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The Impact of Pore Water Chemistry on Carbonate Surface Charge and Oil Wettability

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Abstract Water chemistry has been shown experimentally to affect the stability of water films and the sorption of organic oil components on mineral surfaces. When oil is displaced by water, water chemistry has been shown to impact oil recovery. At least two mechanisms could account for these effects, the water chemistry could change the charge on the rock surface and affect the rock wettability, and/or changes in the water chemistry could dissolve rock minerals and affect the rock wettability. The explanations need not be the same for oil displacement of water as for water imbibition and displacement of oil. This article investigates how water chemistry affects surface charge and rock dissolution in a pure calcium carbonate rock similar to the Stevns Klint chalk by constructing and applying a chemical model that couples bulk aqueous and surface chemistry and also addresses mineral precipitation and dissolution. We perform calculations for seawater and formation water for temperatures between 70 and 130°C. The model we construct accurately predicts the surface potential of calcite and the adsorption of sulfate ions from the pore water. The surface potential changes are not able to explain the observed changes in oil recovery caused by changes in pore water chemistry or temperature. On the other hand, chemical dissolution of calcite has the experimentally observed chemical and temperature dependence and could account for the experimental recovery systematics. Based on this preliminary analysis, we conclude that although surface potential may explain some aspects of the existing spontaneous imbibitions data set, mineral dissolution appears to be the controlling factor.

Keywords Wettability · Wettability change · Geochemistry · Zeta potential · Carbonate

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1 Introduction

Wettability has a significant influence on multiphase flow in porous media. In particular, if the reservoir has a mixed-wettability state, then the porous media may have oil and water films that are continuous. Thus, oil and water are mobile down to very low saturations (Salathiel 1973). Depending on the shape of the pore space (Kovscek et al. 1993), the mineralogy of the pore space and the composition of the crude oil, the pore space can be water-wet, be partly oil and partly water-wet, or be oil-wet (Buckley 2001).

Before it is filled with oil, an oil reservoir is filled with water and all its mineral surfaces are water-wet. When oil enters the reservoir it will do so by moving through the center of the pores and water will continue to wet the pore surfaces. This process is simulated in the laboratory by the aging stage of spontaneous imbibition experiments, as discussed below. In order for the oil to contact the pore wall, water has to be pushed away from the wall. The stability of the water film thus determines if there is a potential for wettability to change (Kovscek et al. 1993). After the water film has collapsed, active components in the oil can adsorb to calcium or carbonate sites in the calcite lattice and change the wettability. The nature of the oil components (chain length, number of carboxylic groups, etc.) and the density of adsorption sites will determine if the rock becomes strongly oil-wet or more moderately oil wet (Buckley 2001; Thomas et al. 1993a,b). The water film is stable if it can resist the pressure in the oil phase. More precisely, the collapse of the water film is controlled by the disjoining pressure (Kovscek et al. 1993; Bergeron and Radke 1995), as reviewed in Israelachivili (1985). A thick water film prevents active components in the oil from adsorbing to the surface. However, a high pressure in the oil phase can reduce the thickness of the water film sufficiently to allow active components in the oil phase to adhere to the rock mineral surface. Thus, the wetting state in a reservoir should be dependent on the difference between the oil and water pressure (e.g., the capillary pressure; Melrose 1982; Hirasaki 1991). The rock should be more water-wet close to the oil-water contact, than in the overlying oil reservoir where, due to buoyancy, the oil pressure is higher. Experiments support this basic thesis (Hamon 2004).

Temperature also plays a role, and in practice changes in wettability can involve non-obvious complexities. Schembre et al. (2006) suggest that the change in temperature that results when flooding waters are introduced to a reservoir causes the surface oil-wet fines to detach, leaving a clean, water-wet surface. One implication is that changes in wettability during water displacement of oil may differ from those during oil displacement of water.

The situation is thus complicated even if disjoining pressure is the only wettability control. In the last decade, it has also been found that the chemistry of the aqueous phase influences the water wetness of the pore surface. Brines with low salinity seem to wet the pore surface more, and reducing the salinity of flooding waters has been found to enhance oil production (Tang and Morrow 1999; Lager et al. 2006; Zhang et al. 2006). In fractured chalk fields, such as Ekofisk, spontaneous imbibition of water from the fractures into the matrix is believed to be an important recovery mechanism (Hamon 2004). The concentration of calcium, magnesium, and sulfate in water spontaneously imbibed into chalk cores affects the amount of oil expelled (Strand et al. 2006; Zhang et al. 2006, 2007; Zhang and Austad 2006). One explanation could be that sulfate, calcium, and magnesium adsorb to the pore surfaces, change the surface charge, and could thereby potentially influence the ability of polar oil components to adsorb. Regardless of cause, the effect of calcium, magnesium, and sulfate ions on oil production is clearly illustrated in spontaneous imbibition experiments (Strand et al. 2006; Zhang et al. 2006, 2007; Zhang and Austad 2006; Karoussi and Hamouda 2007).

Injection of water into a reservoir could cause mineral dissolution, and this could change the wettability and perhaps even cause pore collapse that could expel oil. The chemistry of the

Table 1 Composition of synthetic seawater (SW), Ekofisk formation (EF) brine, "modified" seawater with 4 times calcium concentration (SW w/4× Ca^{2+}), "modified" seawater with no calcium (SW u/Ca^{2+}), "modified" seawater with no sulfate (SW u/SO_4^{2-}), and "modified" seawater with three times the sulfate concentration (SW w/3× SO_4^{2-})

Ion	SW w/4×Ca^{2+} (mol/l)	SW (mol/l)	SW u/Ca^{2+} (mol/l)	SW u/SO_4^{2-} (mol/l)	SW w/3× SO_4^{2-} (mol/l)	EF (mol/l)
Na^+	0.333	0.45	0.489	0.5	0.429	0.684
K^+	0.01	0.01	0.01	0.01	0.01	–
Mg^{2+}	0.0445	0.0445	0.0445	0.0445	0.0445	0.025
Ca^{2+}	0.052	0.013	–	0.013	0.013	0.231
Cl^-	0.486	0.525	0.538	0.623	0.408	1.196
HCO_3^-	0.002	0.002	0.002	0.002	0.002	–
SO_4^{2-}	0.024	0.024	0.024	–	0.072	–

oil is definitely also important. Pressure, temperature, and pore water and oil chemistry can all change wettability and can also influence oil production through dissolution and induced compaction.

The variations and combinations of the above processes are difficult to assess without a capable chemical model. The purpose of this article is to develop a geochemical model that couples aqueous and surface chemistry and use it to analyze the data now available. The next section presents experimental data that shows how aqueous chemistry affects oil recovery in imbibition experiments. Section 3 presents the chemical model. Section 4 shows that the model can predict surface potential and sulfate adsorption on calcite. Section 5 applies the surface potential model to oil wettability and shows that surface potential changes cannot explain the oil recovery data. Section 6 shows that calcite dissolution could explain the experimental data. The last two sections provide discussion and summarize the conclusions reached in the previous discussion.

2 Review of Experimental Data

The data to which we will compare our model in this article is from spontaneous imbibition experiments. All the experiments we summarize used Stevns Klint outcrop chalk from Denmark. This chalk is a relatively clean mainly calcite carbonate with a non-carbonate content lower than 0.2%. The specific surface area is 1.8 m^2/g (Hjuler 2007). The chalk porosity is 45–50% and the permeability is 2–5 mD. After being drilled to the correct size, the cores were dried at 90°C (Strand et al. 2006; Zhang et al. 2006, 2007; Zhang and Austad 2006) and 120°C (Karoussi and Hamouda 2007) until a constant weight was achieved. Before presenting the data, it is important to understand the way spontaneous imbibitions experiments are performed:

- In the initial water phase, the cores are put under vacuum and saturated with fluid. Strand et al. (2006), Zhang et al. (2006, 2007), and Zhang and Austad (2006) used brines with concentrations similar to the Ekofisk formation (EF; see Table 1). Karoussi and Hamouda (2007) used pure distilled water (DW), or DW with Na_2SO_4 or $MgCl_2$ added.

