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A CHEMICAL MODEL FOR THE SEAWATER-CO₂-CARBONATE SYSTEM – AQUEOUS AND SURFACE CHEMISTRY

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ABSTRACT

We present a chemical model of the aqueous and surface chemistry of a calcium carbonate rock in equilibrium with a brine and CO₂(g). The predicted surface chemistry match zeta potential measurements reported in the literature. We calculate the surface charge and potential of a rock in equilibrium with high salinity brines, such as seawater and Ekofisk formation water in the temperature range 25-130°C. We show that a calcium carbonate (chalk) core exposed to seawater at high temperature will experience dissolution and mineralogical change. Experiments performed on Stevns Klint chalk (which is a very clean chalk with a high content of calcium carbonate) show a significant water weakening effect when exposed to seawater at high temperatures. These cores also behave more water wet at high temperatures. From our calculations, we find no clear evidence that the explanation for these experiments could be due to changes in surface potential or charge, simply because the temperature dependence in the surface potential is too weak. Instead we find that dissolution of calcite have the right temperature dependence. We therefore suggest that a dissolution process inside the core could explain the experimental results. We present calculations that show a nice correlation between the oil produced in six imbibition experiments, and the calculated amount of dissolved calcium inside the core.

INTRODUCTION

During the last decade it has become more and more evident that the water chemistry has an impact on the final oil recovery (Lager, Webb et al. 2006; Schembre, Tang et al. 2006; Zhang, Xie et al. 2007). The extra increase in oil recovery due to the water composition has been interpreted as a change in wettability. Experiments performed on outcrop chalk cores a small changes in the concentration of divalent ions has shown to increase production of oil in imbibition experiments dramatically (Strand 2005; Zhang 2006).

The aqueous chemistry also impact the rock mechanical strength, flooding outcrop chalk cores with brines of different composition gives a different hydrostatic yield point (Korsnes 2007). Lowering the hydrostatic yield point of a material could lead to an

enhanced subsidence, this would of course be positive for oil production, but it can also lead to well instabilities. The observed effect in rock mechanical experiments has much in common with the wettability change observed in imbibition experiments. Imbibition of seawater into Stevns Klint (chalk) cores, enhance production of oil at elevated temperatures (70-130°C). Hydrostatic tests on the same type of outcrop chalk cores, gives a lower hydrostatic yield point with seawater compared with fresh water. Similar experiments have been performed on Rørdal chalk, this is a chalk with slightly different mineralogy than Stevns Klint (Rørdal has a higher content of silica). The Rørdal core material is difficult to make oil wet and also no significant effect on the rock mechanical strength is observed when different brines are used in rock mechanical tests (unpublished work performed at University of Stavanger (UiS)).

When there is a large effect on the oil recovery or the rock mechanical strength by changing the concentration of individual ions in the solution, there must be a great potential for improving the process. This clearly calls for a modelling effort where the individual ions are incorporated into a chemical model. In addition, when discussing the effect of water chemistry on oil recovery or rock mechanical strength, the mineralogy of the core should be specified. In this paper we will focus on the calcium carbonate chemistry, both the chemistry of the fluid in contact with this type of carbonate and the surface chemistry. Thus, the results we present in this paper will not be applicable to all type of reservoirs, but rather those who mainly are controlled by the calcium carbonate chemistry. The results of the modelling will be compared to experiments performed on Stevns Klint outcrop.

The outline of the paper is as follows, first we present the chemical model, and then we compare our calculations to measured zeta potential. Then we discuss how to interpret our results in light of experiments performed on Stevns Klint outcrop.

