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Author(s)	Hao, Xingjuan; Abu-Al-Saud, Moataz; Ayirala, Subhash et al.
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1 **Influence of carbonate impurities on smartwater effect: evaluation of wettability**  
2 **alteration process by geochemical simulation**

3

4 Xingjuan Hao <sup>1</sup>, Moataz Abu-Al-Saud <sup>2</sup>, Subhash Ayirala <sup>2</sup>, Yogarajah Elakneswaran <sup>1,\*</sup>

5

6 <sup>1</sup> Division of Sustainable Resources Engineering

7 Faculty of Engineering, Hokkaido University

8 Kita 13, Nishi 8, Kita-ku, Sapporo, 060-8628, Japan

9

10 <sup>2</sup>EXPEC Advanced Research Center, Saudi Aramco, Dhahran 31311, Saudi Arabia

11

12 \* Corresponding author

13 E-mail: elakneswaran@eng.hokudai.ac.jp

14 Tel: +81-11-706-7274

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18 **Highlights**

- 19 ➤ Equilibrium of carbonate impurities contributed to carbonate/brine than oil/brine.
- 20 ➤ Brine with  $\text{SO}_4^{2-}$  results in higher water-wet condition compared to other solutions.
- 21 ➤ The measured adhesion force is inversely related to calculated disjoining pressure.
- 22 ➤ An increase of -COOH/-NH ratio shows more water-wet state.

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26

27 **Abstract**

28 Low salinity water flooding (LSWF) has been considered as a promising technique for enhanced oil  
29 recovery (EOR). The wettability alteration towards a more water-wet state is recognised as the main  
30 mechanism for the positive LSWF effect. Electrokinetic interactions occurring at crude oil/brine and  
31 rock/brine interfaces affect the wettability alteration. Most of the studies reported in the existing  
32 knowledge considered synthetic calcite to understand the electrokinetics of natural carbonate with  
33 brines. The mineral impurities present in natural carbonate could influence the electrokinetics and  
34 subsequently wettability alteration. In this study, the surface complexation model, thermodynamic  
35 equilibrium model, and extended Derjaguin-Landau-Verwey-Overbeek (DLVO) theory were  
36 combined to evaluate the effect of impurities (dolomite and anhydrite) in natural carbonate on  
37 wettability alteration. The surface complexation modelling parameters were first estimated by fitting  
38 the calculated zeta potential to that of measured value in various brines and then validated in  
39 smartwater. The thermodynamic equilibrium of impurities is largely insensitive to crude oil/brine  
40 interface properties. However, the calculated carbonate/brine surface or zeta potential changed from  
41 positive to negative with anhydrite equilibrium in the brines containing  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions. The  
42 attractive or repulsive forces between crude oil and carbonate were estimated from disjoining pressure  
43 using extended DLVO theory and compared with measured adhesion forces. The computed disjoining  
44 pressure was used as an indicator to evaluate wettability alteration. It is found that brine with  $\text{SO}_4^{2-}$   
45 ions can result in highest water-wet condition, followed by smartwater (brine with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  
46  $\text{SO}_4^{2-}$ ) and brine with either  $\text{Ca}^{2+}$  ions or  $\text{Mg}^{2+}$  ions. The de-ionic (DI) water is unfavourable for  
47 wettability alteration. The effect of impurities equilibrium and the crude oil surface site densities on  
48 the disjoining pressure were also discussed.

49

50 **Keywords:** Triple-layer surface complexation model; Zeta potential; Smartwater; Carbonate  
51 impurities; Disjoining pressure; Adhesion force

52

53 **1. Introduction**

54 More than 60% of crude oil is present in carbonate reservoirs, most of which were described as  
55 naturally fractured and oil-wet [1,2]. Due to low recovery efficiency with conventional waterflooding,  
56 many enhanced oil recovery technologies have been investigated for tertiary oil recovery [3-11]. Low  
57 salinity water flooding (LSWF) or smartwater flooding (SWF) has recently attracted more attention  
58 for enhanced oil recovery (EOR) due to its low cost and eco-friendly nature. Various mechanisms  
59 such as fines migration, permeability reduction, osmotic effects, viscoelasticity, micro-dispersion  
60 formation, mineral dissolution, pH, desorption of polar oil components, expansion of electrical double  
61 layer (EDL), multi-component ionic exchange (MIE), and wettability alteration have been proposed  
62 for the positive effect of smartwater flooding [12-24]. However, the dominant mechanism is still  
63 uncertain, which can hinder the mechanistic modelling to accurately guide the design and  
64 implementation of this recovery technology for large-scale applications in different reservoirs.

65  
66 Some researchers have recognized wettability alteration as a major physiochemical process for LSWF  
67 effect, which was affected by different factors including ionic composition and interface properties.  
68 Divalent potential determining ions (PDIs) of calcium, magnesium, sulphate have a significant  
69 influence on wettability alteration. Karimi et al. investigated the impact of  $Mg^{2+}$ ,  $SO_4^{2-}$ , and cationic  
70 surfactant on wettability alteration in calcite [25]. Their results showed that both  $Mg^{2+}$  and  $SO_4^{2-}$   
71 could act as wettability modifying agents for the oil-wet calcite, and the modified low salinity brine  
72 solutions effectively changed the wettability towards more water-wet state. Purswani and Karpyn  
73 conducted a series of waterflooding experiments using synthetic high salinity water and observed that  
74 the surface charge of limestone rocks was linearly affected by  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $SO_4^{2+}$  ions [26]. In  
75 general, crude oil is negatively charged due to the dissociation of carboxylate groups ( $-COOH$ )  
76 whereas calcite, the main composition of carbonate, is positively charged [9,11]. These opposing  
77 surface charges result in the strong affinity of crude oil to the calcite surface to develop the oil-wet  
78 conditions.

79  
80 Reservoir carbonate rocks are primarily composed of calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), and  
81 other impurities including quartz, anhydrite, clay minerals, organic matter, and apatite [27]. To further  
82 understand the electrostatic properties of carbonate reservoirs, limestone was widely studied. Song et  
83 al. selected Indiana limestone as the representative of carbonate minerals to evaluate the effect of ions  
84 on “smart water”-induced carbonate wettability alteration [28]. That study used zeta potential  
85 experiments, disjoining pressure, and surface complexation modelling to evaluate the electrostatic  
86 interactions. In addition, Alroudhan et al. studied the electrostatic properties of Portland limestone  
87 [29]. Their measured zeta potential was negative at high pCa or pMg (i.e., low  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$   
88 concentration) and become less negative with decreasing pCa or pMg. Tetteh et al. analysed the effect  
89 of several factors including ionic composition, temperature, and solution pH on Indiana limestone  
90 rock system and used double layer surface complexation model (SCM) of calcite/brine interface to  
91 predict zeta potentials of limestone [30]. In addition, they evaluated the significance of magnesium  
92 ions in the solution for EOR in limestone rock through wettability alteration [31]. The magnesium  
93 ions had a positive effect on wettability alteration whereas calcium ions had a detrimental effect. In  
94 these studies [30, 31], they did not analyse the effect of limestone impurities on the results, which  
95 might affect the magnesium concentration in the solution. Mahani et al. conducted a detailed  
96 experimental and surface complexation modelling study to examine the effect of rock type, brine  
97 composition and pH on the electrokinetics of carbonate/brine interface [32]. In this study [32], the  
98 surface complexation model and the parameters were considered for calcite surface to understand the  
99 measured zeta potential. Brady and Thyne used a double layer SCM based on calcite surface to  
100 predict oil recovery trends in carbonate reservoir [33]. Chen et al. study showed that surface chemistry  
101 of oil/brine and calcite/brine strongly affects the wettability of oil-brine-carbonate system [34], which  
102 is governed by crude oil composition and water chemistry. However, they did not evaluate the effect  
103 of carbonate impurities (quartz and ankerite) on the resulting of water chemistry changes.