- The initial water is displaced by oil in a Hassler cell until a residual water saturation (S_{wr}) of 20–35% is reached.
- In a process called aging, the core is then left in a heated cabinet for a period of time to equilibrate the water with the oil and the rock. Strand et al. (2006), Zhang et al. (2006, 2007), and Zhang and Austad (2006) aged their cores for 4–5 weeks at 90°C . Karoussi and Hamouda (2007) aged their cores for 18 days at 90°C . These last two steps simulate the initial migration of oil into a reservoir.
- Different oils were used by different workers. Strand et al. (2006), Zhang et al. (2006, 2007), and Zhang and Austad (2006) used crude oil diluted with *n*-heptane. Increasing the amount of *n*-heptane lowers the concentration of polar components. The polar component content is quantified by the acid number. In Karoussi and Hamouda (2007), they used *n*-decane with a concentration of 0.005 M stearic acid (equivalent to an acid number of 0.3 mg KOH/g). Stearic acid promotes a very oil-wet surface (Thomas et al. 1993a,b).
- During the spontaneous imbibition phase of the experiment, the aqueous phase that entirely surrounds the core is spontaneously imbibed into the core and oil is expelled. The chemistry of the imbibed water affects the amount of oil that is produced (expelled from the core). This step simulates some of the processes involved in oil recovery.
- The production of oil in the spontaneous imbibition tests decreases to near zero after several weeks or months. When this occurs, the chemical parameters or the temperature of the system is usually changed. For example, the temperature is increased and/or the surrounding aqueous fluid is replaced with a fluid with a different chemical composition. When this is done the production of oil may increase. This is interpreted as a wettability change. The core is thought to have become more water-wet, and hence, more oil was expelled. The additional amount of oil expelled can be comparable to the amount expelled in the initial spontaneous imbibitions phase.

Tables 1, 2, 3, 4, and 5 summarize spontaneous imbibitions data. Table 1 gives the chemical composition of the brines in the later tables. Table 2 shows the oil recovery from cores aged with EF water at 90°C for 42 days and then invaded by seawater with variable amounts of Ca^{2+}. The spontaneous imbibition was at 70°C and the post-plateau change was to increase the temperature to 100°C . The table shows that except at 130°C , increasing Ca^{2+} in the imbibing water greatly increases the amount of oil recovered. The higher the Ca^{2+} concentration in the displacing brine the greater the oil recovery. Table 3 shows the percent oil recovery for oils with an acid number of 0.3 mg KOH/g aged with distilled water.

Cores 1–4 have been aged with distilled water, thus they should have a similar wettability. The imbibing waters were distilled water with either sulfate or magnesium ions added. The post-plateau changes involved heating in two steps of 30°C each. The recovery was substantially independent of the imbibing fluid composition, and the recovery for Mg^{2+} and SO_4^{2-} is very similar. The increase in recovery during post-plateau heating is almost entirely attributable to thermal expansion of the pore fluids. Cores 6–9 have been aged with different fluid chemistry. The cores aged with MgCl_2 is clearly much more oil-wet than cores aged with distilled water or $\mathrm{Na}_2\mathrm{SO}_4$. Later, we will show that this is consistent with changes in surface charge.

Table 4 shows that adding sulfate to the imbibing fluid increases the oil recovery dramatically. The chalk cores were aged with EF water, and the sulfate content varied from that of seawater as indicated. During the spontaneous imbibition experiment, temperature was kept constant at 110°C . Table 5 shows that the oil recovery is also greater when Mg^{2+} is in the imbibing fluid. The recovery increases quite strongly with increasing temperature. Some of this is due to thermal expansion of the pore fluids, but most is not. In order to summarize,

Table 2 Recovery factors and physical properties of the cores used in Zhang et al. (2007)

Core id	Porosity (%)	S_{wr} (%)	Aging Time (days)	Imb. Temp. (°C)	Imb. brine	Recovery (%)
CS2-1	47.6	20.4	42	70 → 100	SW w/4× Ca^{2+}	30.9 → 42.2
CS2-2	48.9	20.3	42	70 → 100	SW	23.8 → 34.8
CS2-3	48.5	22.4	42	70 → 100	SW u/Ca^{2+}	8.9 → 22.5
CS3-1	48.1	29.2	30	100 → 130	SW w/4× Ca^{2+}	29.4 → 39.8
CS3-2	48.9	27.2	30	100 → 130	SW	24.6 → 50.8
CS3-3	48.2	28.1	30	100 → 130	SW u/Ca^{2+}	22.5 → 45.1

All the cores were aged at 90°C, crude oil with acid number 2.07 mg KOH/g was used as the oil phase. The lengths of the cores were in the range 4.85–6.33 cm, and the diameter was in the range 3.51–3.55 cm. The composition of the brines used in the experiments can be found in Table 1

Table 3 Summary of the experimental results in Karoussi and Hamouda (2007)

Core id	Porosity (%)	S_{wr} (%)	Saturation fluid	Imb. fluid	Imb. Temp. (°C)	Recovery (%)
1	48.01	30	DW	DW	40 → 70 → 90	9 → 12 → 17
2	48.32	32	DW	0.03 M Na_2SO_4	40 → 70 → 90	9 → 15 → 20
3	49.74	32	DW	0.1 M Na_2SO_4	40 → 70 → 90	10 → 16 → 23
4	49.23	31	DW	0.06 M $MgCl_2$	40 → 70 → 90	13 → 18 → 23
5	48.1	33	DW	0.1 M $MgCl_2$	40 → 70 → 90	21 → 26 → 34
6	47.94	34	0.03 M Na_2SO_4	0.03 M Na_2SO_4	40 → 70 → 90	7 → 13 → 18
7	47.67	34	0.1 M Na_2SO_4	0.1 M Na_2SO_4	40 → 70 → 90	9 → 14 → 20
8	48.22	35	0.1 M $MgCl_2$	0.1 M $MgCl_2$	40 → 70 → 90	3 → 9 → 16
9	48.16	32	0.06 M $MgCl_2$	0.06 M $MgCl_2$	40 → 70 → 90	2 → 7 → 13

The cores were aged for 18 days

Table 4 Summary of some of the experimental data presented in Strand et al. (2006), temperature was 110°C during the experiment and saturation fluid was EF brine

Core id	Porosity (%)	PV (ml)	S_{wr} (%)	Imb. fluids (%)	Recovery (%)
5/1	48.2	19.2	28.1	SW u/SO_4^{2-} → SW → SW w/3× SO_4^{2-}	8 → 15 → 25
6/1	49.4	31.8	26.1	SW u/SO_4^{2-} → SW → SW w/3× SO_4^{2-}	8 → 13 → 23

The cores were aged for 4–5 weeks at 90°C

oil recovery by spontaneous imbibition increases with increasing solution concentration of SO_4^{2-}, Ca^{2+}, and Mg^{2+}, and also increases strongly with increasing temperature.