CHEMICAL MODELLING

The chemistry of high salinity brines, such as seawater and formation waters are different from the chemistry of low salinity brines such as the water in lakes and rivers. The main reason for this is that ions make complexes, this has the effect that calcite is much more soluble in seawater compared to distilled water. By changing the concentration of individual ions in the brine, there will be a reshuffling of all the complexes and calcite can be more or less soluble depending on the type of salt in the brine. In addition minerals can be under or super saturated, which would lead to a change in the porous texture. This change in porous texture might very well lead to water weakening effect or even wettability change. We follow the standard approach described in e.g. (Garrels and Christ 1965). The value of the equilibrium and dissociation constants are evaluated using the HKF equation of state (Helgeson and Kirkham 1974; Helgeson and Kirkham 1974; Helgeson, Kirkham et al. 1981) and the SUPCRT thermodynamic data (Johnson, Oelkers et al. 1992), these are calculated by the use of EQAL (Cathles 2006). In the following we will first review the basic equations describing the aqueous chemistry and then review how to incorporate the surface chemistry in the total chemical picture.

AQUEOUS CHEMISTRY

In order to have a simple mathematical description of the chemical reactions in seawater we need to choose a set of basis species, we will choose the following ions: H^+ , Ca^{2+} , HCO_3^- , H_2O , Na^+ , Cl^- , Mg^{2+} , SO_4^{2-} and K^+ . This set could of course be expanded, but these are the main ions that normally exist in seawater. The complexes that can be formed in the aqueous phase will then be linear combinations of the basis set above, e.g.:



For each of the reactions above there is a corresponding law of mass actions with a known dissociation constant.

$$A \rightleftharpoons B + C \Leftrightarrow K = \frac{a_B a_C}{a_A}. \tag{2}$$

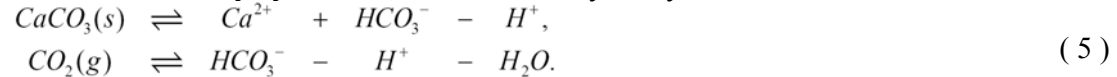
The activities are related to the concentrations in the following way:

$$a_i = m_i \gamma_i \text{ and } \log_{10} \gamma_i = \frac{Z_i^2 A(T) \sqrt{I_o}}{1 + a B(T) \sqrt{I_o}}, \tag{3}$$

m_i is the molar concentration of ion i , γ_i is the corresponding activity coefficient, and A and B are functions that depend on the temperature (Helgeson, Kirkham et al. 1981). Z_i is the charge of the i 'th species and I_o is the ionic strength:

$$I_o = \frac{1}{2} \sum_i Z_i^2 m_i. \tag{4}$$

In this work we only consider the buffer mineral $CaCO_3$ and gaseous CO_2 , with a given partial pressure. This means that once the pH is fixed the concentration of HCO_3^- and Ca^{2+} is determined solely by a buffer, and can not vary freely:



The pH is determined by charge balance:

$$\sum_{i \in \text{species}} Z_i m_i = 0. \tag{6}$$

In order to know which minerals are super or undersaturated, we need to know the concentration of the reactive part of the ions. To clarify things a bit, we can take a closer look at sulphate. Sulphate in solution will make a complex with positively charged ions in the solution: Na^+ , Ca^{2+} , Mg^{2+} , etc. The free part of the sulphate concentration that can react with calcium to make anhydrite (or another sulphate bearing mineral), is not the total concentration of sulphate in solution but:

$$m_{SO_4^{2-}} = m_{SO_4^{2-}}^{Tot} - m_{CaSO_4^0} - m_{MgSO_4^0} - m_{NaSO_4^-} - \dots - m_{\text{surface}}. \tag{7}$$

To summarize, the Ca^{2+} and HCO_3^- concentration is determined by the mineral $CaCO_3(s)$ and the partial pressure (activity) of CO_2 . For each of the other ions in the brine there is a

corresponding mass conservation equation of the type in equation (7). In addition the concentration of H^+ (pH) is determined by charge balance. The equations are quite involved, but this way of attacking the problem is well known and described in standard text books, such as (Garrels and Christ 1965).

