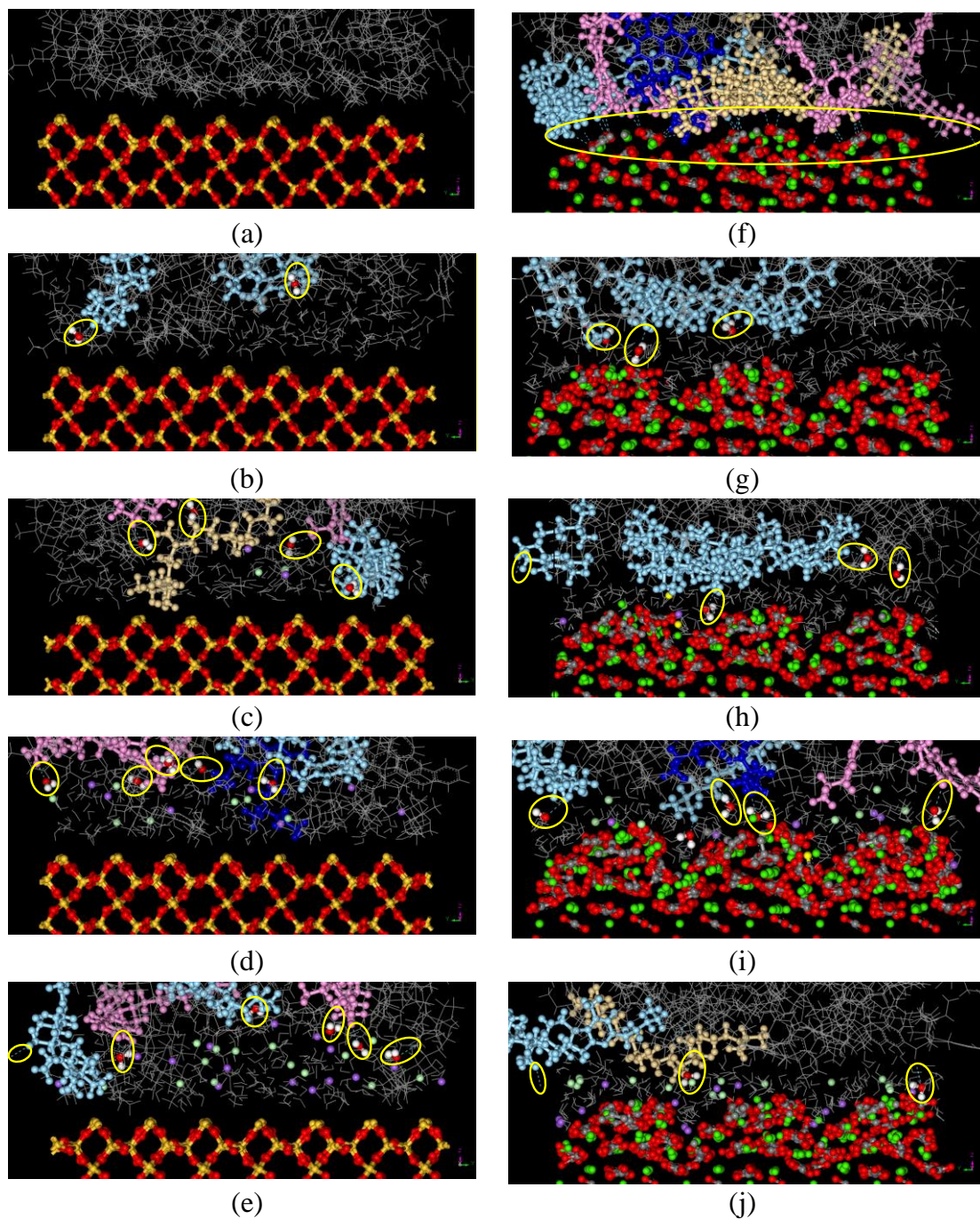
246 After dynamic equilibrium, the cross-sectional distribution of the NaCl solution is characterized to
247 observe the aggregation of aqueous solution, as shown in Fig. 6. The water molecules in 0% NaCl
248 solution are not uniformly distributed at the SiO₂ interface, tending to agglomerate. The presence of 3%
249 NaCl allows the water molecules to be more evenly distributed at the interface. This might be explained
250 by the fact that ions promote the agglomeration of water molecules on the asphalt, due to the greater
251 polarity than water molecules [49]. As the NaCl concentration increases, the aqueous solution is
252 promoted to agglomerate at the interface [50]. And the water molecules are already evenly distributed on
253 CaCO₃ at 0% NaCl solution. And there is no significant change in the distribution of water molecules
254 with NaCl concentration.



255
256 Fig. 6. Cross-sectional distribution of NaCl solution at the interfaces (the light blue areas represent areas
257 where the aqueous solution accumulates; the display style of the asphalt components is line, saturates are
258 yellow, aromatics are pink, resins are light blue, asphaltenes are dark blue); (a) asphalt-0% NaCl solution-
259 SiO₂; (b) asphalt-3% NaCl solution-SiO₂; (c) asphalt-10% NaCl solution-SiO₂; (d) asphalt-20% NaCl
260 solution-SiO₂; (e) asphalt-0% NaCl solution-CaCO₃; (f) asphalt-3% NaCl solution-CaCO₃; (g) asphalt-
261 10% NaCl solution-CaCO₃; (h) asphalt-20% NaCl solution-CaCO₃.