3 Chemical Model

At temperatures greater than about 70°C pore fluids in nature are generally in chemical equilibrium with the rock minerals they contact. Methods have been developed to calculate the chemical composition and pH of a fluid that is in equilibrium with a specified set of buffer

Table 5 Summary of some of the data in Zhang and Austad (2006). The authors state that they add Ca^{2+}or Mg^{2+}in a similar concentration as in SW

Core id	ϕ (%)	S_{wr} (%)	Imb brine	Imbibition Temperature	Recovery (%)
CM1	47.1	22.8	SW/uCa^{2+},Mg^{2+}	70 → 100°C	9 → 12
			add Mg^{2+}	100°C	32
				100 → 130°C	51.5
CM2	49.2	22.8	SW/uCa^{2+},Mg^{2+},SO_4^{2-}	70 → 100°C	9 → 12
			add Mg^{2+}	100°C	12 → 22
				100 → 130°C	26
CM3	47.6	21.2	SW/uCa^{2+},Mg^{2+},w/2×SO_4^{2-}	70 → 100°C	9 → 12
			add Ca^{2+}	100°C	24
				100 → 130°C	29
CM4	48.6	22.2	SW/uCa^{2+},Mg^{2+},w/4×SO_4^{2-}	70 → 100°C	9 → 12
			add Mg^{2+}	100°C	42
				100 → 130°C	61

We assume that 0.0445 M $MgCl_2$ or 0.013 M $CaCl_2$ is added, although this is not explicitly stated in the paper. All the cores were aged with 1.452 M NaCl brine as the aqueous phase, and crude oil with acid number 2.07 mg KOH/g. Aging time was 42 days at a temperature of 90°C . Lengths of the cores were in the range 5.9–6.25 cm, and diameter 3.57 cm

minerals at a specified temperature, pressure and chlorinity. Dissolution constants describe how each mineral dissolves to a minimum set of chemical basis species that fully describe (span) the solution composition. Dissolution log K for the mineral buffer set allows the ratio of the basis species activity to the H^+ activity (known as the activity ratios) to be determined. The hydrogen ion concentration (H^+) is determined by requiring charge balance, taking also into account the total chlorinity of the solution. Substituting the hydrogen ion activity into the activity ratios yields the equilibrium activity of each basis species. Knowing the disassociation log K for all solution complexes (secondary species) to the basis species allows the activity of all the ion solution complexes to be calculated. Activities are then converted to concentrations using the Debye Hückel equation (e.g., Bethke 1966, p. 109):

$$\log_{10} \gamma_i = -\frac{A\, Z_i^2 \sqrt{I_o}}{1 + B\, \text{å} \sqrt{I_o}}. \tag{1}$$

where A and B are solvent parameters that depends on temperature (Helgeson and Kirkham 1974b), å is an ion size parameter (∼ 3.5–9), Z_i is the valence of species i. γ_i is the activity coefficient, and is defined as the ratio between the activity and concentration of a species. I_o is the ionic strength of the solution:

$$I_o = \frac{1}{2} \sum_{i=1}^{N_b} Z_i^2\, m_i + \frac{1}{2} \sum_{i=1}^{N_c} Z_i^2\, n_i. \tag{2}$$

where m_i is the concentration of the basis species and n_i is the concentration of the aqueous complexes. N_b (N_c) is the number of basis species (aqueous complex; for the bulk solution chemistry $N_b = 9$, as discussed below). The full equilibrium chemical composition of the fluid in equilibrium with a specified set of buffer minerals at the specified pressure and temperature (including the concentrations of all individual basis species, all their complexes, and pH) can thus be calculated assuming only that the solution is in chemical equilibrium with a specified set of buffer minerals. An appropriate buffer is the partial pressure of a gas phase. Specifying the total solution concentration of a basis species (and all its complexes) is also a valid constraint that can be substituted for a buffer mineral.

This method of calculating solution composition has been developed and extensively tested over many years, first by Garrels (Garrels and Christ 1965) and then particularly by Helgeson and co-workers. We utilize an implementation of this method we call EqAlt (Cathles 2006). In our implementation, we determine the dissolution and dissociation constants from the HKF equation of state (Helgeson and Kirkham 1974a,b; Helgeson et al. 1981) using thermodynamic data in the SUPCRT database (Johnson et al. 1992). For a recent review of the HKF equation of state, see (Oelkers et al. 2009). In the chemical modeling, considered here, the basis species are H^+, Ca^{2+}, HCO_3^-, H_2O, Na^+, Cl^-, Mg^{2+}, SO_4^{2-}, K^+, and the solution chemistry is constrained by the total concentration of K^+, Na^+, Mg^{2+}, SO_4^{2-}, and Cl^- in the brine, an imposed partial pressure of CO_2, and the requirement that the solution is in equilibrium with calcite. If anhydrite becomes supersaturated, it is precipitated from the bulk solution until it is no longer supersaturated. The determination of solution composition described above is completely standard and the methods involved are described in many standard textbooks (e.g., Garrels and Christ 1965; Bethke 1966).

In the same way, as the ions make complexes in the bulk aqueous fluid, they can also make complexes at the solid surface that contacts the aqueous fluid. For example, sulfate can make a surface complex with calcium sites at the calcium carbonate mineral surface. Calculating the surface complexes requires that the magnitude and sign of the surface potential is known (in this study, we do not distinguish between surface or zeta potential). For a positively charged surface, the concentration of negative ions will follow a Boltzmann type of distribution. That is, the concentration will be high close to the surface and fall off exponential away from the surface. We follow the approach of Van Cappelen et al. (1993). For similar type of models, see Pokrovsky and Schott (1999, 2001, 2002), and Pokrovsky et al. (1999a,b). Our study differs from previous authors in that we predict the surface properties and complexes at the higher temperatures, pressures, and salinities that are found in petroleum reservoirs. We make the following assumptions:

(1) The dominant mineral is calcium carbonate ($CaCO_3$).
(2) There are 2 sites/(nm)^2 on the carbonate surface where surface complexes of $>CaH_2O^+$ and $>CO_3^-$ are present. These positive and negative surface complexes (the sign $>$ indicates that they are surface complexes) are present in equal number. The number of sites per unit area is usually taken to be 5 site/(nm)^2 (Davis and Kent 1990), but we find that 2 sites/(nm)^2 gives a much better fit with the experimental data, as discussed below. Note that calcium and carbonate at the surface share one of the electrons; this is why there is only one plus charge on calcium and one minus charge on carbonate.
(3) The thermodynamic equilibrium constants at the surface have the same temperature dependence as the equilibrium constants in the aqueous phase.

Clearly assumption 1 above can be relaxed and more minerals can be incorporated in the model. Assumption 3 is the most crucial one, and it is probably not 100% correct, but it should be close to being the case. At this stage, we are not seeking a perfect match with the experimental data, but are interested rather in determining if there are significant changes in surface charge and potential when temperature is changed that could affect the stability of the water film and oil wettability in the ways observed experimentally. As in the bulk solution chemistry, all of the other possible surface complexes can be expressed in terms of the two basis surface complexes, we selected above. For example,

$$\begin{aligned}
>\mathrm{CaCO_3^-} &\rightleftharpoons >\mathrm{CaH_2O^+} + \mathrm{HCO_3^-} - \mathrm{H^+} - \mathrm{H_2O},\\
>\mathrm{CaOH^0} &\rightleftharpoons >\mathrm{CaH_2O^+} - \mathrm{H^+},\\
>\mathrm{CaHCO_3^0} &\rightleftharpoons >\mathrm{CaH_2O^+} + \mathrm{HCO_3^-} - \mathrm{H_2O},\\
>\mathrm{CaSO_4^-} &\rightleftharpoons >\mathrm{CaH_2O^+} + \mathrm{SO_4^{2-}},\\
>\mathrm{CO_3H^0} &\rightleftharpoons >\mathrm{CO_3^-} + \mathrm{H^+},\\
>\mathrm{CO_3Ca^+} &\rightleftharpoons >\mathrm{CO_3^-} + \mathrm{Ca^{2+}},\\
>\mathrm{CO_3Mg^+} &\rightleftharpoons >\mathrm{CO_3^-} + \mathrm{Mg^{2+}}.
\end{aligned} \tag{3}$$