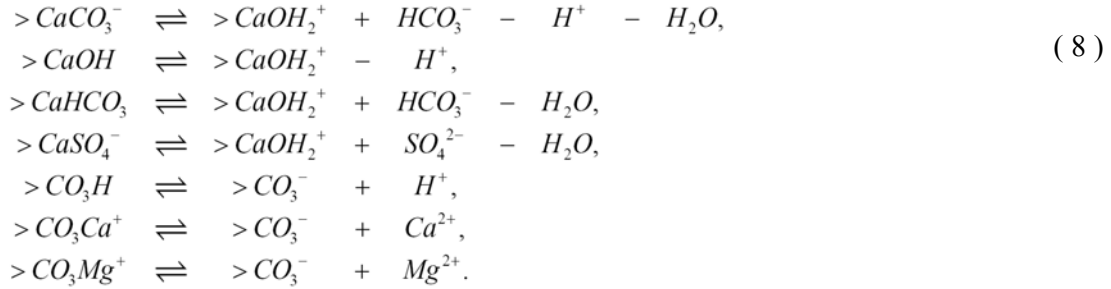
SURFACE CHEMISTRY

In much the same way as the ions make complexes in bulk, they can also make complexes at the surface. In particular sulphate can make a surface complex with calcium sites at the calcium carbonate mineral surface. Calculating the impact of the surface complexes are a bit more involved as the activity of ions close to a charged surface is dependent on the magnitude and sign of the surface potential. For a positive charged surface, the concentration of negative ions will follow a Boltzman type of distribution. The concentration will be high close to the surface and fall off exponential away from the surface. We will follow the approach of (Van Cappelen, Charlet et al. 1993; Pokrovsky and Schott 1999; Pokrovsky, Schott et al. 1999; Pokrovsky, Schott et al. 1999; Pokrovsky and Schott 2002). Our work differs from others by the fact that we perform calculations for high salinity brines and extrapolate the results to higher temperatures. This will make our results more relevant for the situation one normally deals with in petroleum, high temperature and pressure and high salinity brines. We will make the following assumptions:

1. The dominant mineral is calcium carbonate, $CaCO_3$.
2. There is an equal number of calcium and carbonate sites at the surface, this number will be taken to be $5 \text{ sites}/(\text{nm})^2$ (Davies and Kent 1990).
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 2 is simply a choice we make, but it is a reasonable value. Assumption 3 is of course the most crucial one, and it is probably not 100% correct. The temperature dependence might be a little different for the aqueous complexes compared with the surface complexes, but it should not be completely off. At this stage we are not interested in a perfect match with experimental data, but rather study the trend when temperature is changed. If we have access to a large amount of data, we can fit our model to the data and obtain better results. We would like to answer questions of the type; are there significant changes in surface charge and potential, when temperature is changed? Any significant changes in surface potential should have direct impact on the properties of the water film covering the surface.

In the same way as the calculation of the aqueous chemistry, we need to choose a set of basis species for the surface. We choose $>CaOH_2^+$ and $>CO_3^-$, thus we can express all the surface complexes in terms of these two and the basis species introduced in the previous section:



Note that the calcium and carbonate at the surface share one of the electrons; this is why there is only one plus on calcium and one minus sign on carbonate. For each of the above equations there is a corresponding law of mass action:

$$>A \rightleftharpoons >B + C \quad \Leftrightarrow \quad K = \frac{a_{>B} a_C \exp\{-Z_C F \psi / (RT)\}}{a_{>A}}, \tag{9}$$

where F is Faradays constant, ψ the surface potential, R the ideal gas constant, T the absolute temperature, and Z_C the valence of the aqueous species. Note that the activity of the aqueous species is dependent on the surface potential, if the zeta potential has a negative sign then positively charged ions will have a high activity close to the surface and vice versa. In order to solve the equation above, we need to know the surface potential. The surface potential is related to the surface charge by the Grahame equation (Israelachivili 1985):

$$\sigma^2 = 2 \varepsilon \varepsilon_0 k_B T \left(\sum_i m_i \exp\{-Z_i F \psi / (RT)\} - m_i \right), \tag{10}$$

ε_0 is the dielectric constant of vacuum and ε is the dielectric constant of water, k_B is Boltzmann's constant, and σ is the surface charge. The surface charge is the sum of all the charged surface complexes :

$$\sigma = F \left(m_{>CaOH_2^+} - m_{>CaCO_3^-} - m_{>CaSO_4^-} - m_{>CO_3^-} + m_{>CO_3Mg^+} \right). \tag{11}$$

The unit for the surface concentrations are mol/m². Solving the set of equations described in equations (1)-(11), will give the aqueous and surface chemistry.