262 The lengthwise distribution of molecules at the interfaces is used to observe the lengthwise diffusion

263 results of the NaCl solution, as illustrated in Fig. 7. Comparing the asphalt-SiO₂ system and asphalt-
264 CaCO₃ system at dry, the hydrogen bonds between asphalt components with CaCO₃ are found. Hydrogen
265 bonding is an electrostatic connection between electronegative atoms and hydrogen atoms, the presence
266 of which can strengthen the adhesion between them [51]. And NaCl is beneficial to the formation of
267 hydrogen bonds between water molecules and asphalt components. This may be due to the polarity
268 induction effect of increased polarity of NaCl solution on asphalt components. It can be observed from
269 Fig. 7 that the distribution of sodium and chloride ions present certain rules, so their mass densities
270 toward lengthwise direction are quantitatively calculated, as illustrated in Fig. 8. In the asphalt-SiO₂
271 system, the sodium ions mainly accumulate on the SiO₂ surface, and diffuse to the asphalt molecules to
272 a certain extent. Chloride ions also accumulate mainly on the SiO₂ surface, but the red area indicates that
273 chloride ions diffuse more easily to asphalt than sodium ions. This might be explained by the fact that
274 metal ions are more inclined to agglomerate on the surface of minerals, while chloride ions are
275 nucleophilic ions, the polarization induction effect of which makes them more inclined to approach
276 positively charged atoms in asphalt [52]. In asphalt-CaCO₃, the accumulation of sodium ions on CaCO₃
277 is more obvious, while the tendency of chloride ions to be attracted by asphalt is also more obvious. This
278 might be explained by the fact that sodium ions can be attracted by the negatively charged oxygen atom
279 on CO₃²⁻, it is easier to occupy the active site on the surface of CaCO₃ and indirectly promote the diffusion
280 of chloride ions to asphalt.



281

282 Fig. 7. Lengthwise distribution of molecules at the interfaces (blue dashed line represents hydrogen bonds

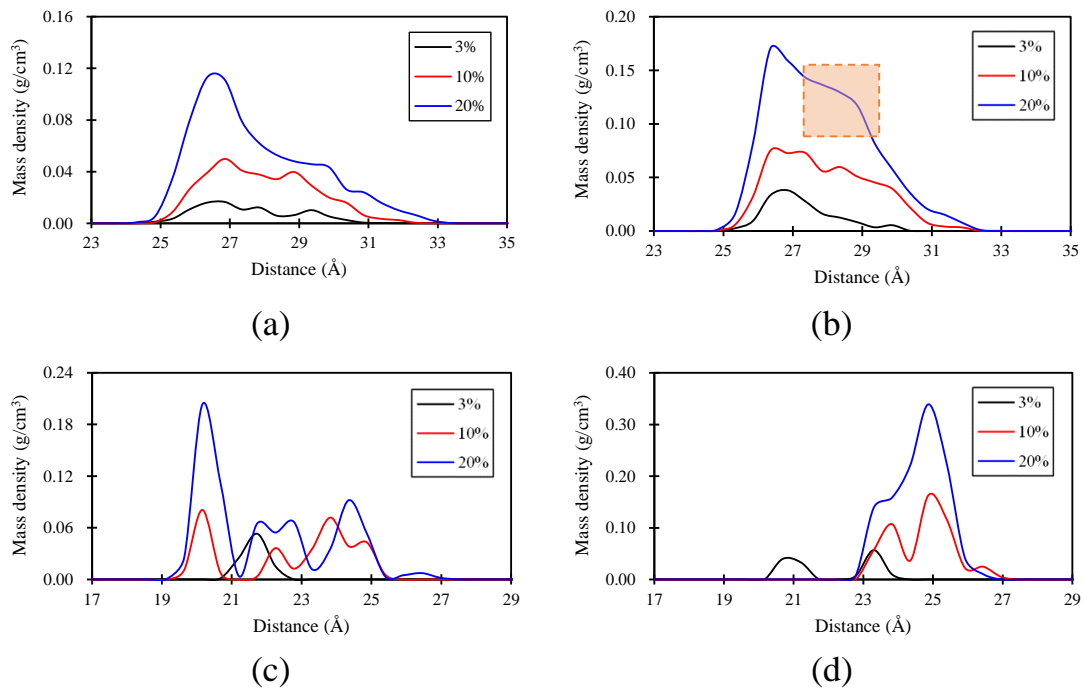
283 that were circled by yellow thread, grey lines represent asphalt components that are not hydrogen bonded

284 to water or mineral); (a) asphalt-SiO₂; (b) asphalt-0% NaCl solution-SiO₂; (c) asphalt-3% NaCl solution-

285 SiO₂; (d) asphalt-10% NaCl solution-SiO₂; (e) asphalt-20% NaCl solution-SiO₂; (f) asphalt-CaCO₃; (g)

286 asphalt-0% NaCl solution-CaCO₃; (h) asphalt-3% NaCl solution-CaCO₃; (i) asphalt-10% NaCl solution-