104

105 The zeta potential of the natural carbonate is typically more negative than that of synthetic calcite or  
106 pure calcite crystal such as Iceland spar [35], which indicates the impurities significantly affected the  
107 surface chemistry of natural carbonate. However, only a few studies have been reported to evaluate  
108 the effect of impurities on the surface charge of natural carbonate. The influence of organic carboxylic  
109 acids and inorganic silica impurities was evaluated by using an extended SCM [35]. The presence of  
110 anhydrite and dolomite in the carbonate affects the pH and solution composition due to their  
111 dissolution and consequently, it could affect the interaction between crude oil and carbonate.  
112 Therefore, the mineral impurities in the carbonate should be considered in characterising the  
113 wettability alteration. This study aims to evaluate the carbonate impurities of dolomite and anhydrite  
114 on wettability alteration through coupled triple-layer surface complexation and thermodynamic  
115 equilibrium model. The zeta potential, surface complexation model, and disjoining pressure were  
116 used to assess the wettability changes in smartwater. Moreover, the calculated disjoining pressure  
117 was compared with the measured adhesion force. Finally, a sensitivity analysis was performed to  
118 evaluate the effect of crude oil surface site densities on disjoining pressure.

119

## 120 **2. Model description and literature data**

### 121 **2.1 Geochemical model**

122 To investigate the effect of carbonate impurities on wettability alteration with smartwater, the triple-  
123 layer surface complexation model built-in the geochemical code PHREEQC was used. This model  
124 could describe the electrical properties of system due to the interactions including thermodynamic  
125 reactions, dissociation of surface species and adsorption of ions. Herein, a brief description of the  
126 model is given for crude oil/brine interface and the similar model was adopted for calcite/brine  
127 interface. A detailed description of the model can be found elsewhere [9,36]. According to the  
128 previous studies [9,10,37], the carboxyl groups ( $-\text{COOH}$ ) and nitrogen bases ( $-\text{NH}$ ) from asphaltenes  
129 and resins are the main surface-active substances in crude oil which have a predominant effect on the  
130 electrical properties of emulsion. These two groups could determine the surface charges of emulsion

131 due to the dissociation and adsorption. It was assumed that both groups can affect the surface charges  
 132 and thereby resulting in the formation of the triple-layer. In addition, the potential determining ions  
 133 (PDIs) including magnesium and calcium ions influence the change in surface charges. The charge  
 134 distribution ( $\Delta z_i, i = 0,1,2$ ) at three layers for  $-NH$  association,  $-COOH$  dissociation, and the  
 135 adsorption of magnesium, calcium, and sodium were assumed as shown in **Table 1** based on ref. [9]  
 136 (**Table 2** for calcite/brine interface). The intrinsic equilibrium constants for crude oil/brine interface  
 137 were calculated as follows:

$$139 \quad -NH + H^+ \leftrightarrow -NH_2^+, \quad K_{-NH_2^+} = \frac{(NH_2^+)}{(-NH) \times a_{H^+}} \exp\left(-\frac{\Delta z_i F \varphi_i}{RT}\right) \quad (1)$$

$$140 \quad -COOH \leftrightarrow -COO^- + H^+, \quad K_{-COO^-} = \frac{(-COO^-) \times a_{H^+}}{(-COOH)} \exp\left(-\frac{\Delta z_i F \varphi_i}{RT}\right) \quad (2)$$

$$141 \quad -COOH + Ca^{2+} \leftrightarrow -COOCa^+ + H^+, \quad K_{-COOCa^+} = \frac{(-COOCa^+) \times a_{H^+}}{(-COOH) \times a_{Ca^{2+}}} \exp\left(-\frac{\Delta z_i F \varphi_i}{RT}\right) \quad (3)$$

142  
 143 where  $K_{-NH_2^+}$ ,  $K_{-COO^-}$ , and  $K_{-COOCa^+}$  respect the intrinsic equilibrium constants for the protonation  
 144 of nitrogen bases, the deprotonation of carboxyl groups and the adsorption of calcium respectively.  
 145 Similar equations as Eq. (3) are used for magnesium and sodium adsorption as well.  $(-M)$  is the  
 146 concentration of the surface species;  $a_i$  denotes the activity of ionic species  $i$ ;  $F$  is the Faraday  
 147 constant equal to  $96485 \text{ C} \cdot \text{mol}^{-1}$ ;  $\varphi_i$  is the potential of the plane- $i$ ;  $R$  is the molar gas constant equal  
 148 to  $8.31451 \text{ J}/(\text{mol} \cdot \text{K})^{-1}$ , and  $T$  is the absolute temperature ( $K$ ).

150 **Table 1** Charge distribution values for the dissociation and adsorption of calcium, magnesium, and  
 151 sodium on crude oil

Ions	$\Delta z_0$	$\Delta z_1$	$\Delta z_2$
$OH^-$	-1	0	0
$H^+$	1	0	0
$Ca^{2+}$	-1	2	0
$Mg^{2+}$	-1	2	0

Na <sup>+</sup>	-1	0	0
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152

153 **Table 2** Charge distribution values for calcite/brine interface

Ions	$\Delta z_0$	$\Delta z_1$	$\Delta z_2$
OH <sup>-</sup>	-1	0	0
H <sup>+</sup>	1	0	0
Ca <sup>2+</sup>	-1	2	0
Mg <sup>2+</sup>	-1	2	0
Na <sup>+</sup>	-1	0	0
SO <sub>4</sub> <sup>2-</sup>	0	-2	0
HCO <sub>3</sub> <sup>-</sup>	0	-1	0

154

155 The thermodynamic equilibrium between minerals and solutions were considered through  
 156 “EQUILIBRIUM\_PHASES” keyword in PHREEQC. The amount of minerals, the type of phase, and  
 157 the specified saturation index were essential input parameters in PHREEQC. The equilibrium  
 158 constant ( $\log K_p$ ) at standard condition and the standard heat of reaction ( $\Delta_r H^0$ ) for the dissolution  
 159 reactions of calcite, dolomite, and anhydrite used in the geochemical modelling were given in **Table**  
 160 **3** [36,38].

161

162 **Table 3** Thermodynamic properties of minerals used in the geochemical simulation

Phase	Reactions	$\log K_p, 25^\circ \text{C}$	$\Delta_r H^0$ (kcal/mol)
Calcite	$\text{CaCO}_3 \leftrightarrow \text{CO}_3^{2-} + \text{Ca}^{2+}$	-8.48	-2.970
Dolomite	$\text{CaMg}(\text{CO}_3)_2 \leftrightarrow 2\text{CO}_3^{2-} + \text{Ca}^{2+} + \text{Mg}^{2+}$	-17.09	-9.436
Anhydrite	$\text{CaSO}_4 \leftrightarrow \text{SO}_4^{2-} + \text{Ca}^{2+}$	-4.36	-4.037

163

164 **2.2 Extended DLVO theory and disjoining pressure calculation**

165 To further understand the interactions between crude oil and carbonate, the total disjoining pressure  
 166 was used, which is comprised of van der Waals, structural and electrical forces and can be written as  
 167 [11,39,40]:

168

169

$$\Pi_{total}(h) = \Pi_{van}(h) + \Pi_{str.}(h) + \Pi_{ele.}(h) \quad (8)$$

170

171 where  $\Pi_{total}(h)$  is the total disjoining pressure;  $\Pi_{van}(h)$  represents the van der Waals force;

172  $\Pi_{str.}(h)$  is the structural force, and  $\Pi_{ele.}(h)$  is the electrical force. The van der Waals can be

173 calculated as follows:

174

175

$$\Pi_{van}(h) = \frac{-A(15.96h/\lambda+2)}{12\pi h^3(1+5.32h/\lambda)^2} \quad (9)$$

176

177 where  $A$  is the Hamaker constant of crude oil/brine/carbonate interface, which was assumed to be

178  $6.6 \times 10^{-21} J$  [41];  $\lambda$  is the London wavelength, and  $h$  is the separation distance of the two surfaces.