TEST OF THE MODEL

In Figure 1 we have compared our calculations with zeta potential measurements performed by Thomson and Pownall (Thompson and Pownall 1989). The fit with experimental data is very good. Note that we calculate the surface potential and not the zeta potential, it is therefore not expected that the match should be perfect. The reason for the change in sign of the surface potential at high pH, can be understood from Figure 2. At pH 10 there is an increase in $>CO_3Ca^+$ concentration, which neutralize the negative carbonate sites.

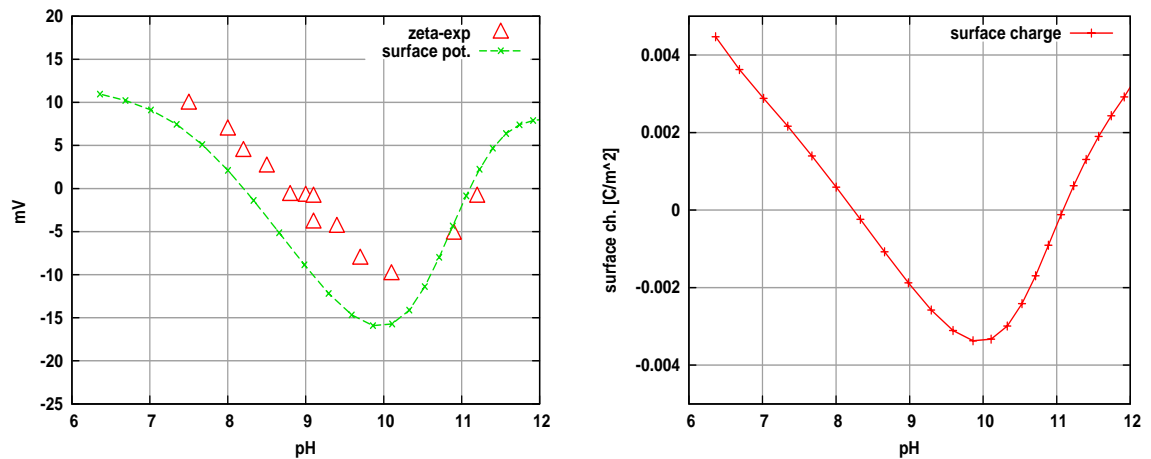


Figure 1: (Left) Measured zeta potential (Thompson and Pownall 1989) and our prediction (solid line), (right) corresponding surface charge. Calculation and measurements performed at 25 °C in 0.005M NaCl brine, and pH is changed by changing partial pressure of CO₂.

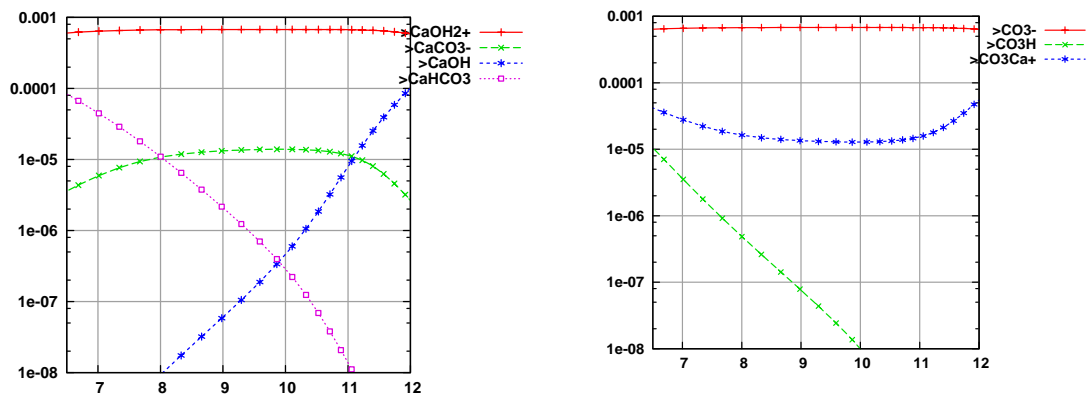


Figure 2: Surface species for the same case as in Figure 1, calcium sites (left) and carbonate site (right).

