

## **DIRECT EXPERIMENTAL EVIDENCE OF WETTABILITY MODIFICATION BY LOW SALINITY**

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### **ABSTRACT**

It has been observed by several parties in the past years that injection of low salinity water leads to the production of additional oil compared to injection of water at reservoir salinity or higher. While this process is already applied in the field, so far the microscopic mechanism is not fully clear. A mechanism proposed by several researchers is that low salinity water leads to a wettability change of the sandstone rock, which then causes release of oil that previously was attached mostly to clay minerals. So far all experimental evidence for this mechanism is macroscopic and indirect, i.e. in the form of an increase in produced oil. The main motivation for this study is to provide direct evidence and to directly visualize detachment of crude oil from clay minerals. In a small lab scale experimental study in a flow cell we observed the release of crude oil from a substrate covered with solidly attached clay particles when changing the brine from high salinity to low salinity. For very low salinity we observed a massive release of crude oil (up to 80%) but also a decomposition of the Montmorillonite clay minerals and release of fines (formation damage). For a brine composition with somewhat higher salinity and in addition presence of divalent ions, we observed release of oil but only insignificant amount of clay swelling ("controlled formation damage").

### **INTRODUCTION**

The concept of injecting low salinity water into an oil reservoir is not a new topic. Jadhunandan (1990) has shown that injection of brine can lead to improvement of oil recovery in sandstone oil reservoirs [11]. Webb (2004) and Secombe (2008) have demonstrated the effect in the laboratory and in field tests [29][22]. Initially, the mechanism was not very clear. Lager (2008) give a very comprehensive overview of the historical development of a deeper understanding of the effect [16]. Since the effect occurred on sandstone but not in fired or acidized sandstones, Tang (1996) and Lager (2006) concluded that the effect is related to the presence of clays. On that basis, a large variety of mechanisms have been proposed in literature:

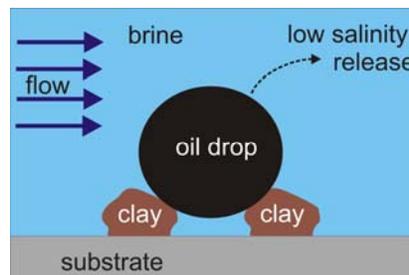
1. McGuire (2005) proposed a pH-induced in-situ surfactant generation and IFT reduction and emulsification [20]
2. Tang (1999) proposed fines migration [25] and stripping of oil bearing fines from pore walls [26]

3. Zhang (2006) argued that selective plugging of predominantly water saturated pore networks [30] causing increase of differential pressure in oil-bearing pores and viscous stripping described already in Anderson (1986) [3]
4. Tang (1996) propose a wettability modification by decrease in ion binding [27]
  - a) Lager (2008) and Tang (2002) favor (multicomponent) ionic exchange [16][28]
  - b) Ligthelm (2009) see evidence for double layer expansion [17]