287 CaCO₃; (j) asphalt-20% NaCl solution-CaCO₃.



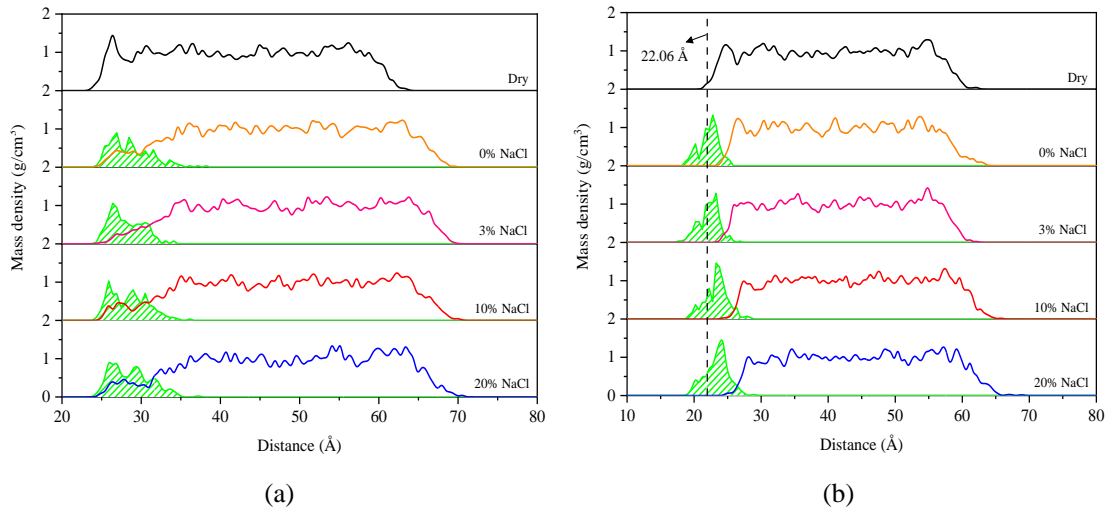
288

289 Fig. 8. Mass density of sodium and chloride ions towards the lengthwise direction; (a) sodium ions in the
 290 asphalt-SiO₂ system; (b) chloride ions in the asphalt-SiO₂ system; (c) sodium ions in the asphalt-CaCO₃
 291 system; (d) chloride ions in the asphalt-CaCO₃ system.

292 **3.4. Spatial arrangement of interfacial molecules at the interface in the NaCl environment**

293 *3.4.1. Distribution of NaCl solution and asphalt molecules*

294 The spatial arrangement of interfacial molecules plays an important function in adhesion properties,
 295 and the lengthwise distribution of asphalt molecules and NaCl solution is plotted in Fig. 9. At dry, the
 296 asphalt agglomerates at 25-30 Å in the asphalt-SiO₂ system, manifesting asphalt agglomerates at the
 297 interface due to the interaction energy. However, NaCl prevents asphalt from the SiO₂, and 3% NaCl
 298 solution presents the greatest effect. In the asphalt-CaCO₃ system, the CaCO₃ thickness is 22.02 Å, and
 299 the asphalt molecules are embedded in CaCO₃ at dry. NaCl solution can replace the asphalt embedded in
 300 the CaCO₃, debonding the asphalt away from CaCO₃. The greater the NaCl concentration, the further the
 301 distance between asphalt and CaCO₃.



302

303 Fig. 9. Mass density of molecules towards the lengthwise direction (green area represents NaCl solution);

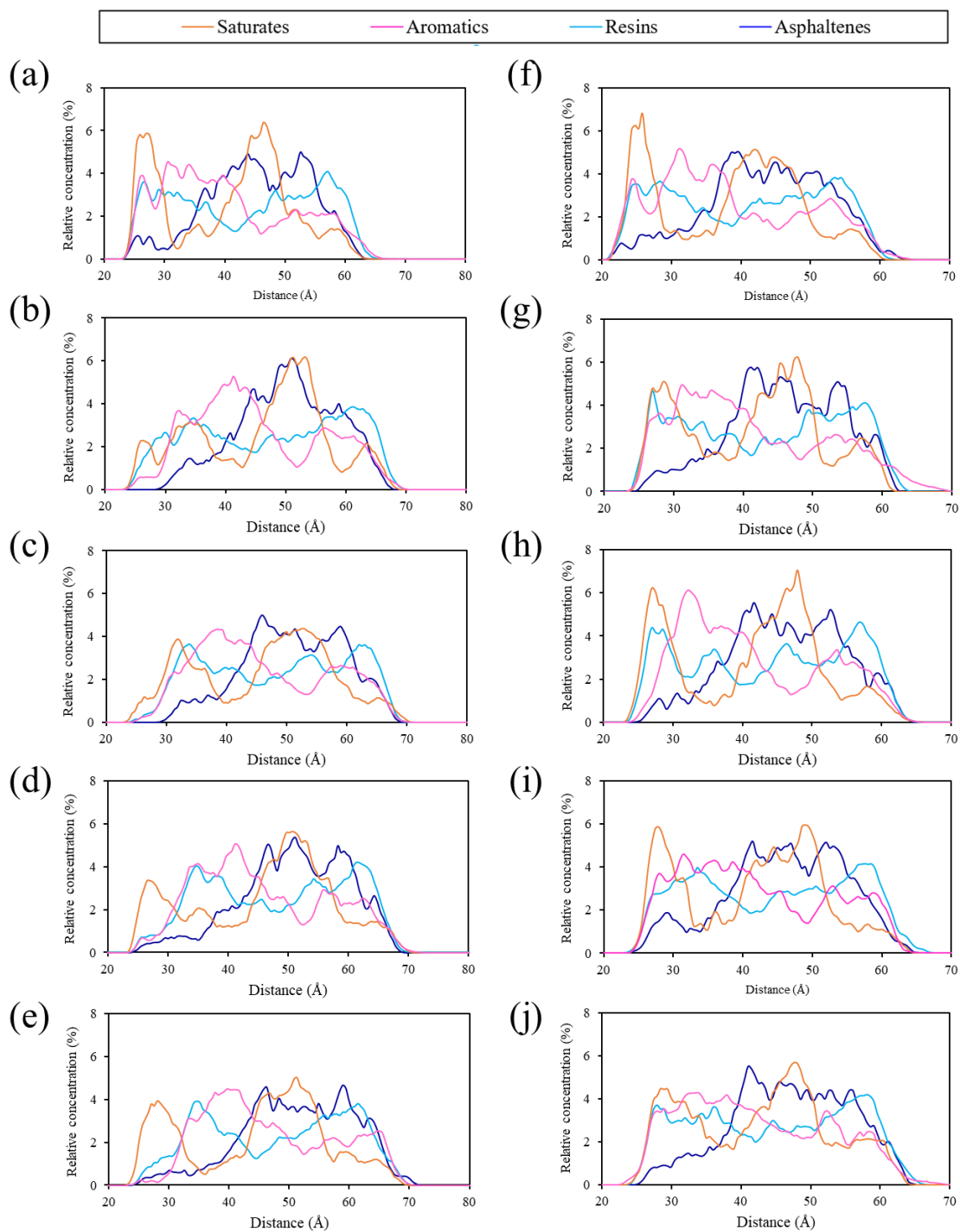
304 (a) asphalt and NaCl solution in the asphalt-SiO₂ system; (b), asphalt and NaCl solution in the asphalt-