We have also compared our model to measurements performed at UiS (Zhang 2006), the result is shown in Figure 3. It is very intriguing to see that we get excellent results in both cases. This suggests strongly that the modelling approach capture basic features of the charging mechanism on the calcium carbonate mineral. As is also clearly illustrated in Figure 3 is the fact that the surface charge or surface potential can be both positive and negative at the same pH.

SURFACE CHEMISTRY OF HIGH SALINITY BRINES

From the previous section, it is clear that our model reproduce zeta potential measurements at room temperature. To our knowledge there is no data on zeta potential of calcium carbonate at high temperatures and high salinity. We can therefore use this model to predict the expected temperature dependence for chalk in contact with formation water and

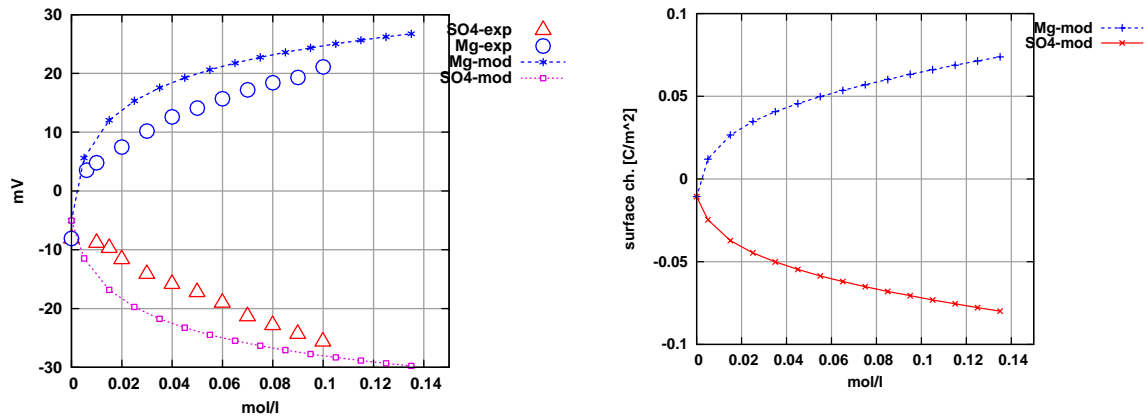


Figure 3: (Left) Zeta potential measurements performed by (Zhang 2006) (points). Measurements were performed at ambient conditions in 0.573 M NaCl brine, and MgCl₂ or Na₂SO₄ where added gradually. The pH was kept constant at 8.4. Model calculations (solid lines) were performed by assuming $P_{\text{CO}_2}=10^{-3.5}$ and equilibrium with CaCO₃ and CO₂(g), predicted pH was 8.4. (Right) Corresponding surface charge.

seawater. To the left in Figure 4 we have plotted the surface potential for the brines to the right in Figure 4 and distilled water. The temperature dependence follows almost a linear trend:

$$\psi(T) = \psi(T_0)(1 + \theta(T - T_0)), \quad (12)$$

$$\theta_{\text{Ekofisk Formation Water}} = 0.005 \text{ K}^{-1}, \theta_{\text{Seawater}} = 0.009 \text{ K}^{-1}, \theta_{\text{Distilled water}} = 0.85 \text{ K}^{-1}.$$