179 The structural force is a short-range force when compared with the other two forces, which primarily

180 acts within 1 nm [11,39]. The structural force was determined by three parameters, such as a

181 coefficient ( $A_k$ ),  $h$ , and the characteristic decay length ( $h_s$ ), given as:

182

183

$$\Pi_{str.}(h) = A_k \exp\left(-\frac{h}{h_s}\right) \quad (10)$$

184

185 where the coefficient and the characteristic decay length were assumed to be  $1.5 \times 10^{10} Pa$  and 0.05

186 nm, respectively [11,42]. The electrical force can be attractive or repulsive based on the sign of

187 surface charge and the ionic composition in the solution. For a constant surface potential, it can be

188 calculated as follows:

189

190

$$\Pi_{ele.}(h) = n_b k_B \left( \frac{2\psi_{r1}\psi_{r2} \cosh(kh) - \psi_{r1}^2 - \psi_{r2}^2}{(\sinh(kh))^2} \right) \quad (11)$$

191

192 where  $n_b$  is the ion density in the bulk brine,  $k_B$  is the Boltzmann constant ( $1.38064 \times 10^{-23}$ ),  $\Psi_{ri}$   
 193 is the reduced potential, and  $k$  is the reciprocal Debye-Hückel double layer length. The reduced  
 194 surface potential and the reciprocal of Debye-Hückel double layer length were determined by  
 195 equations below:

$$196 \quad \Psi_{ri} = \frac{ze\Psi_0}{k_B T} \quad (12)$$

$$197 \quad k = \sqrt{\frac{2e^2 z^2 n_b}{\epsilon_0 \epsilon_r k_B T}} \quad (13)$$

198  
 199 where  $z$  denotes the valence of a symmetrical electrolyte brine;  $e$  is the electron charge  
 200 ( $1.6 \times 10^{-19}$  C);  $\Psi_0$  is the surface potential;  $\epsilon_0$  is the dielectric permittivity of a vacuum  
 201 ( $8.85 \times 10^{-12}$ ), and  $\epsilon_r$  represents the relative permittivity of electrolyte brine.

202

### 203 **2.3 Source and application of literature experimental data**

204 The literature data to evaluate the carbonate impurities on smartwater effect were collected from  
 205 previous works [43,44] and tabulated in **Table 4**. To run the established model, key parameters  
 206 including specific surface area and the surface site densities are necessary. According to the result  
 207 reported by Alotaibi and Yousef [43], the oil droplets were spherical, and the mean size distribution  
 208 could be obtained directly, which were used for calculating the specific surface area. However, the  
 209 calcite particles were smaller with irregular shapes and their specific surface area was larger than that  
 210 of oil droplets. Meanwhile, Takeya et al. (2019) proposed the logarithmic equation to estimate the  
 211 site density of  $-\text{COOH}$  based on TAN at 50 °C, and they did not provide any suggestion to estimate  
 212  $-\text{NH}$  site density [10]. In this study, the modelling was performed to fit and predict the experimental  
 213 data at 22 °C and thus, the proposed equation by Takeya et al. (2019) [10] cannot be used. Moreover,  
 214 this study considered both  $-\text{COOH}$  and  $-\text{NH}$  sites in crude oil/brine/carbonate system. Therefore, for  
 215 the consistency in estimating both site densities, the equations proposed by Eftekhari et al. [45] have  
 216 been used to calculate the surface site densities of  $-\text{COOH}$  and  $-\text{NH}$  as follows [45]:

217

218

$$N_{S,-COOH} = \frac{0.602 \times 10^6 \times TAN}{10^3 \times a_{oil} \times MW_{KOH}} \quad (14)$$

219

$$N_{S,-NH} = \frac{0.602 \times 10^6 \times TBN}{10^3 \times a_{oil} \times MW_{KOH}} \quad (15)$$

220

221 where  $N_{S,-COOH}$  and  $N_{S,-NH}$  represent the carboxylic and nitrogen sites per  $\text{nm}^2$  respectively;  $TAN$  and222  $TBN$  are the total acid and base numbers;  $a_{oil}$  is the specific surface area of the crude oil, and  $MW_{KOH}$ 

223 is the molecular weight of potassium hydroxide (KOH). The natural carbonate considered in this

224 study contained 80% calcite, 13% dolomite, 6% anhydrite and less than 1% quartz [44].

225

226 **Table 4** Brine and oil related properties and the experimental data for zeta potential and adhesion

227 force

Items	DI Water	Brine1	Brine2	Brine3	Brine4
pH	7.04	6.32	6.05	6.27	6.67
Na <sup>+</sup> /ppm	–	–	–	1865	1824
Mg <sup>2+</sup> /ppm	–	1471	–	–	211
Ca <sup>2+</sup> /ppm	–	–	2080	–	65
SO <sub>4</sub> <sup>2+</sup> /ppm	–	–	–	3896	429
Cl <sup>-</sup> /ppm	–	4290	3681	–	3220
HCO <sub>3</sub> <sup>-</sup> /ppm	–	–	–	–	12
TDS/ppm	0	5761	5761	5761	5761
Ionic strength/M	0	0.18	0.16	0.12	0.12
Oil droplet/ $\mu\text{m}$ (d)	14.25	15.51	19.74	9.50	21.53
$\zeta$ -potential/mV (oil-brine) *	-156.11	-33.58	-14.15	-46.84	-51.66
$\zeta$ -potential/mV (carbonate-brine)	-27.44	8.92	12.32	-30.15	-10.54
Adhesion force/ $\mu\text{N}$ (oil-brine-carbonate)	140	111.4	110.7	98.9	103

228 \*where TAN of oil is 0.19 mg/g KOH; TBN is 0.08 mg/g KOH. The zeta potential was measured at

229 room temperature.

230

### 231 3. Results and discussion

#### 232 3.1 Triple layer surface complexation model for crude oil/brine and carbonate/brine:

##### 233 Parameter optimisation and validation

234 In the triple layer surface complexation model, the equilibrium constants for  
235 protonation/deprotonation and ionic adsorption were determined by fitting the experimental zeta  
236 potential results with that of modelling where inner and outer capacitance of the model varies  
237 according to PDIs. From the particle size distribution of crude oil in various brines [43], the specific  
238 surface area and site densities of  $-\text{COOH}$  and  $-\text{NH}$  (eqs. (14-15)) were determined and tabulated in  
239 **Table 5**. Initially, the fitting was performed for crude oil/DI water to determine equilibrium constants  
240 ( $K_{O,1}$  and  $K_{O,2}$  in **Table 5**) for protonation/deprotonation. It was assumed that only water molecules  
241 were attached to inner and outer Stern layers and the calculated  $C_{1,oil}$  and  $C_{2,oil}$  for emulsion formed  
242 by crude oil and DI Water was  $2.510 \text{ F/m}^2$ . The fitting of measured zeta potential with that of  
243 predicted result is shown in **Fig. 1**, and the estimated equilibrium constants are given in **Table 5**.  
244 These values were used to estimate equilibrium constants for the adsorption of calcium, magnesium,  
245 and sodium ions ( $K_{O,3}$ ,  $K_{O,4}$ , and  $K_{O,5}$  in **Table 5**). For Brine1 ( $\text{MgCl}_2$ ) and Brine2 ( $\text{CaCl}_2$ ), the  
246 distances of the inner and outer Stern layers were respectively determined by the presence of  
247 magnesium (diameter  $1.30 \text{ \AA}$ )/calcium ions (diameter  $1.98 \text{ \AA}$ ) and water molecules (diameter  $2.75$   
248  $\text{ \AA}$ ), which were used to calculate inner and outer capacitance (**Table 5**). The predicted zeta potential  
249 result was fitted to measured data of each brine by only adjusting  $K_{O,3}$  or  $K_{O,4}$  (**Fig. 1**). To fit the zeta  
250 potential data in Brine3 ( $\text{Na}_2\text{SO}_4$ ), the effect of sodium ion was considered because sulphate ions does  
251 not influence the potential changes at crude oil/brine interface. It was assumed that there is only water  
252 molecules in inner and outer Stern layers, and the calculated  $C_{1,oil}$  and  $C_{2,oil}$  were equal to  $2.253 \text{ F/m}^2$   
253 for the solution dielectric constant of 70. The estimated equilibrium constant values are tabulated in  
254 **Table 5**, which are rather smaller than those reported in literatures [9,10,37,46]. This is due to  
255 temperature difference between this study and previous studies as the equilibrium constant is a