Lager (2006) give a comprehensive overview of the different mechanisms including the most relevant bibliography [15]. Lager (2006) and Lager (2008) warn that some of the above listed mechanisms are rather effects than causes [16][15] like pH induced IFT reduction, which has been ruled out as cause by Ligthelm (2009) [17]. In Lager (2006) and most of the other studies, the effects of low salinity flooding are studied in core flooding experiments where observations are indirect via an increase of oil production in a recovery curve [15]. Many microscopic mechanisms would be seen macroscopically from a reservoir engineering perspective as wettability modification. Jerauld (2006) argue that the effect of low salinity flooding on a recovery curve can then be modeled as a modification of the relative permeability [12] and Maas (2001) had already proposed a modification of the capillary pressure saturation functions [18]. Already Tang (1996) proposed wettability modification as microscopic mechanism already for a long time [27]. In the past 2-3 years, most publications argue that wettability modification is the dominating microscopic mechanism but the other effects are not clearly ruled out as discussed by McGuire (2005) [20]. Drummond (2002) and (2004) have observed wettability modification based on pH and salinity for model silicate surfaces [8][7]. In a 2-dimensional parameter space spanned by pH and electrolyte concentration, distinct regions where oil adheres to the surface and regions of no or less adhesion have been observed. The underlying mechanism is based on forces and molecular interactions between charged surfaces separated by liquid described by the DLVO theory summarized in Adamson (2007) [1]. Crude oil contains several components that can interact with and adhere to rock surface. Buckley (1998) makes these components responsible for wettability modification [4]. In the context of low salinity flooding, Lager (2008) point in particular on polar components [16]. Clementz (1976) describes clay minerals as very reactive [5] and Clementz (1982) provides evidence that they offer possible binding sites for those polar components leading to oil wetness [6]. Ligthelm (2009) points out that in particular dispersed clays can act as anchor points to pin contact lines of oil droplets [17]. While the end faces of clays can be positively charged, their top faces carry a negative charge over most of the relevant pH range. Lager (2007) sketch binding mechanisms where positively charged polar crude components like amines can directly bind on such a surface [14]. But polar crude components with negatively charged polar groups, e.g. carboxylic head groups, experience a repulsive electrostatic interaction. This repulsion is however screened by positively charged cat-ions in the context of the diffusive double layer with a screening length that is inversely proportional to the square root of the electrolyte concentration as summarized in Adamson (2007) [1]. A reduction of the electrolyte concentration leads to an increase of the screening length and double layer expansion that can eventually separate adsorbed molecules from the charged surface. Webb (2004) make cation exchange reactions substituting double valent "bridging" ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  by mono valent ions responsible for the de-sorption of crude components from the clay surface [29]. These two mechanisms are illustrated in Figure 9 in the discussion section. Ligthelm (2009) recently presented evidence that in sandstone rock cation exchange is

present but double layer expansion gives the dominating contribution to wettability modification [17]. Sharma (1985) argue that in reservoir rock, the stability of clays composed of layered silicate platelets that are bound by electrostatic interactions follows similar principles [24]. Khilar (1984) demonstrated in experimental studies that at a critical salt concentration, the clays start to swell, de-flocculate and migrate as fines [13]. Mays (2007) show examples where this de-flocculated clay leads to clogging of pore throats and formation damage [19]. Clays are stable for high enough concentrations of mono-valent and/or multi-valent ions. For each clay specific stability regions are visualized in phase diagrams introduced by Scheuerman (1990) [21].

The main difficulty in uncovering the microscopic mechanisms is that, so far, mostly core flooding experiments and field trials have been performed so that the effect of low salinity flooding is seen as an additional recovery in a recovery curve observed for instance by Lager (2006) [15], which is an indirect measurement. Tang (1996) point out that core flooding experiments are sometimes not un-ambiguous with large influence from initial sample preparation [27] and from experimental artifacts such as the capillary end effect described in detail by Huang (1996) [9]. The aim of this work is to study the microscopic mechanism of low salinity water flooding on a fundamental and microscopic level. The main focus is on obtaining direct experimental evidence that is supporting wettability modification as the most relevant mechanism.



**Figure 1:** Sketch of the experiment: an oil droplet is attached to clay particles anchored on a solid substrate. When flooding with low salinity water, the droplet detaches.

The effect was studied in an open flow model geometry that allows to directly track the release of single oil droplets. This model geometry represents the situation inside a pore in the rock where some of the residual oil (e.g. after a primary and secondary recovery) is bound to clay particles that are attached to rock grains. In Figure 1, the principle of our experiment is sketched: an oil droplet is attached to clay particles anchored on a solid substrate (simulating the rock grain) under high salinity water. If wettability modification is the main microscopic mechanism, detachment of the oil droplet it is expected when flowing with low salinity water. In case that the bond does not break between oil and clay, but within the clay particle by the same or a similar mechanism and one (or few more) clay layer(s) are released together with the oil droplet, which in our experiment cannot be distinguished, the phenomenon would still appear in the context of wettability in porous rock still as a wettability modification because a more hydrophilic interface is left behind.