Each of these exchange reactions has a corresponding mass action equation from which an exchange log K can be defined. For example, for

$$>\mathrm{CaCO_3^-} \rightleftharpoons >\mathrm{CaH_2O^+} + \mathrm{HCO_3^-} - \mathrm{H^+} - \mathrm{H_2O}, \tag{4}$$

the mass action equation is:

$$\begin{aligned}
>\mathrm{CaCO_3^-} &\rightleftharpoons >\mathrm{CaH_2O^+} + \mathrm{HCO_3^-} - \mathrm{H^+} - \mathrm{H_2O},\\
K &= \frac{a_{>\mathrm{CaH_2O^+}}\, a_{\mathrm{HCO_3^-}}\, \exp\{F\,\psi/(R\,T)\}}{a_{>\mathrm{CaCO_3^-}}\, a_{\mathrm{H^+}}\, \exp\{-F\,\psi/(R\,T)\}},\\
\log_{10} K &= \log_{10} a_{>\mathrm{CaH_2O^+}} + \log_{10} a_{\mathrm{HCO_3^-}} - \log_{10} a_{\mathrm{H^+}},\\
&\quad + 2\frac{F\psi}{\ln 10\, R\,T} - \log_{10} a_{>\mathrm{CaCO_3^-}}.
\end{aligned} \tag{5}$$

Here, we have assumed the activity of water is 1, $F = 9.648456 \times 10^4$ C/mol is Faraday's constant, ψ the surface (or zeta) potential, $R = 8.314$ J/(K mol) the ideal gas constant, T is the absolute temperature. Note that the activity of the aqueous species is dependent on the surface potential. If the surface potential has a negative sign then positively charged ions will have a high activity close to the surface and vice versa. The activity coefficient for the aqueous complexes is taken to be equal to one, thus the concentration of the surface complexes is equal to the activity of the surface complex.

The surface potential is related to the surface charge by the Grahame equation (Israelachivili 1985):

$$\begin{aligned}
&2\varepsilon\,\varepsilon_0\,k_B\,T \sum_{i=1}^{N_b} m_i\,(\exp\{-Z_i\,F\,\psi/(R\,T)\} - 1)\\
&\quad + 2\varepsilon\,\varepsilon_0\,k_B\,T \sum_{i=1}^{N_c} n_i\,(\exp\{-Z_i\,F\,\psi/(R\,T)\} - 1) - \sigma^2 = 0,
\end{aligned} \tag{6}$$

where ε_0 is the dielectric constant of vacuum and ε is the dielectric constant of water, k_B is Boltzmann's constant, Z_i is the valence of the aqueous species ($Z_i = 0$ for the surface complexes), and ψ is the surface charge. m_i is the concentration of a basis species ($>\mathrm{CaH_2O^+}$and $>\mathrm{CO_3^-}$ are included in the basis set), and n_i is the concentration of the aqueous or surface complex (secondary species). σ is the sum of all the charged surface complexes,

$$\sigma = \frac{F}{S}\left(\sum_{i=1}^{N_b} Z_{sci}\, m_i + \sum_{i=1}^{N_c} Z_{sci}\, n_i\right). \tag{7}$$

where S is the surface area in m^2/l, the concentrations of the surface species are in mol/l, thus the surface charge has the correct dimension of C/m^2. Z_{sc} is the valence of a surface complex. Z_{sc} is zero for all the aqueous complexes, and Z is zero for all the surface complexes. N_b (N_c) is the number of basis species (aqueous and surface complex), respectively.

By adding a new basis species $\log_{10} E \equiv F\ \psi / \ln 10RT$ (and two surface basis species, $>CaH_2O^+$ and $>CO_3^-$), all aspects of the solution and surface chemistry can be computed by procedures identical to those used in solving for the bulk solution chemistry alone (now $N_b = 12$). The total concentrations, partial pressure of CO_2 and buffer minerals specify the theoretical equilibrium concentration of all species in solution and on the calcite surface and the bulk solution pH. The calculation procedure is as follows:

(1) Set the basis species to the total solution concentration of that species and all complex concentrations to zero.
(2) Find the activity ratios for all basis species subjected to the specified partial pressure of CO_2 and the total basis species concentration of the solution.
(3) Calculate the ionic strength of the solution, the activity coefficients of all basis species and complexes, at a specified pH.
(4) Find the pH that provides charge balance.
(5) Calculate the surface charge and determine the surface potential.
(6) Return to step 4 and iterate until the pH and surface charge change less than a specified amount.

At the end of this procedure, some minerals may be supersaturated or undersaturated. If this is the case one of the minerals, i.e., out of equilibrium with the solution may be selected and precipitated or dissolved in small stoichiometric increments until it is in equilibrium with the solution. Here, we remove only anhydrite and ignore other supersaturated minerals. However, in general, if other minerals remain supersaturated after anhydrite is removed, they could in turn be similarly titrated. When a supersaturated mineral is precipitated, we keep P_{CO_2} and calcite as buffers for $Ca^{2+}$and HCO_3^-, and also maintain the total solution composition constraints. The buffers allow the total concentration of basis species to change. In addition, the distribution of species among solution and surface complexes and pH may also change.

In order to summarize, the procedure for titrating out a mineral is:

(1) Calculate the equilibrium chemistry.
(2) Pick a mineral such as anhydrite to be titrated and remove small stoichiometric quantities of calcium and sulfate until the solution is in equilibrium with anhydrite.
(3) For each step, where calcium and sulfate are removed, the ionic strength, surface charge, surface potential, and activity coefficients are updated.

4 Comparison of Model Predictions of Surface Chemistry to Experimental Data

Figure 1 compares the zeta potential, we calculate for calcite surrounded by a 0.005 M NaCl brine that is in equilibrium with CO_2 gas at various pressures to zeta potential measurements made by Thompson and Pownall (1989) for an experiment of identical design. The higher the CO_2 pressure the lower the pH. There is a good match between the experimental data and the model, especially considering that we have made no attempt to fit the model to the data. We use the $\log_{10}$ K values as in Van Cappelen et al. (1993), and the theoretical curve is completely specified by the CO_2 partial pressure and the requirement that the solution should be in equilibrium with calcite.

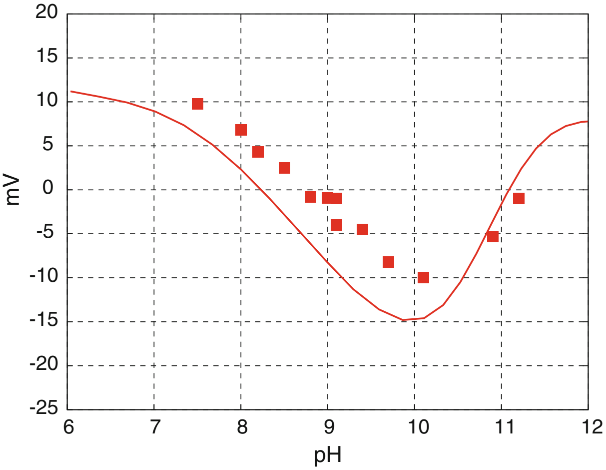


Fig. 1 Variation in the surface (or zeta) potential of calcite in a 0.005 M NaCl brine at 25° C subjected to various partial pressures of CO_2 gas (which changes the pH of the solution). The squares show the experimentally measured zeta potential (Thompson and Pownall 1989), and the solid line is our prediction

In Fig. 2, we compare our model to an experiment performed by Zhang and Austad (2006) and Zhang (2006) in which $MgCl_2$ or Na_2SO_4 was added to a 0.573 M NaCl brine in contact with powdered Stevns Klint chalk core. In the experiment, the pH was maintained at 8.4 by exposing the solution to the partial pressure of CO_2 required to impose this pH and also adding acid and base as needed. The points in Fig. 2 show how the measured surface (zeta) potential varies as the solution composition is changed. The solid lines show the zeta potential, we predict for these conditions. The addition of SO_4^{2-} ions gives the carbonate surface a negative surface potential. The addition of Mg^{2+} ions gives the surface a positive surface potential. The partial pressure required to produce a pH of 8.4 in our calculations was $10^{-3.5}$ bars. The fit between our calculated zeta potentials and those measured experimentally is again excellent, especially considering that the theoretical curves are calculated without any fitting from thermodynamic data.