AQUEOUS CHEMISTRY – SUPERSATURATED MINERALS

The aqueous chemistry is included in the calculations of the surface chemistry presented in the previous section. We will just comment on the fact that some minerals may be supersaturated, in principle they can also be undersaturated, but in this case the only mineral presented is CaCO₃ and we assume equilibrium with this mineral. In the calculations presented so far we have just assumed that the supersaturated minerals will stay in solution and not affect the surface chemistry. Clearly this is not the case in general but is beyond the scope of this paper to include the effect precipitated minerals may have on the surface chemistry. The degree of supersaturation can be estimated by looking at the ratio between the ionic product and the equilibrium constant. Take anhydrite (CaSO₄) as an example:

$$\frac{Q}{K_{\text{anhydrite}}} \equiv \frac{a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}}{K_{\text{anhydrite}}}. \quad (13)$$

If the ionic product is larger than one, then the solution is supersaturated with respect to anhydrite. Further, we can also calculate how much calcium will be lost from solution if anhydrite precipitates out of solution. This is simplified in an equilibrium situation, where one can just minimize the system by the constraint that equation (13) is to be equal to one.

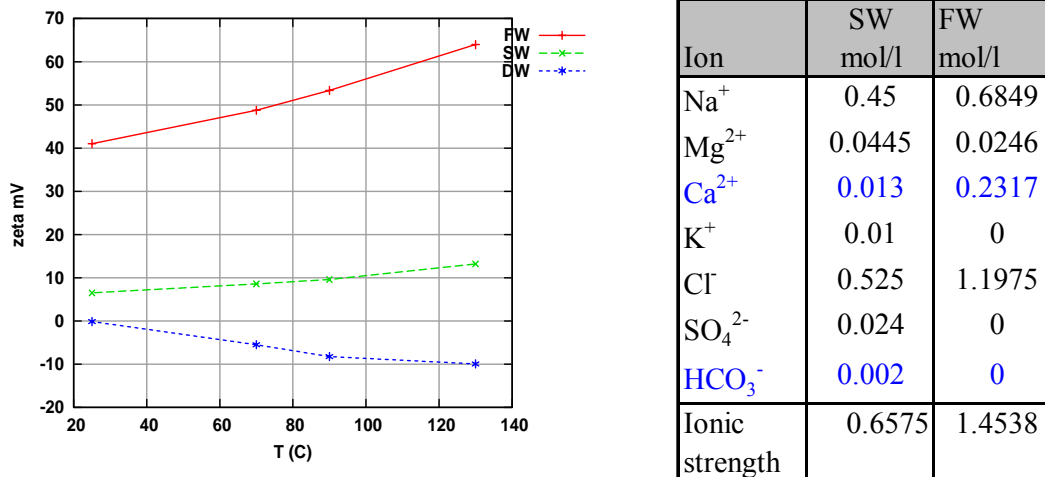


Figure 4: (Left) Predicted surface potential for seawater, Ekofisk formation water and distilled water. The calculations assume equilibrium between aqueous phase, CaCO₃ and CO₂(g), with P_{CO2}=10^{-3.5}. (Right) The Composition of Ekofisk formation water (FW) and seawater (SW) used in the calculation. The calcium and bicarbonate concentration are not used in the calculations, they are determined by the buffer.

At 130°C we find that the minerals in Table 1 are supersaturated.

It is very interesting to see that a lot of minerals are supersaturated at 130°C, which is a relevant temperature for the Ekofisk field. Injecting seawater into a hot reservoir will lead to precipitation of several minerals. If calcium bearing minerals are precipitated, there will be a corresponding dissolution. The water loses calcium and in order to be in equilibrium with calcite, calcium has to dissolve from the formation in order to reach equilibrium. This process will go on until there is established a new equilibrium.

DISCUSSION

It is not feasible from an experimental point of view to explore all kind of brines, pressure and temperature dependence that can occur in the reservoir. By making a chemical model we can easily change temperature, pressure and composition of the brine. The chemical model needs to incorporate the concentration of individual ions. We can use the chemical mode to investigate temperature dependence and verify (or disprove) by comparing with lab experiments.