305 CaCO₃ system.

306 3.4.2. Distribution of asphalt components

307 The spatial distribution of asphalt molecules is associated with the distribution of the four
 308 components. In the asphalt-SiO₂ system, the mass density of component molecules toward the lengthwise
 309 direction is illustrated in Fig. 10a to 10e. In the dry environment, the asphalt components agglomerate at
 310 the asphalt-mineral interface. And saturates have the greatest relative concentration, which is consistent
 311 with previous research findings [49]. This might be explained by the fact that the saturates are a non-
 312 polar component with relatively low molecular weight and weak intermolecular interactions, and
 313 diffusion potential resistance are minimal. The relative concentrations of aromatics and resins are lower
 314 than that of the saturates due to the lower mass fraction in asphalt molecular. Asphaltenes are polar but
 315 also have the highest molecular weight, and macromolecules are strongly hindered and repelled in asphalt,
 316 resulting in the lowest concentration [53]. The agglomeration of each component on the interface is
 317 weakened by 0% NaCl solution and 3% NaCl solution. Due to the decrease in D of the NaCl solution,
 318 the saturates with the lowest molecular weight agglomerate at the interface through 10% NaCl solution,
 319 while there is no obvious change in the distribution of the other components. The distribution
 320 concentration of saturates and resins further increases at the interface because of the further decline in D

321 of 20% NaCl solution. Because the resins are the most polar component of the asphalt components, the
 322 polarity is beneficial to the agglomeration of asphalt components on the SiO₂. It is known that the
 323 agglomeration of components is mainly affected by the D of the NaCl solution and the polarity of asphalt
 324 components, and the components agglomerated on the surface of SiO₂ in the NaCl environment are
 325 mainly saturates.



326

327 Fig. 10. Mass density of asphalt components towards lengthwise direction; (a), (b), (c), (d), and (e)

328 asphalt-SiO₂ at dry, 0%, 3%, 10%, and 20% NaCl solution; (f), (g), (h), (i), and (j) asphalt-CaCO₃ at dry,

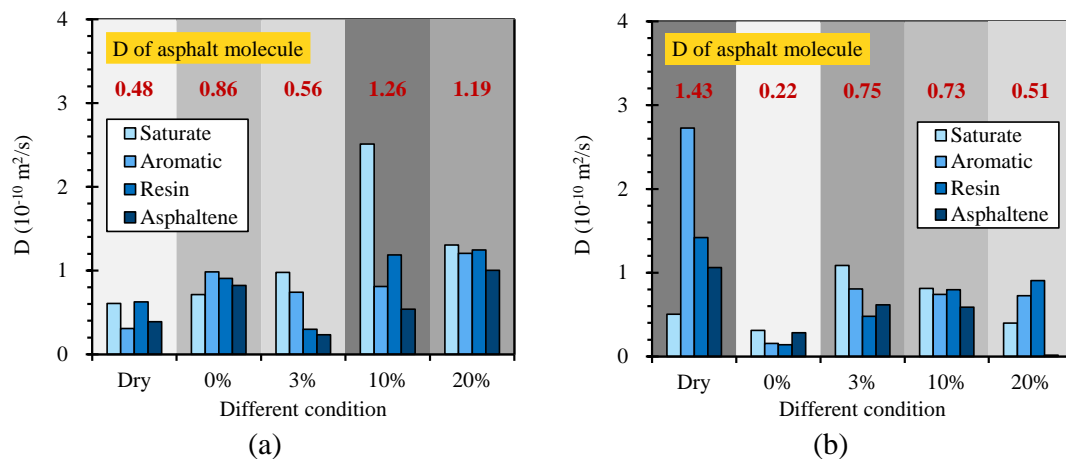
329 0%, 3%, 10%, and 20% NaCl solution.

330 In the asphalt-CaCO₃ system, the spatial distribution of asphalt components is shown in Fig. 10f to
331 10j. In the dry environment, the asphalt components were distributed at the interface in a consistent
332 concentration as in the asphalt-SiO₂ system. In the 0% NaCl solution, all components move away from
333 the interface. The agglomeration of the saturates at the interface was enhanced slightly by 3% NaCl,
334 while it decreases the agglomeration of the other component. However, the agglomeration of all
335 components is gradually weakened by 10% and 20 % NaCl. It manifests that the NaCl concentration has
336 a negative influence on the distribution of the four components at the CaCO₃ interface.