Figure 3 shows the calculated concentrations of the main surface complexes on a calcite surface submerged in seawater in equilibrium with an atmosphere of CO_2 with $P_{CO_2} = 10^{-3.5}$ and various temperatures, assuming 2 sites/(nm)^2 of calcite surface for $>CaH_2O^+$ and $>CO_3^-$. As temperature is increased, the divalent ions adsorb more strongly to the surface. The interaction with H^+, CO_3^{2-}, and HCO_3^- with the surface is of minor importance because their concentration in "seawater-like" brines is lower than the concentration of the divalent ions, such as Ca^{2+}, Mg^{2+}, and SO_4^{2-}.

We can relate the calculated adsorption of sulfate to the adsorption of sulfate in flooding experiments where it has been measured (Strand et al. 2006). Assuming that a surface area of chalk of 2 m^2/g, we can translate the measured total absorption to the adsorption in μ mol per m^2, and compare the temperature dependence of this adsorption with our model calculations. The results are shown in Fig. 4. This figure shows that a surface site density of 2 sites/(nm)^2 gives a good match to the experimental data. At the highest temperature, there is a large discrepancy between the predicted adsorption and the measured adsorption. However, in the experiment, only the loss of sulfate is recorded. This loss might be due to not only adsorption but also precipitation of sulfate bearing minerals, such as anhydrite. From the

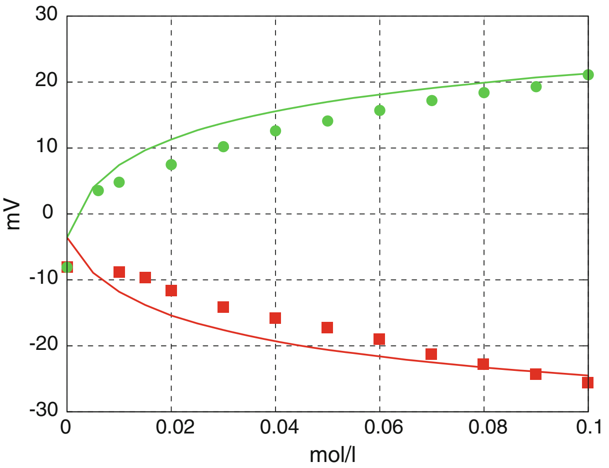
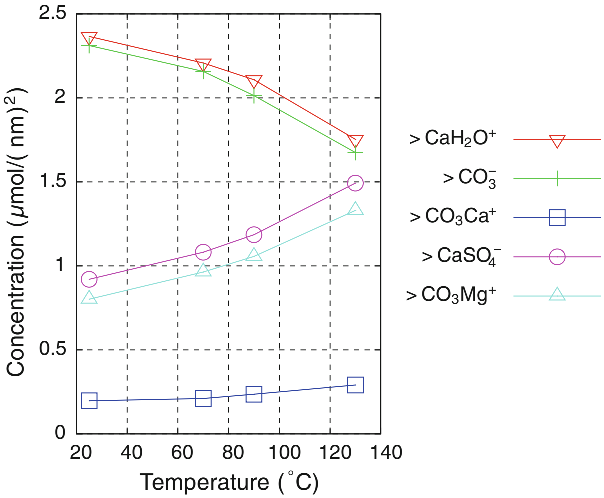


Fig. 2 Zeta potential measured by Zhang and Austad (2006); Zhang (2006) (points) as $MgCl_2$ or Na_2SO_4 was added in steps to a solution of 0.573 M NaCl brine in contact with 4 wt% milled chalk powder and subjected to a partial pressure of CO_2 that maintains the pH at 8.4. The surface (zeta) potential that we calculate for similar conditions is shown by solid lines. 2 sites/(nm)^2 of calcite surface for $>CaH_2O^+$ and $>CO_3^-$ is assumed. The top (*circles*) curve and data points is for Mg additions; the bottom (*squares*) curve and data points is for sulfate additions

Fig. 3 The concentration of the main surface complexes at four different temperatures, 25, 70, 90, and 130°C for seawater in equilibrium with calcite at $P_{CO_2} = 10^{-3.5}$ bars. As the temperature increases, the divalent ions adsorb more strongly to the surface



experimental curves in Strand et al. (2006), one can clearly show that at 130°C, the sulfate concentration never rises to the injected concentration. This suggests an additional sulfate loss due to precipitation. In Fig. 4, we have calculated the contribution to the loss of sulfate due to precipitation of anhydrite and added it to the sulfate adsorption. If sulfate precipitation as anhydrite is taken into account, the calculated “adsorption” gives a much better fit to the measured data (triangular points).

Figures 1, 2, 3, and 4 show that our coupled bulk and surface chemistry model can predict the surface potential of, and the sulfate (and presumably other ions) adsorption to, calcite very well. The predicted surface potential of calcite as a function of pH when Mg^{2+} and

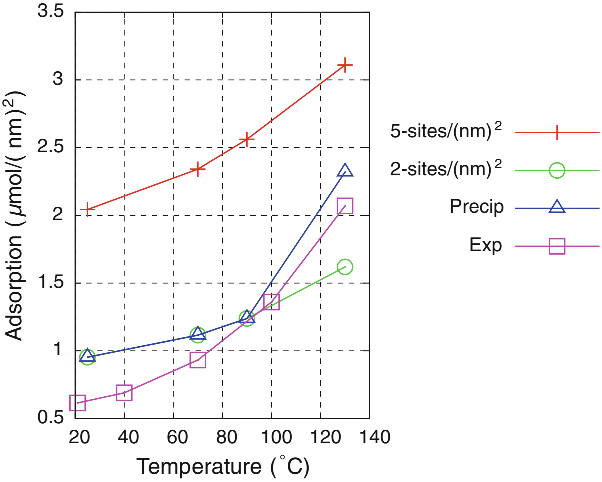


Fig. 4 Adsorption of sulfate on calcite in μmol/m^2 measured as a function of temperature by Strand et al. (2006) compared to our calculated adsorption for 2 sites /(nm)^2 and 5 sites/(nm)^2. The additional loss of sulfate due to precipitation of anhydrite is shown at 130°C (*blue line* and *triangular points*)

SO_4^{2-} are added to solution, all fit the experimental data very well without any modification of standard thermodynamic data or model modifications of any kind.

5 Application to Wettability

We have a model that combines bulk solution and surface chemistry and can predict the zeta (surface) potential and sulfate adsorption to calcite with remarkable accuracy. The next step is to determine what this implies for the stability of water film and thus the adsorption of polar oil components.