256 function of temperature through Van't Hoff equation. The estimated equilibrium constants were  
 257 validated in Brine4 (smartwater). The inner and outer capacitance for crude oil in smartwater is the  
 258 same as the values calculated in Brine2 (CaCl<sub>2</sub>) as the calcium ion is the largest one in the solution  
 259 which controls the inner capacitance. The predicted zeta potential of crude oil in smartwater agreed  
 260 reasonably well with the measured data (**Fig. 1**), thereby suggesting the applicability of the model  
 261 and surface complexation parameters in smartwater.

262

263

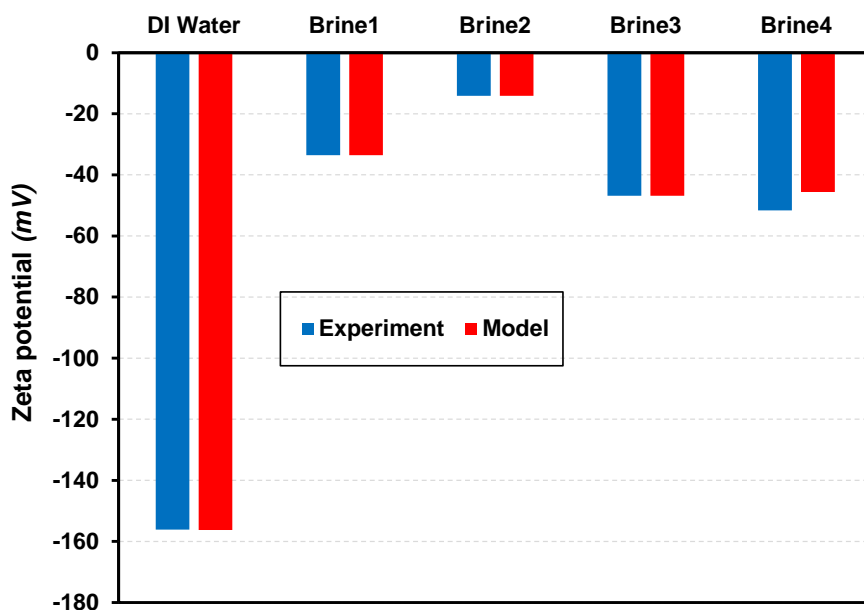
264

265 **Table 5** Determined surface complexation parameters for crude oil

Items	DI Water	Brine1	Brine2	Brine3	Brine4
≡COOH surface site density (sites/nm <sup>2</sup> )	4.28	4.66	5.93	2.85	6.47
≡NH surface site density (sites/nm <sup>2</sup> )	1.80	1.96	2.50	1.20	2.72
Specific surface area (m <sup>2</sup> /g)	0.476	0.437	0.344	0.714	0.315
C <sub>1,oil</sub> (F/m <sup>2</sup> )	2.510	4.765	3.129	2.253	3.129
C <sub>2,oil</sub> (F/m <sup>2</sup> )	2.510	2.253	2.253	2.253	2.253
Surface reaction	Log <sub>10</sub> K (22 °C)		Value		
≡NH + H <sup>+</sup> ↔ ≡NH <sub>2</sub> <sup>+</sup>	K <sub>O,1</sub>		2.79		
≡COOH ↔ ≡COO <sup>-</sup> + H <sup>+</sup>	K <sub>O,2</sub>		-6.32		
≡COOH + Ca <sup>2+</sup> ↔ ≡COOCa <sup>+</sup> + H <sup>+</sup>	K <sub>O,3</sub>		-5.42		
≡COOH + Mg <sup>2+</sup> ↔ ≡COOMg <sup>+</sup> + H <sup>+</sup>	K <sub>O,4</sub>		-8.71		
≡COOH + Na <sup>+</sup> ↔ ≡COONa + H <sup>+</sup>	K <sub>O,5</sub>		-5.02		

266

267



268

269 **Fig. 1.** Measured and predicted zeta potential of crude oil in DI water and brines

270

271 A similar methodology was adopted for carbonate/brine interface to optimise the equilibrium  
 272 constants for surface complexation reactions. It was assumed that the surface electrical properties of  
 273 carbonate/brine are governed by calcite surface. Therefore, in this study, the surface complexation  
 274 modelling parameters for calcite/brine are estimated by fitting the experimental data to modelling  
 275 results, where the dissolution of anhydrite and dolomite was not considered to minimise the number  
 276 of fitting parameters. As reported in the previous studies [47], the calcite surface possesses  $>CaOH$   
 277 and  $>CO_3H$  sites for protonation/deprotonation and adsorption of ions. The site density of both  
 278 surfaces was assumed to be  $4.95 \text{ sites/nm}^2$  and the specific surface area of calcite was  $2.15 \text{ m}^2/\text{g}$  [11].  
 279 The calcium ions from the dissolution of calcite in solution determine the inner capacitance ( $3.129$   
 280  $\text{F/m}^2$ ) whereas  $0.200 \text{ F/m}^2$  was assumed for outer capacitance. To predict the zeta potential of  
 281 carbonate/brine, various ions have been considered and their charge distribution in the triple-layer  
 282 model is given in **Table 2**. At each case, the dissolution of calcite releases calcium and carbonate ions  
 283 into the solution. Therefore, the experimental data for DI Water and Brine2 ( $CaCl_2$ ) needs to be fitted  
 284 at the initial stage to determine  $K_{C,1}$ ,  $K_{C,2}$ ,  $K_{C,3}$  and  $K_{C,4}$  (**Table 6**). Afterwards, the data for Brine1  
 285 ( $MgCl_2$ ) was fitted to estimate  $K_{C,5}$ , and then Brine3 ( $Na_2SO_4$ ) was used to determine  $K_{C,6}$  and  $K_{C,7}$ .

286 It should be noted that the adsorption of  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  is considered on  $>\text{CaOH}_2^+$  surface [28, 47],  
 287 and the appropriate charge distribution is given in **Table 2**. The optimised surface complexation  
 288 modelling parameters are tabulated in **Table 6** and they are comparable to the data reported in the  
 289 previous studies [11,34,39]. Finally, the modelling parameters were validated in predicting the zeta  
 290 potential of smartwater and then comparing with experimental data. The fitting and prediction are  
 291 shown in **Fig. 2**. As can be seen, the model was able to successfully predict the zeta potential of  
 292 carbonate in smartwater.