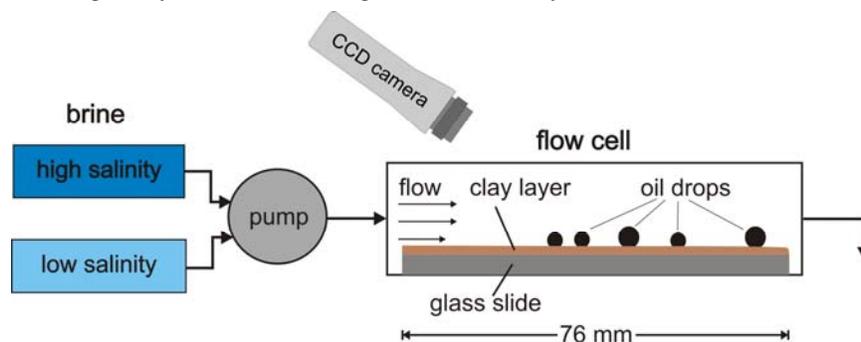
## EXPERIMENTAL

**Materials** - Montmorillonite clay (Na-Montmorillonite, type Swy-2) was obtained from the Source Clays Repository (The Clay Minerals Society, Purdue University, 915 West State Street, West Lafayette, IN 47907-2054, USA). A North sea crude oil with a density of  $0.827 \text{ g/cm}^3$  and a viscosity of 4 cP was used for the oil droplets. The brine compositions used in the experiments are listed in Table 1. The "high salinity" brine is typically in a regime where clays are stable. The "low salinity" brine is typically in the formation damage regime where clay swelling and de-flocculation is expected. Intermediate salinity was obtained by diluting the high salinity brine 2, 4 and 10 times to reach a regime where clays stay intact ("controlled formation damage").

|  | "high salinity" brine      | "low salinity" brine       |
|--|----------------------------|----------------------------|
| <i>substance</i>                       | <i>concentration (g/l)</i> | <i>concentration (g/l)</i> |
| NaCl                                   | 10.85                      | 2.0                        |
| KCl                                    | 13.80                      |                            |
| CaCl <sub>2</sub> · 2 H <sub>2</sub> O | 1.106                      |                            |
| MgCl <sub>2</sub> · 6 H <sub>2</sub> O | 0.194                      |                            |
| <b>TDS</b>                             | <b>25.95</b>               | <b>2.0</b>                 |

**Table 1:** Brine composition

**Setup** - In Figure 2, a simplified sketch of the experimental setup is shown. In a flow cell, flow of brine with specified composition is directed past a clay surface where oil droplets are attached. For simplicity, in the sketch we indicated that the flow is generated by a pump. In the experiment, however, we used reservoirs at constant height difference and gravity driven flow to generate a steady flow.



**Figure 2:** Sketch of the experiment: oil droplets are attached to clay particles glued on a glass slide. When flooding with low salinity water, some droplets detach which is recorded with a CCD camera.