As discussed above, the ability of the oil phase to collapse the water film and adhere to the surface depends on the pressure in the oil phase relative to the water phase which is equal to the disjoining pressure (for a locally flat surface). The disjoining pressure consists of two terms. One term describes the attractive van der Waals forces, and the other term the double layer forces. The double layer forces are strongly dependent on the surface potential and the ionic strength of the solution. In the weak overlap approximation, the formula for the disjoining pressure is (Israelachivili 1985):

$$P(D) = -\left(\frac{A}{10^{-20}}\right) \cdot \frac{10^7}{6\pi D^3} + 1.12 \cdot 10^6 \frac{I_o}{T} \psi_{\text{oil}} \psi_{\text{rock}} \exp\{-\kappa D\} \text{ (Pa)}, \quad \text{where:}$$

$$\kappa = 56.2\sqrt{\frac{I_o}{T}} (\text{nm})^{-1}, \quad A = \text{Hamaker constant}\,(5 \cdot 10^{-19}\,J), \tag{8}$$

where D is the thickness of the water film, A is the Hamaker constant. This formula assumes the surface potential to be expressed in mV, temperature in K, and D in nm. I_o is the ionic strength of the solution, and defined in Eq. 2. If the surface potential for oil and water has an opposite sign, then the water film will collapse immediately.

By combining the above expression for disjoining pressure with our chemical model, we can analyze the experiments performed by Karoussi and Hamouda (2007) that we summarized in Sect. 2. For example, we can calculate the surface charge of the oil by assuming that the surface of the oil is covered by fatty acid. The typical area of a surfactant head group is 0.70 nm^2 (Israelachivili 1985). Each fatty acid contributes one unit of electrical charge.

Table 6 Surface potentials calculated for calcite for various solutions at 90° C

Solution	Surface potential (mV)	Surface potential of oil (mV)
Distilled water	−7.9	−166
0.1 M Na_2SO_4	−63	−118
0.03 M Na_2SO_4	−49	−154
0.1 M $MgCl_2$	46	–
0.03 M $MgCl_2$	43	–

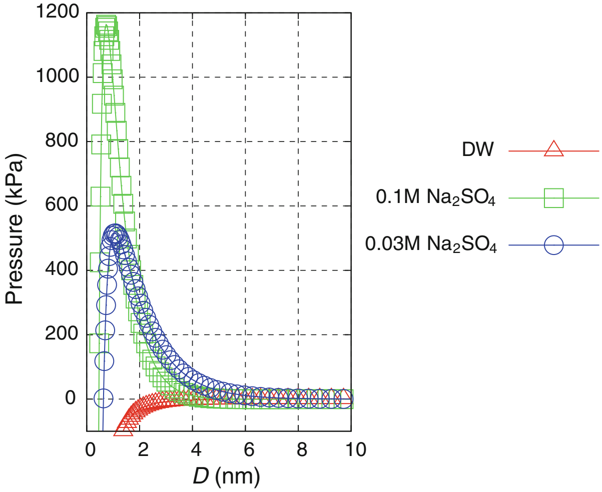


Fig. 5 Disjoining pressure as a function of distance from the calcite surface calculated by our model at 90°C (the temperature used during aging) for the solution compositions given in Table 6

Hence,

$$-1.602 \times 10^{-19}\,C/0.70\,\mathrm{nm}^2 = -0.22\,C/\mathrm{m}^2. \quad (9)$$

Notice that the oil has a negative surface potential. If the calcite surface has a negative surface potential, its water film will be stable and it will be water wet. If, however, the calcite surface potential is positive, the water film will collapse immediately and the surface will be oil wet. The surface potentials we calculate for distilled water and distilled water with addition of Na_2SO_4 and $MgCl_2$ are shown in Table 6.

From these surface potentials, we can calculate the disjoining pressure using Eq. 8, with the results shown in Fig. 5. The value for the surface potential of oil is found by solving Eq. 6 with the value in Eq. 9 as input. The results are listed in the last column in Table 6. Note that the surface potential of oil is not listed for the $MgCl_2$ solutions because they give the carbonate surface a positive potential and the surface is, therefore, oil wet.

Aging a core with a pore fluid containing Na_2SO_4 gives the chalk surface a negative surface charge. Figure 5 shows that the disjoining pressure in this circumstance is such that the oil pressure needs to exceed the water pressure by more than 10 bars for 0.1 M Na_2SO_4 or 5 bars for 0.03 M Na_2SO_4 to collapse the water film. If, on the other hand, $MgCl_2$ is the aging fluid no stable water film is possible because the surface has a positive charge which would immediately collapse any water film. Thus, we can understand why aging the core with waters containing Na_2SO_4 makes the core more water wet and promotes more oil recovery (during spontaneous water imbibition). The same also holds for $MgCl_2$ in the water *during* *aging*, a positive surface charge will promote film collapse and make the core more oil wet (Core 8 and 9 in Table 3). However, during the spontaneous imbibition process, magnesium in the water that enters the core increases the oil recovery, see Table 5. If surface charge controls this process, the effect should be just the opposite.

Aging with distilled water gives the chalk surface a negative charge, but as shown in Fig. 5 the oil pressure needed to displace water is almost three orders of magnitude smaller than in the Na_2SO_4 case. Thus, it is not obvious why cores aged with distilled water should imbibe water as effectively as cores aged with 0.1 M Na_2SO_4. It is possible that (1) the formula in Eq. 8, derived for small double layers, is not completely valid for distilled water, (2) the distilled water case has such large double layers that disjoining pressure is overridden, (3) salt present in the brine could change the surface charge of oil and render the estimated value in Eq. 9 invalid, and (4) the polar components could be packed closer in the presence of positive ions. However, we think these disqualifications of the model predictions are unlikely.

Finally, the predicted temperature dependence of the surface charge does not follow the temperature dependence of the oil recovery that is observed in spontaneous imbibition experiments. As summarized in Sect. 2, oil recovery increases strongly with increasing temperature. Using our chemical model, we can predict the temperature dependence of surface charge for seawater (SW), Ekofisk formation brine (EF), distilled water (DW), and a 1:1 mix of SW and EF brine (Mix). The results are shown in Fig. 6. It is important to remember that during a spontaneous imbibition, there is initially a significant amount of formation water in the core. When seawater enters the core, it will mix with this formation water. Thus, if the aging water was distilled water and the imbibing water seawater, the surface potential of the pore surface will lie between distilled water and seawater. Figure 6 shows that both distilled water and seawater have a roughly linear and relatively flat temperature dependence. The surface potential for distilled water is slightly negative and decreases slightly with increasing temperature. The surface potential for seawater is slightly positive and increases slightly with temperature. The surface potential of Ekofisk brine increases fairly strongly with temperature, but a 50/50 mix with seawater increases much less strongly. Therefore, regardless of the imbibing fluid chemistry, oil recovery should not have the strong temperature dependence observed if surface potential changes are the cause of changes in recovery in experiments (Strand et al. 2006; Zhang et al. 2006, 2007; Zhang and Austad 2006).

6 Enhanced Oil Production Caused by Mineral Precipitation and Dissolution

Changes in solution chemistry do not change the surface potential of carbonate in a fashion that can explain how these changes increase oil recovery in spontaneously imbibition experiments. Can other mechanisms be identified which could explain the experimental imbibition data? We think the answer to this question is yes. A good candidate is carbonate dissolution.

We found in our chemical modeling that dissolution of calcite will take place in the temperature range where enhanced imbibition is observed. At low temperature, seawater is in equilibrium with calcite, but at higher temperature calcium in the seawater reacts with sulfate and anhydrite is precipitated. When anhydrite is formed the aqueous phase loses calcium, and calcium has to be supplied from the rock for the solution to remain in equilibrium with calcite. The source of Ca^{2+} ions must be calcite dissolution. If the calcite dissolution takes place where the oil is adsorbed, then the oil can be liberated from the rock. The dissolution mechanism is illustrated in Fig. 7.