From Figure 4, we see that the surface potential for seawater and formation water increase linearly as the temperature increases. If we assume that our core is dominated by calcium carbonate chemistry, as the work in (Madland 2005; Strand 2005; Zhang 2006; Korsnes 2007), then we can make the following comments:

1. If a change in the surface potential is a dominant mechanism, both in rock mechanical testing and wettability studies, then this should be observed at low temperature and high temperature. There is no significant difference in the surface potential at low and high temperature. That is, by changing from formation water to seawater, the drop in surface potential is approximately the same.

2. The surface potential for formation water is increasing as the temperature is increased. This change in surface potential is quite large and one should expect a difference between an experiment performed at room temperature and high temperature with Ekofisk formation water.

The surface potential dictates the behaviour of the double layer forces; in addition there are short range forces: attractive van der Waals forces and non DLVO forces. These forces will give some refinement to the statements above, but they should be independent of the aqueous chemistry. Therefore we believe that it is possible to make some statements without taking these forces into account. Regarding point 1 above, there has been an extensive experimental activity both on rock mechanical testing and wettability studies, well documented in (Madland 2005; Strand 2005; Zhang 2006; Korsnes 2007). These studies show that seawater is relatively inert at low temperatures; the temperature has to be over 70°C in order for the seawater to behave different than Ekofisk formation water. At high temperature the chalk cores are weaker and they imbibe more seawater, compared with Ekofisk formation water. Based on these facts, it does not seem likely from the model that the change in surface potential can account for the wettability change or water weakening effect observed.

We therefore suggest that dissolution can be an explanation for the observed wettability change and water weakening effect. As stated earlier, when seawater and formation water mix there will be a precipitation of calcium bearing minerals. When these minerals precipitate there will be a corresponding dissolution. The crucial question is of course where does this dissolution take place? If a crystal is under stress, it will tend to lower its surface energy. The intergranular contacts will be in a higher stress state than the rest of the pore space, so it is reasonable to assume that the dissolution takes place at the intergranular contacts. Clearly this hypothesis has to be verified by detecting mineralogical change inside the core, before and after flooding. We are currently working on this and the results will be presented in forthcoming papers.

It also turns out that it is also reasonable to expect an enhanced dissolution, where organic acids in the oil are adsorbed to the rock surface. Enhanced dissolution rates is observed on carbonate minerals such as dolomite (Pokrovsky and Schott 2001) in the presence of lignans. The explanation for this is the fact that the electrons from the organic acids disturb the calcite surface such that a dissolution process will be promoted where the oil is adsorbed. Thus we argue that oil is liberated when a dissolution process is started where the oil is “anchored” to the rock surface. Dissolution at the “anchored” points may induce a large production. We would guess that the nature of the oil components is important, not all oil components have the ability to adsorb so strongly that they would impact the calcium carbonate structure. After dissolution there will be new water wet surface. How to test this hypothesis? Clearly if dissolution is responsible for enhanced oil production in imbibition experiments on chalk, then the oil production in these experiments should be proportional to the amount of dissolved calcium in the core. We have used the data in Fig 6 and Fig 7 in (Zhang, Tveheyo et al. 2006). Seawater enters the core and mix with the formation water. From the steady state levels (see Figure 5) we can find the amount of

produced oil, which is equal to the imbibed seawater, so we know the average composition of the water inside the core. Then we can calculate the amount of calcium dissolution at the given temperature, triggered by the precipitation of anhydrite (CaSO_4). In Figure 5 the result of the calculation is shown, we see clearly a very nice correlation. The dissolution hypothesis has the right temperature dependence, no precipitation of anhydrite below 70°C . The imbibition process is a complicated process, and capillary forces are definitely important. Clearly not all oil production can be due to dissolution; this probably explains some of the points which do not lie on the line indicated in Figure 5.