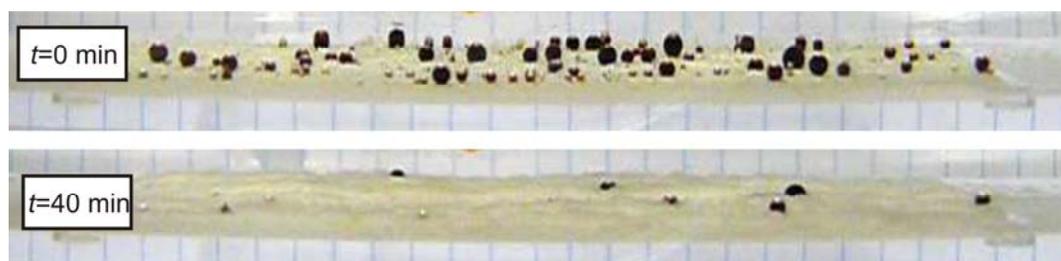
The clay surface is fabricated from a standard microscope glass slide (76 mm x 26 mm, Menzel-Gläser, available through Thermo Scientific) where clay particles were glued on using a 2-component glue (epoxy glue Bison kombi-rapide, Bison International, Postbus 160, 4460 AD Goes, The Netherlands). Clay particles that were not firmly attached were first blown off by pressured air and then removed by brine flow. Oil droplets were attached from a syringe needle ( $\text{Ø}0.60 \times 80 \text{ mm}$ ) to the substrate immersed in high-salinity brine which is a favorable condition for binding. The experiments commenced by creating a steady flow with high salinity brine at a flow rate of 200-500 ml/min corresponding to linear flow velocities on the order of 1 cm/s. In the first few seconds, typically few oil droplets that are not firmly attached are released and swept away by the flow. After few minutes, a steady state is reached where all oil droplets are stable. Even after 1 hour, no additional oil drops are released.

The main purpose of the water flow is to change between high and low saline brine and keeping all other conditions, i.e. flow speed, constant. In our experiments, we compared two different brine salinities with compositions specified above. When the brine of lower salinity displaced the high saline brine initially present in the flow cell, Schlieren patterns (see Settles (2001) [23]) due to index of refraction differences were observed. This point serves as a reference time " $t_0$ ". A typical experiment lasts 20-40 minutes. Videos of the experiments were recorded with a digital camera (Lumix DMC-FZ50, Panasonic Corporation) at a resolution of 640 x 480 pixels and up to 30 fps. The camera images the substrate with the oil droplets from the side at an angle of approximately 30 degrees. The release of oil droplets is quantified via Image Analysis with ImageJ [10]. After thresholding (oil=black, everything else=white) the particle analysis function of ImageJ computes the area of each individual oil droplet where the majority of droplets has circular or slightly elliptical cross sections. Assuming that we see a projection of a spherical drop, we calculate the volume of the drop from the cross sectional area. The total volume of oil is then the sum of all individual droplet volumes.

Main source of error originates from droplets in the line of view partially hiding other droplets and swelling of the clay layer. Large droplets become partially and small droplets become entirely embedded. Droplets seem to have disappeared or shrunk when in reality they are still in place. In the automatic image analysis, the invisible oil volume due to swelling is counted by mistake as produced oil. In our analysis, the effect of clay swelling is partially corrected. Due to the depth of view, droplets close to the camera appear larger than the ones in the back of the flow cell. Moreover, the automatic particle counter of ImageJ often mistakes a group of droplets for one object, resulting in incorrect volume calculations which is based on spherical droplets. Droplets hidden behind other droplets are initially not counted. Consequently, when one droplet detaches, another one may become visible instead. The overall relative error in volume calculation ranges from 5-60%.