337 *3.4.3. Diffusion coefficient of asphalt components*

338 The D of the asphalt components and the D of asphalt molecule in the system towards the mineral
339 surface can describe the adhesion kinetic behavior between asphalt components and minerals. These
340 indexes in the asphalt-SiO₂ system are depicted in Fig. 11a. The color intensity of the background plate
341 corresponds to the D of asphalt molecule, which is convenient to observe the behavior of asphalt
342 molecules more intuitively. Saturates and resins have the larger D at dry, followed by asphaltenes and
343 aromatic. The D of all components increases at 0% NaCl solution. And the aromatics with the lowest
344 molecular weight have the greatest D, followed by the polar components resins and asphaltenes, and the
345 saturates have the minimum D. The cross-sectional D of 3% NaCl solution hinders the diffusion of all
346 components except the saturates are reduced, in the order of saturates > aromatics > resins > asphaltenes.
347 That can be because the saturates has a relatively low molecular weight with non-polar and weak
348 intermolecular interactions and therefore diffuses more easily to the surface of SiO₂. And it is suggested
349 that the diffusion of polar components towards the SiO₂ surface is inhibited by the polarization-inducing
350 effect of low concentrations of Cl⁻ [25]. The diffusion of the components was facilitated by the decrease
351 in cross-sectional D of the 10% and 20% NaCl solutions, with 10% NaCl contributing the most to the
352 diffusion of the saturated fraction, and 20% contributing more to the other three components. The D of

353 asphaltenes is almost minimum in different environments, which is because asphaltenes have the highest
 354 molecular weight and the highest molecular resistance to movement. Therefore, the diffusion of the
 355 saturates is promoted to dominate the diffusion of asphalt at the interface in the NaCl environment, and
 356 it is promoted most by 10% NaCl. The diffusion of the other components decreases and then increases
 357 with increasing NaCl concentration, reaching a minimum at 3% NaCl.



358 (a) (b)
 359 Fig. 11. Diffusion coefficient of asphalt components; (a) asphalt-SiO₂ system; (b) asphalt-CaCO₃ system.

360 From Fig. 11b, in the asphalt-CaCO₃ system, the aromatics have the larger D at dry, followed by
 361 polar components containing resins and asphaltenes, and the saturates have the smallest D . The order of
 362 polarity of asphalt components is the saturates, aromatics, asphaltenes, and resins. And resins and
 363 asphaltene as polar components are more adsorbed by the ionic bonding of CaCO₃. As a nonpolar
 364 component, the aromatics contain a benzene ring which gives the greater electron cloud density and
 365 dipole moment and has the smallest molecular weight and the smallest kinematic site resistance. These
 366 may be responsible for its maximum D under the ionic bonding of CaCO₃. The diffusion of all
 367 components is strongly limited by 0% NaCl solution, and the asphalt diffusion is dominated by saturates
 368 and asphaltenes. The diffusion of the components is slightly facilitated by 3% NaCl solution compared
 369 to 0% NaCl solution and the D values of the components are inversely proportional to the polarity. The
 370 10% NaCl solution increases the D of the resins and decreases the D of the other components. This trend
 371 was further facilitated by the 20% NaCl solution and the D of the asphaltenes was close to 0. Thus, NaCl

372 facilitated the diffusion of all the components and the diffusion of the resins is increased as the increasing
373 NaCl concentration, while the D of the other components reaches a maximum at 3% NaCl solution. That
374 indicates that the resins are the most sensitive to NaCl in the asphalt-CaCO₃ interface, and its diffusion
375 restricts the movement of the other components.

376 **3.5. Effect of NaCl solution on adhesion of asphalt-mineral interface**

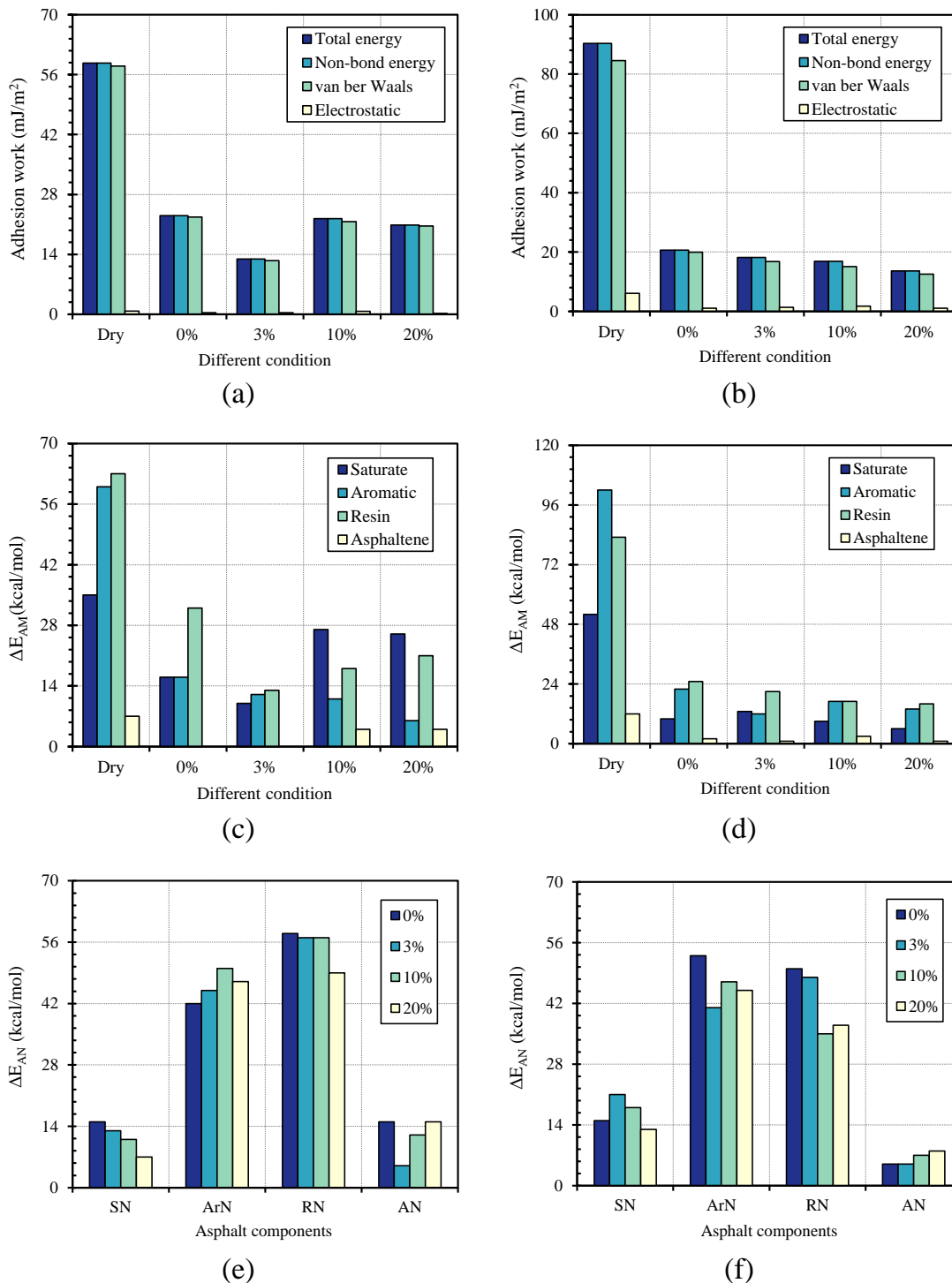
377 *3.5.1. Adhesion work between asphalt molecules and minerals*