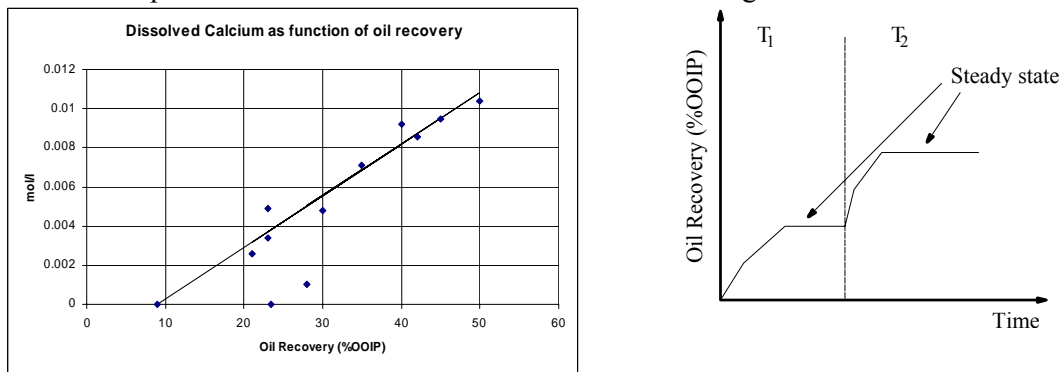


Figure 5: (Left) Calculation of the expected dissolution of calcium carbonate, and plotted against the oil recovery. The data are taken from six imbibition experiments. (Right) Schematic shape of the imbibition curve. We have used the steady state value as indicated on the curve.

CONCLUSION

We have developed a chemical model that includes both the aqueous chemistry and surface chemistry. This is necessary in order to discuss how the water chemistry may impact petrophysical parameters such as wettability and rock mechanical strength. We have compared the model with zeta potential measurements. The match is very good, and we have extrapolated these results to higher temperatures. Based on the calculations it does not seem likely that changes in the surface potential may be responsible for the observed wettability change observed in imbibition experiments on chalk. We suggest that dissolution could be a possible explanation for both wettability change and water weakening of chalk. It is important to note that our model does not contain the oil components, but we believe that when oil components adsorb to a rock surface they adsorb strongly and irreversibly. Therefore a change in the water chemistry should not affect the equilibrium between the rock surface and the oil phase.

We find a nice correlation between the expected dissolution of calcium inside the chalk core and the produced oil. The correlation is encouraging, but no proof. In order to verify our hypothesis one needs to observe mineralogical change inside the core. It would also be great to see this change on a scanning electron microscope image. Anyway, we would like to stress the need to discuss chemical mechanism inside a well defined setting. The type of modelling we suggest in this paper is one case of such a setting. Chemistry is complicated and the details are very important, this makes it very hard to draw conclusions from core

scale experiments without making some calculations. Finally we would like to make the comment that if dissolution turns out to be a correct description for the wettability change observed on chalk cores, it would be very interesting to pursue this idea for low salinity water flooding in sandstone.

ACKNOWLEDGEMENTS

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NOMENCLATURE

Symbol	Description	Unit
ψ	Surface potential	V
σ	Surface charge	C/m ²
R	Ideal gas constant	8.314 J/(kg K)
F	Faradays constant	96485 C/mol
T	Temperature	K
I_o	Ionic strength	M=mol/l
m	Concentration	mol/l
a	Activity	
γ	Activity coefficient	
ϵ	Relative permittivity	
ϵ_0	Permittivity of vacuum	8.85·10 ⁻¹² C ² /(J m)
Z _i	valency	
>	prefix for surface species	
Å	Debye diameter	
θ	fitting parameter	1/K

Table 1: Supersaturated minerals at 130 °C and 8 bar.

Mineral	Log ₁₀ Q/K	
	Seawater	EF
Dolomite CaMg(CO ₃) ₂	2.16	0.7
Dolomite(ordered) CaMg(CO ₃) ₂	2.17	0.7
Dolomite(disord.) CaMg(CO ₃) ₂	1.18	-0.29
Huntite CaMg ₃ (CO ₃) ₄	1.98	-2.42
Brucite Mg(OH) ₂	1.37	-0.1
Magnesite MgCO ₃	1	-0.46
Anhydrite CaSO ₄	0.22	-
Calcite CaCO ₃	0	0

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