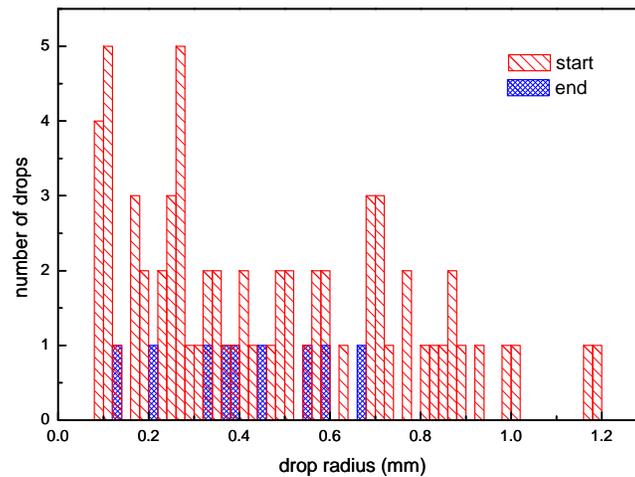
## RESULTS

In Figure 3 we show an example of a typical experiment with low salinity brine where approximately 87% of the crude oil is released. In most of the experiments with low salinity brine, a release of more than 80% of crude oil is observed. In porous rock, 5-15% increased recovery as observed as demonstrated by Zhang (2006) [30] and between 60-80% by Agbalaka (2009) [2]. The recovery is also expected to depend on the density of clay on the rock surface which in this experiment is very high and typically lower in oil reservoirs. In Figure 4 we show the histogram of the droplet size distribution from the low salinity flooding experiment from Figure 3. It is evident that the low salinity brine causes droplets of almost all sizes to detach.



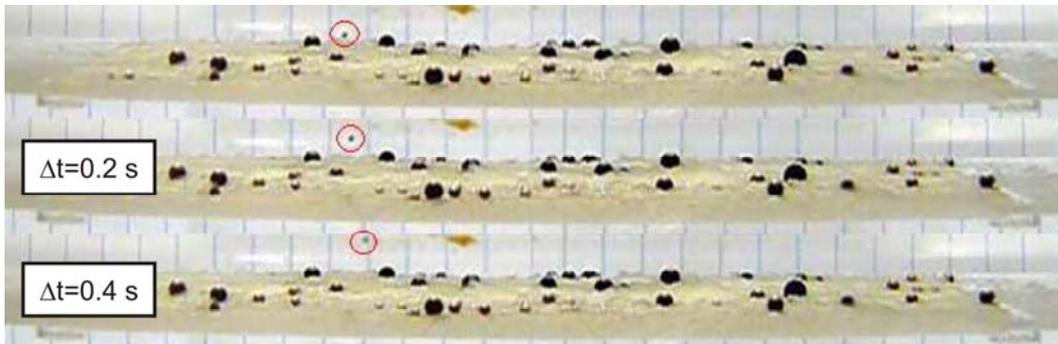
**Figure 3:** Snapshots at the start and the end of an experiment with low salinity brine. Approximately 87% of the crude oil is released. There is substantial clay swelling and de-flocculation.

Apart from the release of crude oil, a substantial amount of clay swelling and de-flocculation is observed. During the flow, the clay layer swells by several 100% of its original thickness and clay particles detach and are carried along with the flow. Due to the increase in clay layer thickness, the smaller droplets are not visible at the end of the experiment because they are hidden behind the clay layer and therefore also missing in the histogram. In calculations of the produced oil fraction, we attempted to correct for that effect. The correction is only partially successful. Major uncertainties arise when small droplets disappear entirely under the swollen clay layer. In our future work, we intend to improve our analysis method by tracking the release of individual droplets and discard droplets that become invisible.



**Figure 4:** Drop size distribution (histogram) from Figure 3 at start and end of the experiment.

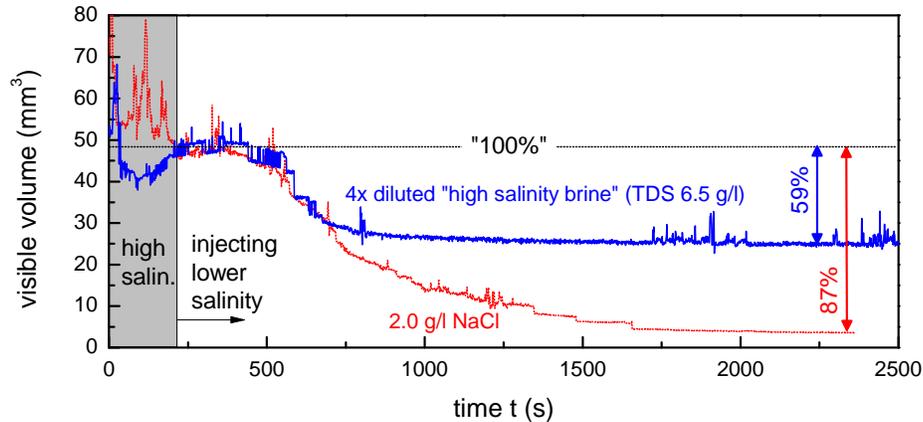
In Figure 5 we display a sequence of snapshots taken during an experiment with low salinity brine where a released oil drop is tracked over several frames.