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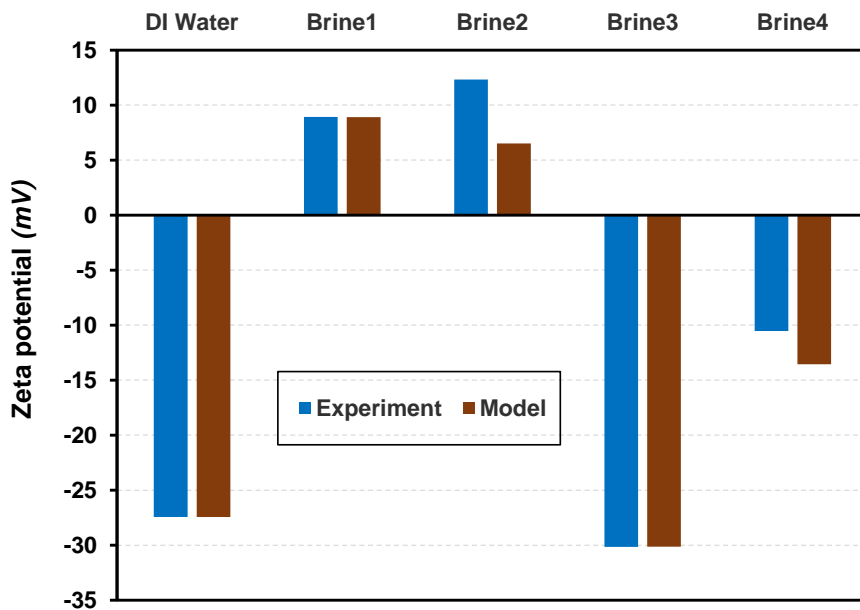
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296

297 **Table 6** Determined surface complexation parameters for carbonate core particles

Items	Value	
$>\text{CaOH}$ surface site density (sites/nm <sup>2</sup> )	4.95	
$>\text{CO}_3\text{H}$ surface site density (sites/nm <sup>2</sup> )	4.95	
Specific surface area (m <sup>2</sup> /g)	2.15	
$C_{1,\text{carbonate}}$ (F/m <sup>2</sup> )	3.129	
$C_{2,\text{carbonate}}$ (F/m <sup>2</sup> )	0.200	
Surface reaction	Log <sub>10</sub> K (22 °C)	Value
$>\text{CO}_3\text{H} \leftrightarrow >\text{CO}_3^- + \text{H}^+$	$K_{C,1}$	-3.37
$>\text{CaOH} + \text{H}^+ \leftrightarrow >\text{CaOH}_2^+$	$K_{C,2}$	11.70
$>\text{CO}_3\text{H} + \text{Ca}^{2+} \leftrightarrow >\text{CO}_3\text{Ca}^+ + \text{H}^+$	$K_{C,3}$	-1.00
$>\text{CaOH}_2^+ + \text{HCO}_3^- \leftrightarrow >\text{CaOH}_3\text{CO}_3$	$K_{C,4}$	5.05
$>\text{CO}_3\text{H} + \text{Mg}^{2+} \leftrightarrow >\text{CO}_3\text{Mg}^+ + \text{H}^+$	$K_{C,5}$	0.04
$>\text{CO}_3\text{H} + \text{Na}^+ \leftrightarrow >\text{CO}_3\text{Na} + \text{H}^+$	$K_{C,6}$	-1.15
$>\text{CaOH}_2^+ + \text{SO}_4^{2-} \leftrightarrow >\text{CaOH}_2\text{SO}_4^-$	$K_{C,7}$	10.70

298



299

300 **Fig. 2.** Measured and predicted zeta potential of carbonate in DI water and brines

301

### 302 **3.2 Effect of carbonate impurities on interface properties**

303 The crushed carbonate core sample used to measure zeta potential composed of 80% calcite, 13%

304 dolomite, 6% anhydrite, and less than 1% quartz [44]. The presence of impurities and their amount

305 were considered in the phase-equilibrium model as given in **Table 3**. In the phase-equilibrium model,

306 the amounts of minerals' moles were selected with respect to their composition in the carbonate for

307 dissolution. Dolomite and anhydrite impurities dissolve into the solution and change pH and ionic

308 composition of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ , which could influence the interface properties through

309 the reactions given in **Table 6**. It should be noted that the surface complexation model for either

310 dolomite or anhydrite is not considered in this study because the dissolution is more significant than

311 surface complexation reaction for anhydrite or dolomite. **Fig. 3** shows the effect of impurities

312 equilibrium on the calculated zeta potential of carbonate and its comparison with experimental data.

313 The calculation was performed without considering the crude oil. The equilibrium of anhydrite

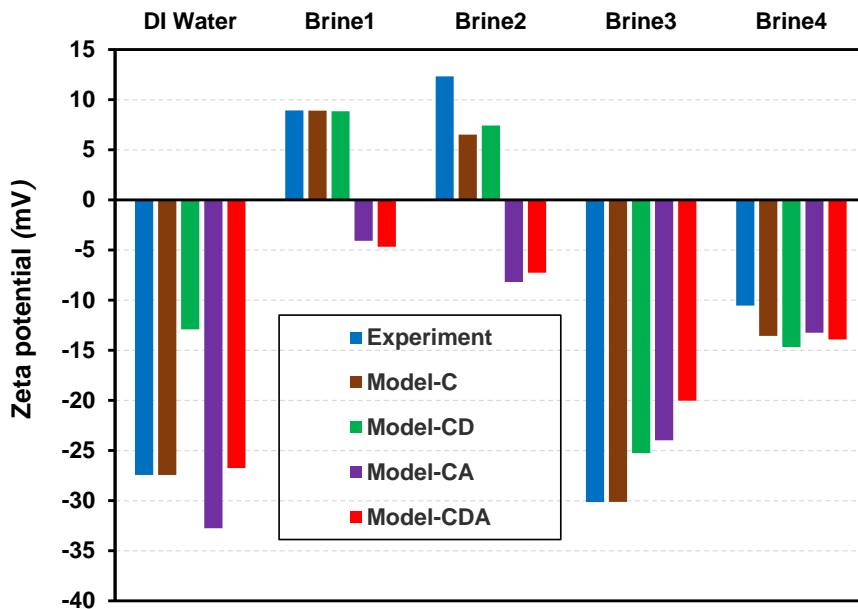
314 releases enough sulphate ions into the solution and reverses the calculated zeta potential from positive

315 to negative in Brine1 ( $\text{MgCl}_2$ ) and Brine2 ( $\text{CaCl}_2$ ) solution, which is opposite to the measured data.

316 It is important to note that the equilibrium of calcite or impurities of dolomite and anhydrite does not

317 have a significant influence on the zeta potential of carbonate in smartwater (Brine4). This is mainly  
 318 due to the reason that smartwater contained enough PDIs and as a result, their compositions did not  
 319 change considerably with the minerals' equilibrium.

320



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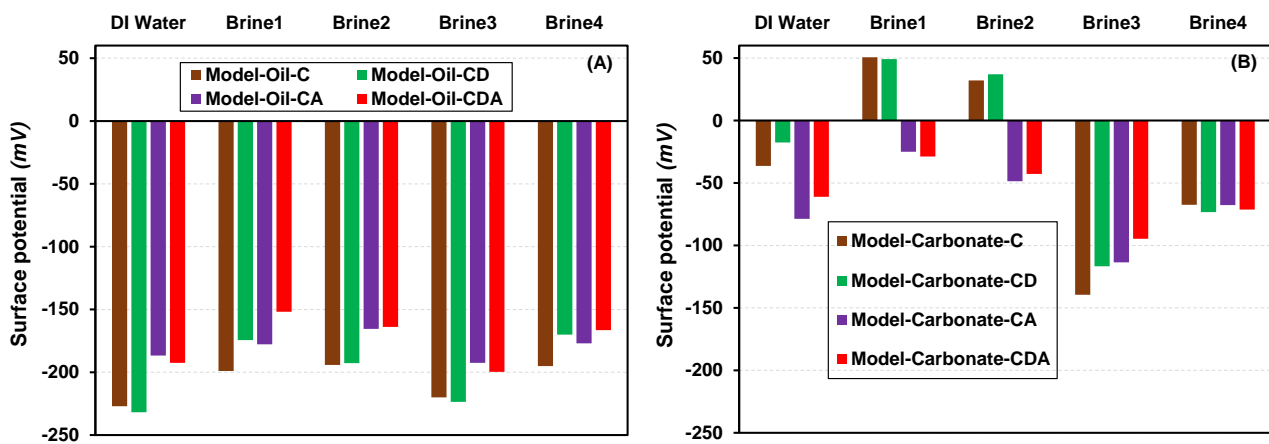
322 **Fig. 3.** Influence of impurities equilibrium on zeta potential of carbonate in DI water and brines. C:  
 323 Equilibrium with calcite; CD: Equilibrium with calcite and dolomite; CA: Equilibrium with calcite  
 324 and anhydrite; CDA: Equilibrium with calcite, dolomite, and anhydrite. [Carbonate-DI water/brines  
 325 system]