378 The adhesion work is used to evaluate the impact of NaCl solution on the adhesion property of the
379 asphalt-mineral interface. The work required to separate the asphalt from the mineral at the interface is
380 known as the adhesion work and it determines the resistance to separation at the interface [54]. The
381 adhesion work of asphalt-mineral in NaCl environments was calculated by Eq. (7) [55].

$$W_{AM} = \frac{\Delta E_{AM}}{A} = \frac{E_A + E_M - E_{AM}}{A} \quad (7)$$

382 where W_{AM} and ΔE_{AM} express the adhesion work and interaction energy of asphalt-minerals, respectively;
383 E_B , E_M , and E_{BM} express the potential energies of asphalt, mineral, and asphalt-mineral, respectively; and
384 A expresses the area of contact between the asphalt and minerals, quantified using the Connolly area of
385 the surface of the mineral. From Fig. 12a and 12b, the adhesion work of asphalt-SiO₂ is mainly controlled
386 by the non-bonding energy generated by van der Waals forces, and the electrostatic interactions are
387 negligible. This might be explained by the fact that there is no hydrogen bond between SiO₂ and asphalt
388 from Fig. 7a. The adhesion work at dry is 58.72 mJ /m², which is close to the previously reported
389 experimental data [56]. And the adhesion of asphalt to SiO₂ can be deteriorated by NaCl, and 3% NaCl
390 solution has the most obvious effect. The adhesion work of asphalt-CaCO₃ is controlled by the non-
391 bonding energy resulting from the interaction of electrostatic forces and van der Waals forces. The
392 adhesion work provided by van der Waals forces is reduced by 76.43% by 0% NaCl solution, and the
393 adhesion work provided by electrostatic forces is reduced to 1.03 mJ /m², resulting in a significant
394 reduction in the interfacial adhesion work. This might be explained by the fact that the hydrogen bond

395 between the asphalt and CaCO_3 is replaced by the NaCl solution, and the adhesion work provided by the
 396 electrostatic force is almost 0. And the adhesion work generally decreases with NaCl concentration. The
 397 adhesion work is closely related to the agglomeration state of asphalt molecules at the mineral surface.



398 (a) and (b) contribution of
 399 Fig. 12. Adhesion work and interaction energy in the asphalt-mineral system; (a) and (b) contribution of
 400 non-bonding energy for adhesion work in asphalt-SiO₂ and asphalt-CaCO₃; (c) and (d) interaction energy
 401 of asphalt components-SiO₂ and asphalt components-CaCO₃; (e) and (f) interaction energy of system

402 components-NaCl solution.

403 3.5.2. Interaction energy between asphalt components and minerals

404 The interaction energies between asphalt components and minerals were further analyzed to
405 investigate the damage characteristic of adhesion work changing with NaCl concentration, as shown in
406 Fig. 12c and 12d. In the asphalt-SiO₂ system, the ΔE_{AM} of resins and aromatics, which have the greater
407 mass fraction, was greater, followed by saturates and asphaltenes at dry. The 0 % NaCl solution reduces
408 the ΔE_{AM} of all components, among which the ΔE_{AM} of resins is the largest, and the ΔE_{AM} of asphaltene
409 was close to 0 mJ /m². The ΔE_{AM} of all components are further reduced by 3% NaCl solution. Both 10%
410 and 20% NaCl solutions enhance the ΔE_{AM} of saturates, resins, and asphaltenes, and weaken the ΔE_{AM} of
411 aromatics. In the NaCl environment, the main components that provide the ΔE_{AM} for the asphalt-SiO₂
412 interface are saturates and resins. In the asphalt-CaCO₃ system, the aromatics provide the greatest ΔE_{AM}
413 for the interface at dry, followed by the resins, saturates, and asphaltenes. With the increase of NaCl
414 concentration, the ΔE_{AM} of all asphalt components decline in volatility, indicating that the polarization
415 induction effect of NaCl has a negative effect on the interfacial adhesion.