**Figure 5:** Release of a single oil droplet at horizontal flow rate of approx. 1 cm/s.

In Figure 6 the area fraction of oil as function of time is plotted for the low salinity flooding experiment shown above which is in the formation damage regime where clays swell and de-flocculate and detach. Superimposed is an experiment with a 4 times diluted high salinity brine where still oil detaches but no clay detaches and the clay layer swells only insignificantly. The error due to oil drops hidden behind others and oil droplets hidden underneath the swollen clay layer ranges from 20-60%. Therefore the incremental recovery is over estimated. The large scatter in the first 200 s is an

initialization artefact. The stable base line is established right when low salinity injection starts.



**Figure 6:** Decrease of the visible oil on the surface as function of time when flooding with "low salinity brine" (experiment from Figure 3) and with 4 times diluted "high salinity brine".

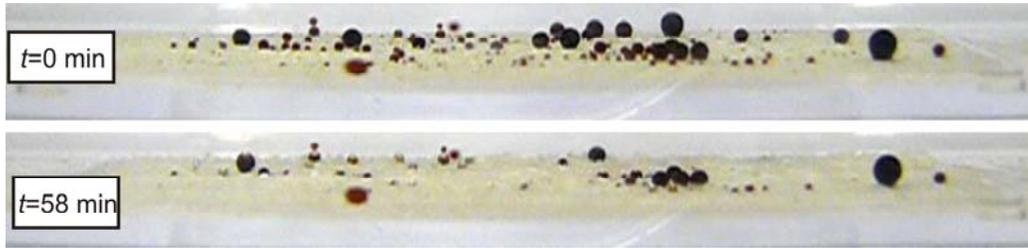
In Table 2 an overview of all successful experiments is given. The majority of our experiments has been conducted with Montmorillonite clay and a low salinity brine of 2 g/l NaCl. In those experiments, on average,  $66.6 \pm 20$  vol-% of oil has been released. Note that not in all experiments, clay swelling and release of oil has been observed which we attribute to unknown experimental artefacts and handling mistakes.

| #  | Oil released | % of released oil volume | Clay type       | Low salinity brine composition | Formation damage |
|----|--------------|--------------------------|-----------------|--------------------------------|------------------|
| 11 | Yes          | (20 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 12 | Yes          | (48 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 14 | No           | N.A.                     | Smectite-illite | 2,0 g/l NaCl                   | Yes              |
| 17 | Yes          | (16 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 18 | Yes          | (79 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 19 | Yes          | (98 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 20 | Yes          | (69 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 22 | Yes          | (82 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 23 | Yes          | (93 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 24 | Yes          | (87 ± 30) %              | Montmorillonite | 2,0 g/l NaCl                   | Yes              |
| 28 | Yes          | (54 ± 30) %              | Montmorillonite | 1/10 high salinity brine       | Yes              |
| 29 | No           | -                        | Montmorillonite | High salinity brine            | No               |
| 30 | No           | -                        | Montmorillonite | 1/2 high salinity brine        | No               |
| 31 | Yes          | (59 ± 30) %              | Montmorillonite | 1/4 high salinity brine        | little           |

**Table 2:** Overview of all successful experiments.

In a control experiment flowing only with high salinity brine, no additional oil was produced and no clay swelling was observed (experiment 29). In order to approach the regime where oil is produced by clays stay intact, we started diluting the high salinity brine with demineralised water (experiments 28, 30 and 31). For 4 times dilution of the high salinity brine we observed release of oil but only a very minor amount of clay swelling. In Figure 7 we show snapshots at the start and the end of that experiment. Approximately 59% of the oil is released (see Figure 6). There is only very minor clay

swelling. The clay layer thickness slightly increases but there is no de-flocculation or release of clay particles.