326

327 A similar calculation was performed for crude oil-brine-carbonate system in the presence of crude oil.  
 328 The calculated surface potential of crude oil and that of carbonate is shown in **Fig. 4**. The effect of  
 329 impurities on carbonate surface potential in the presence of crude oil showed similar trend as obtained  
 330 for zeta potential (**Fig. 3**). However, the equilibrium of carbonate minerals does not remarkably affect  
 331 the surface potential of crude oil, and the crude oil surface still shows negative charge. The potential  
 332 variation with the equilibrium of mineral relates to pH change. For example, in Brine2 ( $\text{CaCl}_2$ ), pH  
 333 was around 9.4 when considering the equilibrium of calcite or both of calcite and dolomite, but it was  
 334 reduced to 8.8 with anhydrite equilibrium. These pH variations correspond to the change of surface

335 potential. The distribution of surface species of crude oil and carbonate without or with the  
 336 equilibrium of calcite, dolomite and anhydrite is shown in **Fig. 5**. Again, the impurities equilibrium  
 337 has no effect on crude oil surface species whereas the release of sulphate ions from anhydrite  
 338 equilibrium forms  $>\text{CaOH}_2\text{SO}_4^-$  which controls the calcite surface. The  $>\text{CaOH}_2\text{SO}_4^-$ ,  $>\text{CO}_3\text{Mg}^+$ ,  
 339 and  $>\text{CO}_3\text{Ca}^+$  are the main surface species when the carbonate equilibrates with various solutions,  
 340 where the density of  $>\text{CO}_3^-$  and  $>\text{CaOH}_2^+$  are negligible on calcite surface. In smartwater, the  
 341 concentration of surface species is almost equal with or without impurities equilibrium, which clearly  
 342 explains the independence of surface/zeta potential with impurities equilibrium for this case.

343



344

345 **Fig. 4.** Effect of impurities on surface potential of crude oil and carbonate in DI water and brines.

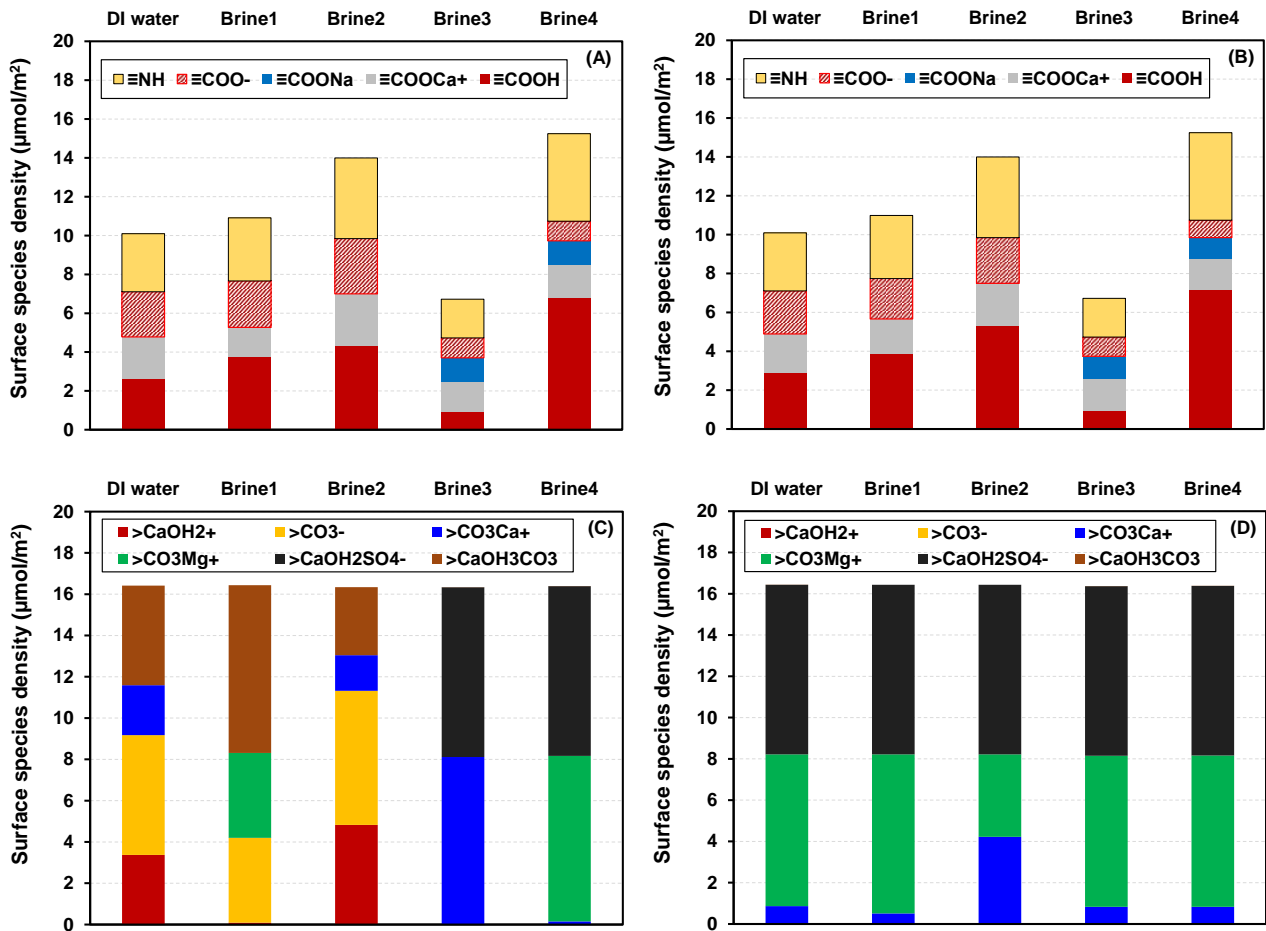
346 (A) Surface potential of crude oil; (B) Surface potential of carbonate. C: Equilibrium with calcite;

347 CD: Equilibrium with calcite and dolomite; CA: Equilibrium with calcite and anhydrite; CDA:

348 Equilibrium with calcite, dolomite, and anhydrite. [Crude oil- DI water/brines- carbonate system]

349

350



351

352 **Fig. 5** (A) Surface species density of crude oil in the system without impurities equilibrium; (B)  
 353 Surface species density of crude oil in the system with the equilibrium of calcite, dolomite and  
 354 anhydrite; (C) Surface species density of carbonate in the system without impurities equilibrium; (D)  
 355 Surface species density of carbonate in the system with the equilibrium of calcite, dolomite and  
 356 anhydrite