416 3.5.3. Interaction energy between NaCl solution and asphalt components

417 The ΔE_{AM} between NaCl solution and asphalt components is characterized to investigate the
418 stripping effect of NaCl solutions on asphalt components on mineral materials, as shown in Figure 12e
419 and 12f. In the asphalt-SiO₂ system, the ΔE_{AM} of the non-polar saturates is small, and decreases with the
420 increase of NaCl concentration. And NaCl increases the ΔE_{AM} of the aromatics, which may be due to the
421 hydrogen bonding between NaCl solution and aromatics. The resins have the greatest ΔE_{AM} compared
422 to the other components, but the ΔE_{AM} decreases with increasing NaCl concentration. NaCl weakens
423 the ΔE_{AM} of asphaltenes, but the weakening effect decreases with the increase of NaCl concentration,
424 which is related to the spatial distribution of asphaltenes. That indicates that NaCl can weaken the
425 adhesion between asphalt and SiO₂ by hindering the aggregation of saturates, resins and asphaltenes on
426 the surface of SiO₂, enhancing the interaction between aqueous solution and aromatics to strip the

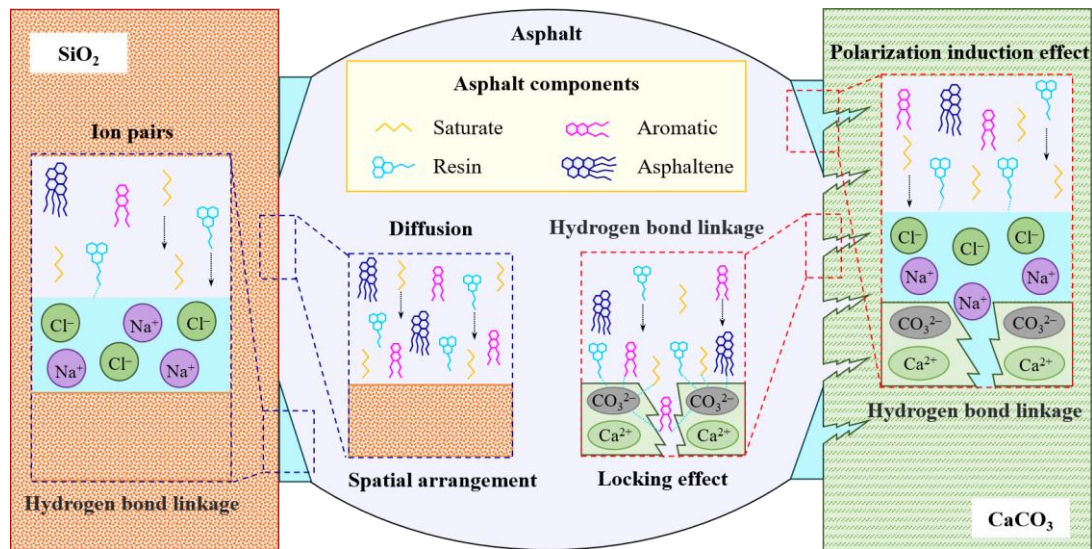
427 aromatics from the surface of SiO₂. In the system of asphalt-CaCO₃, NaCl increases the ΔE_{AM} of
428 saturates and asphaltenes, indicating that NaCl promotes aqueous solution to strip saturates and
429 asphaltenes adhesion on the surface, and saturates is more sensitive to low concentrations of NaCl. The
430 ΔE_{AM} of aromatics and resins are reduced by NaCl as they gradually move away from CaCO₃ from Fig.
431 9f-j.

432 ***3.6. Damage mechanism of NaCl solution to the adhesion of the asphalt-aggregate interface***

433 Considering the above results, the NaCl environment can affect the distribution and diffusion of
434 asphalt components and therefore reduce the asphalt-minerals adhesion. The schematic graph of the
435 adhesion behavior of asphalt with minerals in a NaCl environment is shown in Fig. 13. For the asphalt-
436 SiO₂ system, the polarity of the solution is enhanced by 3% NaCl, and there are more free ions to promote
437 the cross-section diffusion of the solution. Combined with the polarity induction effect, it hindered the
438 diffusion of other components except the saturates to the surface of SiO₂. This might be explained by the
439 fact that the saturates with the relatively low molecular weight is a non-polar component, therefore the
440 intermolecular interaction is weak, and the diffusion potential resistance is extremely small [57]. In
441 addition, the adhesion work between asphalt and SiO₂ is generated by non-bond energy provided by the
442 van der Waals force. The 3% NaCl prevents the accumulation of saturates, resins, and asphaltenes and
443 strips the aromatics on the SiO₂ surface, thus weakening the adhesion between asphalt and SiO₂. At this
444 time, the resins rather than the other components provide the maximum energy for the interface. However,
445 with the increase of NaCl concentration, contact ion pairs gradually increase, resulting in a decrease in
446 the R_g and FFV of the solution. Subsequently, the movement of atoms in the solution is limited, thus
447 inhibiting the diffusion of the solution [58]. And the accumulation of asphalt components except for
448 resins on SiO₂ will not be hindered on a large scale, and the diffusion and distribution of saturates are
449 still dominant. Therefore, the adhesion work between asphalt and SiO₂ at 10% and 20% NaCl solution is
450 greater than that at 3% NaCl solution, and the saturates are divided into the adhesion work at the interface

451 providing the maximum interaction energy.