When seawater (or "seawater-like" brines) is spontaneously imbibed, oil is expelled. Water flows into and oil out of the core. The amount of seawater that enters equals the amount of

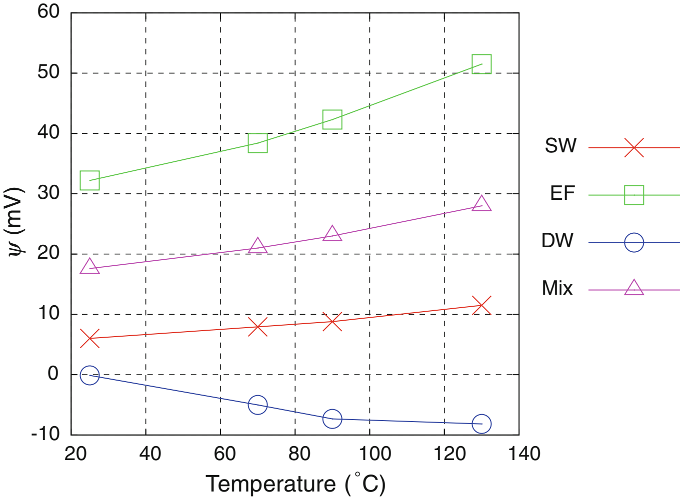


Fig. 6 Predicted surface potential for seawater (SW), Ekofisk formation brine (EF), and distilled water (DW), and a 1:1 mix of SW and EF brine (Mix). The calculations assume equilibrium between aqueous phase, $CaCO_3$(s)and CO_2(g), with $P_{CO_2} = 10^{-3.5}$

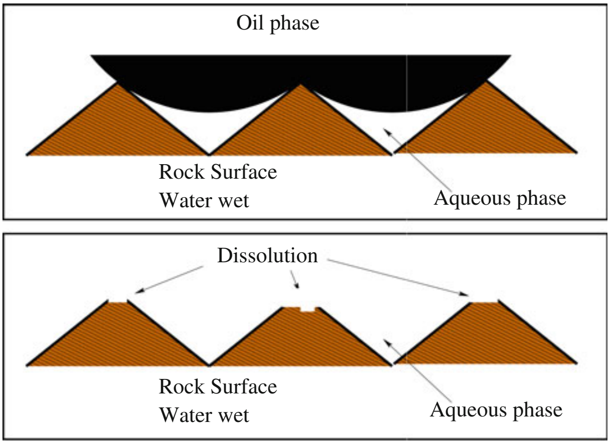


Fig. 7 *Top*: A section of the pore space, before any dissolution reaction. The surface is rough and oil is attached where there is a large curvature and the water film is broken. *Bottom*: Dissolution of the chalk surface has taken place where the oil was attached, and new water-wet rock surface has been created

oil expelled (or produced). When water enters the core it will mix with the formation water present there. For simplicity, we assume that the aqueous phase concentration everywhere inside the core is a mix between the original amount of formation water and the amount of seawater that has entered the core. We can calculate the consequences of this mixing for anhydrite stability using EqAlt. When we do this for the experiments summarized in Table 2, we find that the mixing causes anhydrite to become supersaturated at temperatures used in the experiments. We calculate the amount of anhydrite that will be precipitated, and if we assume that the calcium precipitated with the sulfate is replaced by calcite dissolution, we can calculate the amount of calcite dissolution that will occur in the core as a consequence

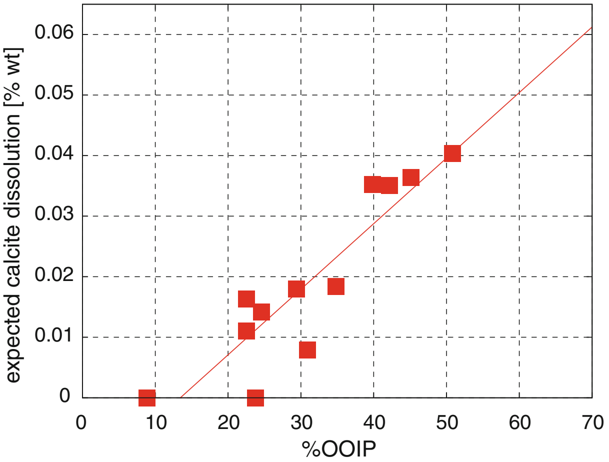


Fig. 8 Calculation of the expected dissolution of calcium carbonate, and plotted against the oil recovery. The data are taken from the six imbibition experiments reported in Table 2. %OOIP is the percent of oil in place that is produced. The expected calcite dissolution is calculated by assuming that the aqueous phase concentration everywhere inside the core is a mix between the original amount of formation water and the amount of brine that has entered the core. Calcite dissolution is expressed as a mass fraction of the original calcite. The line is a regression line

of imbibition (oil expulsion). We use the data for core CS2-1, CS2-2, CS2-3, CS3-1, CS3-2, and CS3-3 in Table 2. The results of this calculation are shown in Fig. 8. It should be noted that the experimental points in Fig. 8 are taken from three different temperatures (70, 90, and 130°C). Figure 8 shows that the mass fraction of calcite dissolved from the core correlates linearly with the produced oil in Zhang et al. (2006). This permits the conclusion that the extra oil production that is observed when seawater is the imbibing fluid may be related to the dissolution of calcite caused by this imbibition. It has been observed in experiments that organic matter attached to a mineral surface enhances the calcite dissolution rate (Stumm 1992, p. 162; Pokrovsky and Schott 2001). Thus, there are reasons to suspect that the calcite dissolution preferentially takes place where the oil is adsorbed. Particularly in this context, the amount of calcite dissolved when seawater enters a chalk formation is quite significant, and liberation of a substantial amount of oil by this mechanism is highly plausible. Moreover, more precipitation of anhydrite will occur at higher temperature, and, therefore, this mechanism for increasing oil production could have the temperature dependence that is observed in experiments.

Finally, as summarized in Sect. 2, magnesium clearly impacts the spontaneous imbibition of water into chalk (Zhang and Austad 2006). The role of magnesium in precipitation and dissolution of calcite is an area of extensive research (for a review, see Morse et al. (2007)), but again it appears that the enhanced oil recovery that is observed, when magnesium is present in the imbibing fluid may be related to the dissolution of calcite. While performing mechanical experiments on Liège chalk at 130°C (an outcrop chalk with mineralogy not very different to that of Stevns Klint) in a case where only magnesium chloride was present in the injected brine, we noted that a large amount of extra calcium was produced, and there was also a significant loss of magnesium (Madland et al. 2009). The loss of magnesium and production of calcium at the outlet could be accounted for if a magnesium-bearing mineral precipitated and calcite dissolved in the core. Modeling the experiments of

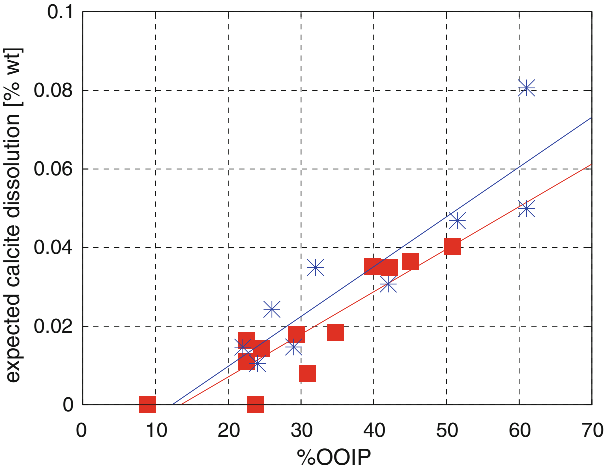


Fig. 9 Calculated dissolution of calcium carbonate in the experiments reported in Table 5 (*star shaped points*). For simplicity, the data points in Fig. 8 are reproduced (*square shaped points*). *Axis labels* are as described in Fig. 8. The expected calcite dissolution is calculated by assuming that the aqueous phase concentration everywhere inside the core is a mix between the original amount of formation water and the amount of brine that has entered the core. This line is a regression line

Madland et al. (2009) using the EqAlt program, we found that huntite ($CaMg_3(CO_3)_4$) was the most super-saturated mineral.