**Figure 7:** Snapshots at the start and the end of an experiment with 4 x diluted high salinity brine. Approx. 59% of the crude oil is released. There is only very minor clay swelling and no de-flocculation or release of clay particles.

## DISCUSSION

The main goal of this study is to provide direct evidence that adhesion forces between oil droplets and clay particles are weakened by low salinity brine. When the adhesion force becomes smaller than the forces responsible for release, droplets are released. The forces responsible for release are a combination of buoyancy forces

$$F_{gravity} = \Delta\rho g \frac{4}{3}\pi r^3 \quad (1)$$

due to the density difference  $\Delta\rho$  between oil drop with radius  $r$  and brine, where  $g$  is the gravitational acceleration constant and viscous forces

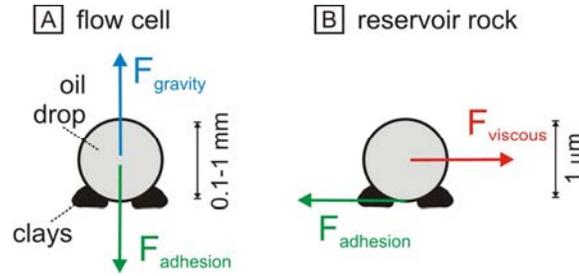
$$F_{viscous} = 6\pi\mu r v \quad (2)$$

approximated via the Stokes drag force for a fluid flow velocity  $v$  and viscosity  $\mu$ .

Gravity forces,  $F_{gravity} \propto r^3$ , have a much stronger dependency on the drop radius  $r$  than viscous forces,  $F_{viscous} \propto r$ . The ratio of viscous and gravity forces for a drop of radius  $r$  is

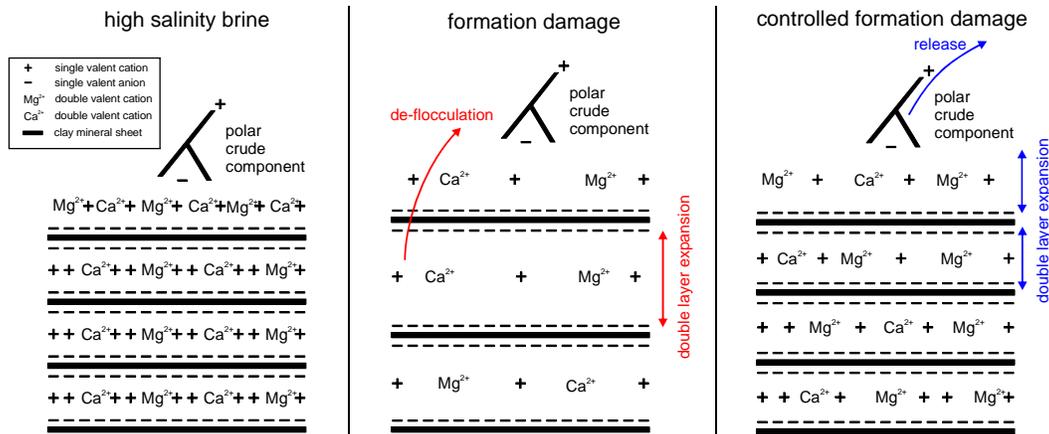
$$\frac{F_{viscous}}{F_{gravity}} \approx \frac{6\pi\mu r v}{\Delta\rho g \frac{4}{3}\pi r^3} \quad (3)$$