452 For the asphalt-CaCO₃ system, there is an embedded locking effect, and the dense hydrogen bonds
453 between asphalt and CaCO₃ exist at dry due to the ion bonds in CaCO₃. The water can break the hydrogen
454 bond between CaCO₃ and asphalt and form hydrogen bonds with asphalt components. The evenly
455 distributed NaCl solution between asphalt molecules and CaCO₃ removes asphalt away from CaCO₃,
456 thus destroying the embedded locking effect between asphalt and CaCO₃. The polar effects of sodium
457 and chloride ions promote the cross-sectional and longitudinal diffusion of NaCl solution at the interface
458 and the diffusion of each component of asphalt. The adhesion work between asphalt and CaCO₃ is
459 generated by the non-bonding energy provided by van der Waals forces together with electrostatic forces,
460 as CaCO₃ consists of ionic bonds [59]. The 3% NaCl increases the interaction between the aqueous
461 solution and the saturates and asphaltenes to strip them from CaCO₃, and makes the aromatics and resins
462 far away from CaCO₃, which weakens the adhesion between CaCO₃ and asphalt. At the same time, the
463 resins provide the maximum interaction energy for interfacial adhesion. With the increase of NaCl
464 concentration, sodium ions can be attracted by negatively charged oxygen atoms on CO₃²⁻, thus
465 occupying the active site on CaCO₃ more easily. That prevents the formation of contact ion pairs in NaCl
466 solution, and makes it easier for chloride ions to penetrate the asphalt molecule and asphalt components
467 to detached from CaCO₃. Therefore, the interface adhesion is continuously weakened with increasing
468 NaCl concentration, and the resins with greater polarity provide the greatest interaction energy for the
469 interface adhesion, which is consistent with the previous study [60].



470

471 Fig. 13. Schematic graph of molecule migration model at asphalt-minerals interface.

472 4. Conclusions

473 In summary, the MD simulations of the asphalt-SiO₂ and asphalt-CaCO₃ interfaces were performed
 474 in an environment with extreme concentrations of NaCl, respectively. The characterizations contain the
 475 diffusion behavior of the NaCl solution at the interface, the spatial arrangement of asphalt components,
 476 and the changing trend of the interfacial adhesion work. It can be concluded that:

- 477 (1) As the NaCl concentration increases, the motion of atoms in the aqueous solution is restricted,
 478 which causes the 3% NaCl solution has the greatest D at the asphalt-SiO₂ interface and the
 479 asphalt-CaCO₃ interface.
- 480 (2) Due to the polarity caused by the ions, contact ion pairs exist abundantly in the NaCl solution,
 481 resulting in the self-aggregation of the NaCl solution at the asphalt-SiO₂ interface. In the
 482 asphalt-CaCO₃ system, the sodium ions are attracted to the negatively charged oxygen atoms
 483 on the CO₃²⁻, readily occupying the active sites on the CaCO₃ surface. That prevents the
 484 formation of contact ion pairs in the NaCl solution and avoids self-aggregation of the NaCl
 485 solution, allowing the NaCl to cover the depressions on the CaCO₃ surface uniformly.
- 486 (3) The distribution and diffusion of asphalt components on the mineral surface are mainly affected
 487 by the D of NaCl solution and the polarity of asphalt components. And NaCl is conducive to

488 the formation of hydrogen bonds between water molecules and asphalt components.

489 (4) The 3% NaCl prevents the accumulation of saturates, resins, and asphaltenes on the SiO₂
490 surface, and strips aromatics from the SiO₂ surface, resulting in the maximum damage of
491 interfacial adhesion work to the 55.93% of that in 0% NaCl solution. And the resins provide the
492 maximum interaction energy. The adhesion work between asphalt and SiO₂ in 10% and 20%
493 NaCl solution is greater than that in 3% NaCl solution. Among the four asphalt components,
494 the saturates provide the greatest interaction energy for the interface.

495 (5) The 3% NaCl solution can strip saturates and asphaltenes from CaCO₃, keeping aromatics and
496 resins away from CaCO₃. As the NaCl concentration increases, the chloride ions and
497 asphaltenes move away from CaCO₃. The interfacial adhesion continued to diminish with
498 increasing NaCl concentration, and the adhesion work is 66.03% of that at 20% NaCl solution.
499 The resin with the highest polarity provides the largest interaction energy for interfacial
500 adhesion.

501 This study exploits molecular dynamics to visualize the erosion process of the asphalt-aggregate
502 interface by sodium chloride solution and explores the failure mechanism of interfacial adhesion. These
503 findings provide new perspectives on the microscopic investigation of the interfacial adhesion behavior
504 of asphalt mixture subjected to salt. The whole process of asphalt-aggregate interfacial separation in salt
505 solution has not yet been visualized, considering the influence of factors such as solution surface tension.
506 The effects of aging and temperature also need to be considered. Therefore, these topics are of interest
507 to future research.

508 **Credit author statement**

509 **Zou Yingxue:** Conceptualization, Experiment, Writing-Original Draft. **Yangming Gao:**
510 Methodology, Software, Writing-Review, Supervision. **Anqi Chen:** Writing Assistance, Supervision.
511 **Shaopeng Wu:** Validation, Supervision. **Yuanyuan Li:** Writing-Review, Methodology. **Haiqin Xu:**

512 Software. **Huan Wang**: Methodology. **Ye Yang**: Data Curation. **Serji Amirkhanian**: Supervision.

513 **Declaration of competing interest**

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

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