In the present case, we can account for the formation of magnesium-bearing minerals inside the core by setting huntite as a buffer mineral (in addition to CO_2, and calcite). The calculations have been be done in a similar fashion as when calculating the results shown in Fig. 8. Calculating the solution chemistry with huntite, calcite, and CO_2 as the buffer minerals and using the composition of the brines and temperatures as reported in Table 5 gives the results shown in Fig. 9 (star shaped points). Note that the cores in Table 5 were aged with sodium chloride brines, and we expected those cores to have a slightly different initial wettability than the cores in Table 2 (Fig. 8). In both cases (the experiments reported in Tables 2 and 5), the calcite dissolution was a consequence of magnesium and/or sulfate bearing mineral precipitation inside the core.

7 Discussion

The results presented ignore changes in the chemistry of the the oil phase. Ions in the solution can influence the concentration of charged oil components at the oil-water interface. This could lead to an increase or decrease in the surface charge of oil. In addition, ions can make complexes with the polar part of the oil components, and this could change the solubility of the polar oil components in the oil phase.

During aging, there is a high capillary pressure, and the oil is pushed toward the solid surface. During imbibition, the capillary pressure is reduced to very near zero. The curvature of the oil-water interface reverses. As the surface charge of the calcite surface is positive and the oil-water interface negative, there is a significant negative disjoining pressure that will tend to hold the oil-water interface close to the surface. When the formation water is *partly* replaced by seawater, the surface charge will become less positive and the disjoining pressure will have a slightly less negative value. This osmotic pressure change could also be a driving force for removing oil components from the surface. We have suggested that the process of removing oil components depends on the calcite surface being thermodynamically unstable, i.e., dissolution (see Figs. 8 and 9). Otherwise, it is very hard to understand why addition of positively charged ions, such as calcium and magnesium, to the invading brine will increase the oil recovery (as reported in Tables 2 and 5).

There are some inconsistencies in the experimental data in Table 2 that could be instructive: an increase in the calcium concentration below 100°C gives an enhanced recovery, but above 100°C the effect is reversed. These inconsistencies could be due to transport effects. When a "seawater-like" brine is spontaneously imbibed into the core at 70°C (core CS2-1, CS2-2, and CS2-3), sulfate is introduced to a large part of the core. And, when temperature is increased to 100°C, sulfate can precipitate as anhydrite and lead to a dissolution. However, when water is spontaneously imbibed into the core at a high temperature (100°C), the brines with a high calcium concentration can lose sulfate as anhydrite before the brine enters the core or very close to the border of the core. In this case, the impact of anhydrite precipitation would be reduced.

In order to investigate the effect of dissolution of calcite on the rock wettability, a coupled core scale model needs to be developed. The core scale model can address where the dissolution inside the core takes place, and link this dissolution to a corresponding change in relative permeability and capillary pressure. We are in the process of developing such a model.

8 Conclusions

Many experiments demonstrate that small changes in water chemistry cause large changes in the way oil displaces water and in the way water displaces oil when it is imbibed. Here, we have used a chemical model that couples bulk solution and surface chemistry to address the causes of these changes. Our analysis is restricted to a solid surface of (calcium) carbonate, but our methods can be extended to incorporate other minerals. We find that pore water chemistry can control how calcite is wet by oil. A negatively charged mineral surface promotes a more water-wet surface, when the oil is negatively charged. Whereas a positively charged mineral surface promotes a more oil-wet surface.

However, it is unlikely that the surface charge dependence of disjoining pressure can be responsible for forcing the desorption of adsorbed oil during water imbibition. This is because this process predicts that the addition of positively charged major ions will promote oil wetting, and the water wetting (i.e., negative surface charge) calculated for negative ions (e.g., SO_4^{2-}) does not have the strong temperature dependence observed in imbibition experiments. On the other hand, the dissolution of calcite could increase water wetness, and this process has the right temperature dependence. The amount of calcite dissolved appears sufficient to account for the extra oil production, especially if, as expected, the calcite is preferentially dissolved exactly where the oil wets the calcite. Our purpose in this article was to develop a chemical model that couples bulk aqueous and surface chemistry, and show how it is useful in analyzing the very complex relationships between oil and water wetting that are fundamental to oil recovery. We have certainly not addressed all the issues such modeling must ultimately address. No single paper could. However, we hope, we have succeeded in showing that coupled models can be useful, and that this demonstration will encourage further developments of such models. It is our strong conviction that without capable integrated models of the kind presented here, it will be impossible to understand the complex

Table 7 Nomenclature

m	Concentration of basis species (mol/l)
n	Concentration of complex (mol/l)
Z_i	Valence of aqueous species
$Z_{\mathrm{sc}i}$	Valence of surface species
I_o	Ionic strength (mol/l)
T	Temperature (K)
ψ	Surface potential (V)
σ	Surface charge (C/m^2)
>	Prefix for surface species
F	Faradays constant (96484.56 C/mol)
R	Ideal gas constant (8.314 J/K mol)
S	Specific surface area (m^2/l)
D	Water film thickness (nm)
A	Hamaker constant (5×10^{-19} J)
κ^{-1}	Debye length (nm)

Table 8 Surface reactions and corresponding equilibrium constants at various temperatures and pressure 8 bar

Reaction	T=25°C	T=70°C	T=90°C	T=130°C
$>CaCO_3^- \rightleftharpoons >CaH_2O^+ + HCO_3^- - H^+ - H_2O$	7.01	6.34	6.08	5.65
$>CaOH^0 \rightleftharpoons >CaH_2O^+ - H^+$	12.9	11	10.48	9.76
$>CaHCO_3^0 \rightleftharpoons >CaH_2O^+ + HCO_3^- - H_2O$	−1.04	−1.2	−1.34	−1.68
$>CaSO_4^- \rightleftharpoons >CaH_2O^+ + SO_4^{2-}$	−2.1	−2.29	−2.44	−2.78
$>CO_3H^0 \rightleftharpoons >CO_3^- + H^+$	−4.9	−4.7	−4.89	−5.48
$>CO_3Ca^+ \rightleftharpoons >CO_3^- + Ca^{2+}$	−1.74	−1.9	−2.04	−2.38
$>CO_3Mg^+ \rightleftharpoons >CO_3^- + Mg^{2+}$	−1.73	−1.93	−2.06	−2.41

The temperature dependence has been calculated with EQAlt (Cathles 2006), the values for the equilibrium constants at room temperature, are similar to the ones used by Van Cappelen et al. (1993), Pokrovsky and Schott (1999, 2001, 2002), and Pokrovsky et al. (1999a,b)

relationships between chemistry and wettability that have been documented by a host of published chemical experiments.

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Appendix: Equilibrium Constants

As stated earlier, we assume that the temperature and pressure dependence of the surface complexes follows the same dependence as the aqueous complexes. The temperature dependence has been calculated with EqAlt (Cathles 2006). In Table 8, we list the values for the equilibrium concentration of each of the surface complexes.

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