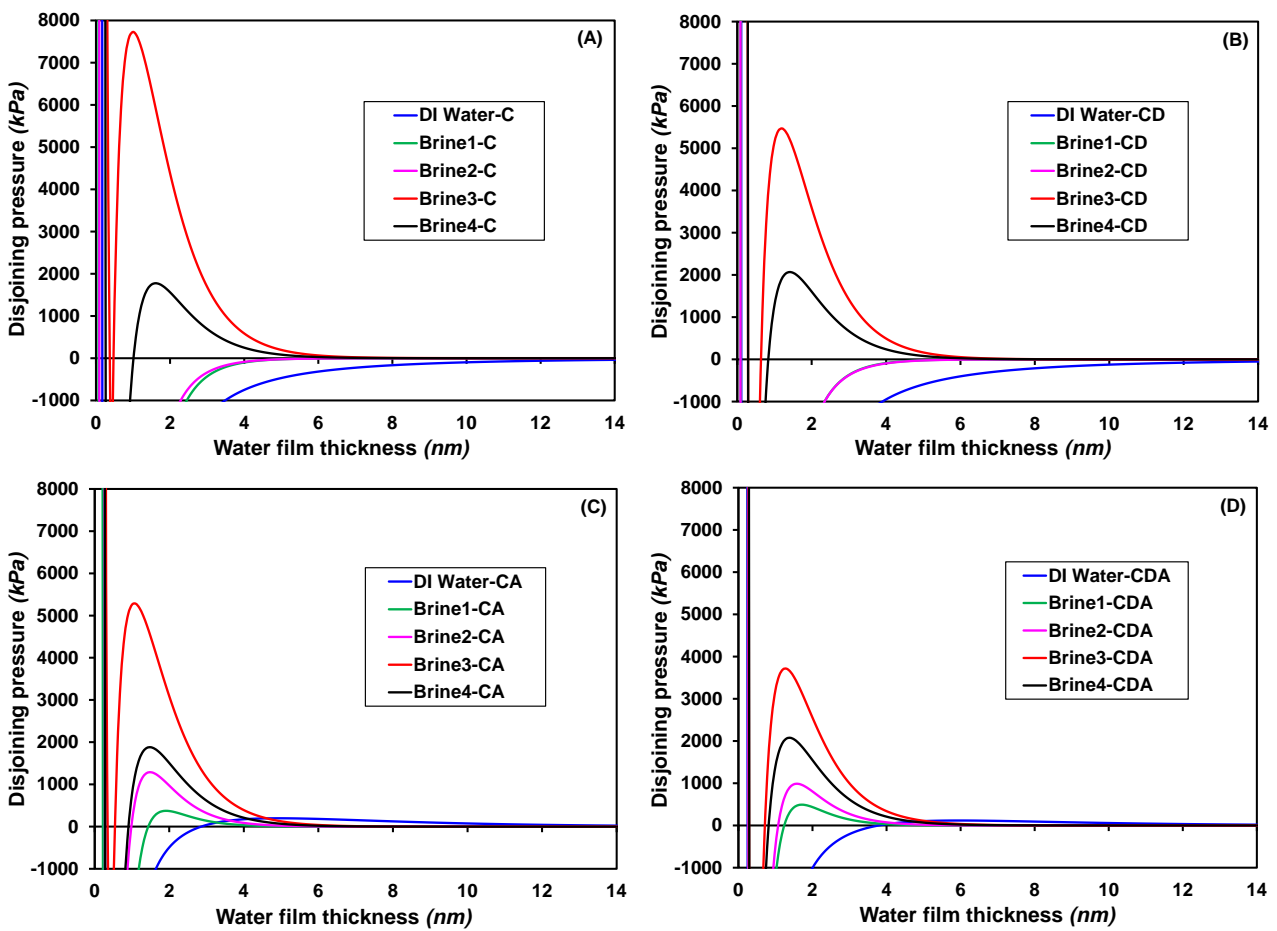
357

### 358 3.3 Impact of carbonate impurities and crude oil properties on disjoining pressure

359 The surface potentials were used to calculate total disjoining pressure which was adopted to evaluate  
 360 the wettability alteration. Consistent with previous studies [11,39,41], the calculated van der Waals  
 361 force was negative whereas the structural force acting at  $< 1\text{nm}$  was positive. Therefore, the electrical  
 362 force controls the total disjoining pressure. The effect of impurities equilibrium on total disjoining  
 363 pressure is shown in **Fig. 6**. The surface potential of crude oil was negative in DI Water/Brines (**Fig.**  
 364 **4(A)**). The positive surface potential of carbonate with the equilibrium of calcite or calcite and

365 dolomite in Brine1 and Brine2 (**Fig. 4(B)**) develops an attractive force (negative disjoining pressure)  
 366 between crude oil and carbonate (**Fig. 6(A)** and (B)). However, the equilibrium of anhydrite reversed  
 367 the surface potential of carbonate from positive to negative and resulted in repulsive (positive  
 368 disjoining pressure) force (**Fig. 6(C)** and (D)). The calculated disjoining pressure shows repulsion  
 369 between crude oil and carbonate in smartwater. Furthermore, the magnitude of disjoining pressure  
 370 varied according to the surface potentials of crude oil and carbonate.

371



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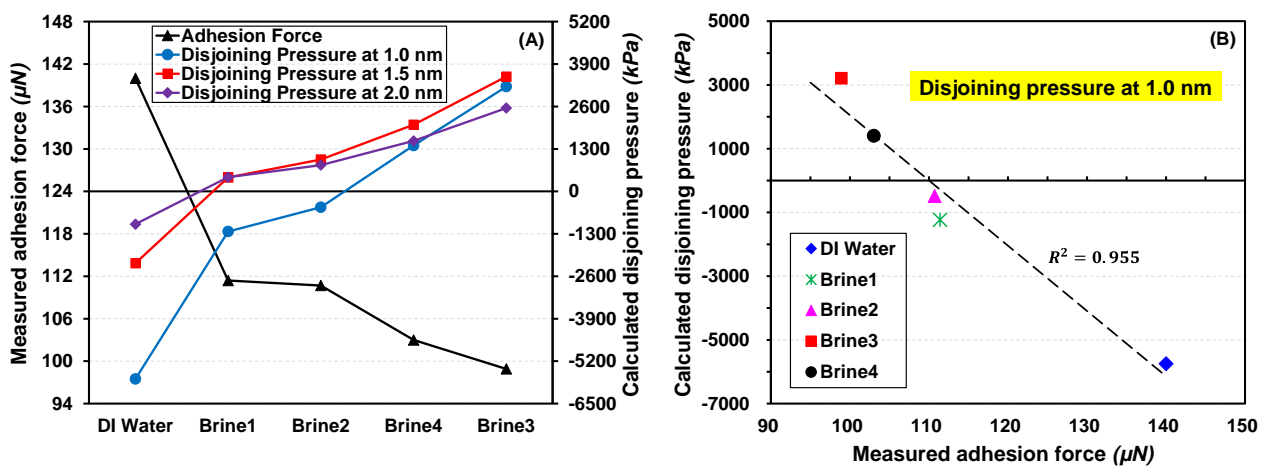
373 **Fig. 6** Calculated total disjoining pressure between crude oil and carbonate in DI water and brines.

374 (A) Equilibrium with calcite; (B) Equilibrium with calcite and dolomite; (C) Equilibrium with calcite  
 375 and anhydrite; (D) Equilibrium with calcite, dolomite, and anhydrite.