In our experiments, droplets have a typical diameter in the range of 0.1-1  $\mu$ m (see Figure 4). In an oil reservoir, oil droplets are typically on the order of 1  $\mu$ m which is a factor of  $10^3$  smaller. For a typical situation in our flow cell with  $v=1$  cm/s and  $r=1$  mm we obtain  $F_{visc} / F_g \approx 0.026 \ll 1$  indicating a dominance of gravity forces. Besides, the two forces are perpendicular to each other. For a typical situation in a pore inside the reservoir rock with  $v=1$  ft/day and  $r=1$   $\mu$ m we obtain  $F_{visc} / F_g \approx 10 \gg 1$  indicating a dominance of viscous forces. Therefore in our experiments, the dominating force balance  $F_{gravity} / F_{adhesion}$  is in the vertical direction as sketched in Figure 8A where buoyancy forces (density of oil was less than the density of brine) are balanced by adhesion forces to the clay substrate.



**Figure 8:** Force balance in the flow cell (A) and in the pore in the reservoir rock (B).

In the oil reservoir with much smaller oil droplets, the dominating force balance  $F_{viscous} / F_{adhesion}$  is in the horizontal direction and adhesion forces are balanced by the viscous forces that the brine flow exerts on the oil droplets via viscous coupling (see Figure 8B). Our study is not attempting to mimic the force balance in the reservoir but to demonstrate the weakening of adhesion forces by low salinity brine which is tested via the viscous-adhesion force balance. In the large majority of experiments with Montmorillonite clay and brine concentrations in the formation damage regime (2 g/l NaCl, see Table 2) the release of 66.6 vol-% of oil on average was observed. The situation is sketched in Figure 9.



**Figure 9:** Stable clays with polar crude component attached (left), formation damage where very low cat-ion concentration causes clay de-flocculation due to strong double layer expansion (middle) and controlled formation damage where moderate double layer expansion weakens the adhesion between the polar crude components and the clay (right).

In the controlled formation damage regime, we have seen one experiment where approximately 59 vol-% of oil has been released (Figure 6). The two experiments are similar in the sense that oil has been released but there are important differences: In the formation damage regime, we observe first noticeable swelling of clay combined with clay de-flocculation and fines migration, before oil is released. In the controlled formation damage regime, we observe first the release of oil and after that very minor expansion of the clay layer but there is no visible de-flocculation or fines migration. We can, however, not completely exclude the possibility that single clay layers or fragments detach together with oil droplets. Experimentally, we do not have to possibility to distinguish those two cases. From a macroscopic perspective, clays stay essentially intact.

Apparently, in the controlled formation damage regime, the clays remain predominantly stable but only adhesion between clays and oil are weakened. This finding has large practical implications because this regime is particularly interesting for field applications. From an academic point of view, there are still many questions open: unfortunately we cannot determine with certainty if oil droplets detach from clay particles or if single clay layers with attached oil separate from the clay assembly or the substrate. So far, our experiments are also not specific enough to determine whether the actual weakening of adhesion forces is caused by double layer expansion or ion exchange reactions. Ongoing studies will shed more light on the details of the mechanisms in the different regimes.

## CONCLUSION

In this paper we provide direct experimental evidence that wettability modification of clay surfaces is the microscopic mechanism for low salinity flooding. Our findings can clearly rule out emulsification, IFT reduction, fines migration and selective plugging of water-bearing pores via clay swelling as most relevant mechanisms. While we can confirm wettability modification as relevant mechanism, ongoing research tries to distinguish between double layer expansion and cation exchange or if a layer of clay detaches together with each oil droplet. While release of oil is seen for very low salinity where also clay de-flocculation and formation damage occurs, at least for Montmorillonite clays there is a regime of intermediate salinity where still oil is released but the clays stay intact ("controlled formation damage"). This regime is in particular interesting for field applications where production of oil is desired but migration of fines (formation damage) has to be avoided. This simple experimental geometry provides a convenient platform to study the onset of oil production and clay swelling and frame the electrolyte concentration ranges. In a more systematic follow-up study, the effect will be studied for different clay types that are more difficult to handle (smaller particle size) and different salinities.

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