376

377 The positive or negative disjoining pressure was obtained due to respective repulsive or attractive  
 378 forces between crude oil and carbonate in the brines (**Fig. 6.**). However, a constant positive adhesion

379 force was measured after the oil droplet detached from the carbonate [44]. The calculated total  
 380 disjoining pressure was compared with the measured adhesion force in **Fig. 7**. As can be seen in the  
 381 figure, the disjoining pressure was calculated at 1.0, 1.5 and 2.0 nm. It should be noted that the  
 382 disjoining pressure was calculated considering the equilibrium of calcite, dolomite, and anhydrite.  
 383 The electrical force is the main contributor to the total disjoining pressure at a separating distance  
 384 higher than 1 nm. Although the measured adhesion force cannot be directly compared to the  
 385 calculated disjoining pressure, the measured adhesion force shows a good relationship with the  
 386 calculated disjoining pressure: high adhesion force shows low disjoining pressure or vice versa. In  
 387 particular, the total disjoining pressure calculated at 1 nm exhibits a good relationship with the  
 388 measured adhesion force (**Fig. 7(B)**). The disjoining pressure and adhesion force results indicate that  
 389 crude oil is closely attached to carbonate in DI water. On the other hand, both the crude oil and  
 390 carbonate repelled with each other in the other solutions where Brine3 ( $\text{Na}_2\text{SO}_4$ ) shows lowest  
 391 adhesion force or highest disjoining pressure. Both Brine4 (smartwater) and Brine3 ( $\text{Na}_2\text{SO}_4$ ) have a  
 392 similar ionic strength, but the higher adsorption of sulphate ions on carbonate in Brine3 ( $\text{Na}_2\text{SO}_4$ )  
 393 shows high negative surface potential of carbonate which strongly repulses the crude oil. These results  
 394 are consistent with the measured contact angle; a smaller contact angle was obtained for Brine3  
 395 ( $\text{Na}_2\text{SO}_4$ ) [44].

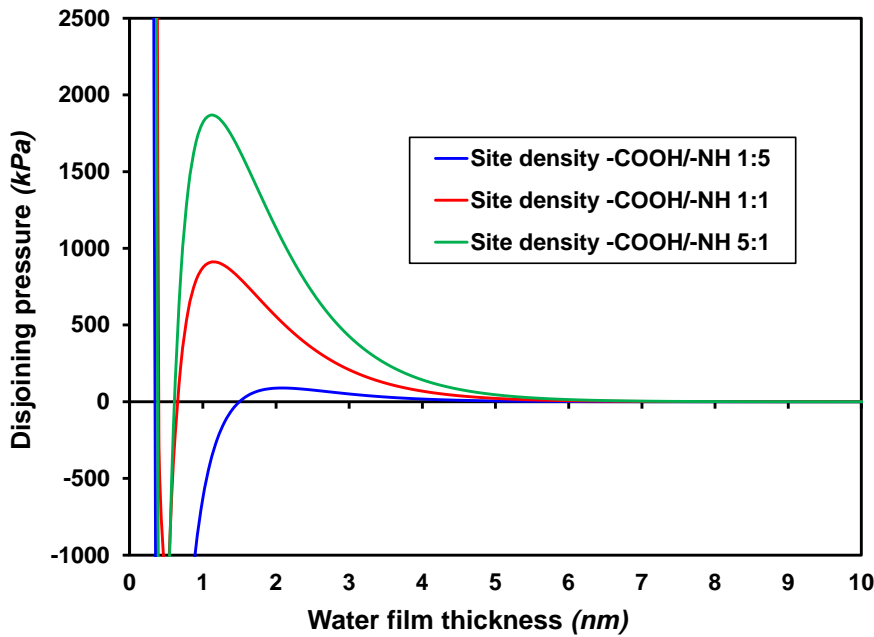


396  
 397 **Fig. 7** (A) Comparison of measured adhesion force with calculated disjoining pressure between crude  
 398 oil and carbonate in DI water and brines; (B) The best relationship between measured adhesion force  
 399 and calculated disjoining pressure at 1 nm.

400

401 The disjoining pressure is governed by electrical force or surface potential which is sensitive to the  
402 surface complexation modelling parameters given in **Table 5** and **Table 6**. Indeed, the equilibrium  
403 constant strongly influences the surface or zeta potential, which is a function of temperature and is  
404 usually derived by fitting the experimental data. In addition to equilibrium constant, the surface site  
405 density is an important factor controlling the surface electrical properties, which was determined by  
406 the structure of minerals or molecules. From the defined structure of calcite, the surface site density  
407 of calcite is constant. On the other hand, it is difficult to estimate the surface functional groups and  
408 their densities from the structure of crude oil. Eftekhari et al. [45] proposed equations (14) and (15)  
409 to estimate site densities while other researchers [10] have suggested a different method. However,  
410 the applicability of these methods to estimate surface site densities of crude oil depends on the TAN  
411 or TBN. A crude oil with TAN of 0.19 g/g KOH and TBN of 0.08 g/g KOH was used to evaluate  
412 wettability alteration using electrokinetics in this study. The effect of crude oil site densities, in other  
413 words TAN/TBN, on total disjoining pressure is shown in **Fig. 8**. The calculations were performed  
414 in smartwater with the equilibrium of impurities. The change of site densities modifies the surface  
415 potential of crude oil, and subsequently it affects the wettability alteration through the change of  
416 disjoining pressure. The calculation results indicate that higher  $-\text{COOH}/-\text{NH}$  ratio shows stronger  
417 repulsion between the crude oil and carbonate.

418



419

420 **Fig. 8.** Calculated disjoining pressure for crude oil/smartwater/carbonate system with different site  
 421 density ratios of  $-\text{COOH}$  and  $-\text{NH}$ .

422

#### 423 4. Conclusions

424 A triple-layer surface complexation model was established and applied to predict the zeta potential  
 425 of crude oil and carbonate in smartwater. The model is coupled with thermodynamic equilibrium  
 426 reactions to analyse the carbonate impurities on wettability changes. The measured and calculated  
 427 zeta potentials of crude oil and carbonate in various solutions were successfully fitted to estimate the  
 428 equilibrium constant of reactions, and it was validated with predicting the zeta potential in smartwater.  
 429 The equilibrium of carbonate impurities of dolomite and anhydrite does not affect the electrokinetic  
 430 properties of crude oil/brine, but the equilibrium of anhydrite changes the carbonate zeta or surface  
 431 potential from positive to negative in  $\text{CaCl}_2$  or  $\text{MgCl}_2$  solution. As a result of impurities equilibrium,  
 432 the surface of carbonate is mainly composed of  $>\text{CaOH}_2\text{SO}_4^-$  and  $>\text{CO}_3\text{Mg}^+$  species, which governs  
 433 the potential. The impurities equilibrium has a less effect in smartwater or  $\text{Na}_2\text{SO}_4$  solution that  
 434 contains sulphate ions. The calculated disjoining pressure is inversely correlated with measured  
 435 adhesion force and the highest disjoining pressure or the lowest adhesion force was obtained in  
 436  $\text{Na}_2\text{SO}_4$  solution. The disjoining pressure and adhesion force results show that the crude oil is closely

437 attached to carbonate surface in DI water, indicating oil-wet condition. This condition did not change  
438 even with the equilibrium of anhydrite. On the hand, the crude oil and carbonate have repelled with  
439 each other in  $\text{Na}_2\text{SO}_4$  or smartwater, suggesting the water-wet condition. Therefore, the wettability  
440 from oil-wet to water-wet in the system was in the following order DI water > brine with  $\text{Mg}^{2+}$  >  
441 brine with  $\text{Ca}^{2+}$  > brine with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  > brine with  $\text{SO}_4^{2-}$ . Lastly, the effect of crude oil  
442 properties on disjoining pressure was evaluated. It is found that  $-\text{COOH}/-\text{NH}$  (TAN/TBN) ratio  
443 strongly affects the disjoining pressure and wettability changes in crude oil/smartwater/carbonate  
444 system.

445

#### 446 **CRedit authorship contribution statement**

447 **Xingjuan Hao:** Conceptualization, Methodology, Formal analysis, Software, Writing-original Draft,  
448 Writing-review & editing. **Moataz Abu-Al-Saud:** Conceptualization, Methodology, Formal analysis,  
449 Writing-review & editing. **Subhash Ayirala:** Conceptualization, Methodology, Formal analysis,  
450 Supervision, Writing-review & editing. **Yogarajah Elakneswaran:** Conceptualization,  
451 Methodology, Formal analysis, Software, Supervision, Writing-original Draft, Writing-review &  
452 editing.

453

#### 454 **Declaration of Competing Interest**

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

457

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461

462

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