

Chemical Mechanism of Low Salinity Water Flooding in Sandstone Reservoirs

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Abstract

Both laboratory and single well field tests have documented that enhanced oil recovery can be obtained from sandstone reservoirs by performing a tertiary low saline waterflood. Due to the complexity of the crude oil-brine-rock interactions, the mechanism behind the low saline EOR process has been debated in the literature for the last decade. Both physical and chemical mechanisms have been proposed, but it appears that none of the suggested processes has so far been generally accepted as the main contributor to the observed low salinity EOR effect. Based on published data and new experimental results on core flooding, effects of pH and salinity on adsorption of acidic and basic organic components onto different clay minerals, clay properties like ion exchange capacity and selectivity, and oil properties, a new chemical mechanism is suggested, which agrees with documented experimental facts. At reservoir conditions, the pH of formation water is about 4 due to dissolved acidic gases like CO₂ and H₂S. At this pH, the clay minerals, which act as cation exchange material, are adsorbed by acidic and protonated basic components from the crude oil, and cations, especially divalent cations, from the formation water, like Ca²⁺. Injection of a low saline fluid, which promotes desorption of Ca²⁺, will create a local increase in pH close to the brine-clay interface because Ca²⁺ is substituted by H⁺ from the water. A fast reaction between OH⁻ and the adsorbed acidic and protonated basic material will cause desorption of organic material from the clay. The water wetness of the rock is improved, and increased oil recovery is observed.

To observe low salinity EOR effects in sandstones, a balanced initial adsorption of organic components and Ca²⁺ onto the clay is needed. Both the adsorption capacity and the pH-window for adsorption/desorption of organic material is somewhat different for various types of clay minerals. A detailed knowledge of the chemical mechanism behind the low saline EOR process together with information on formation brine composition, oil properties and type of clay material present, will make it possible to evaluate the potential for increase in oil recovery by a low salinity waterflood.

Introduction

A great number of laboratory tests by Morrow and co-workers (Tang and Morrow, 1999a; Tang and Morrow, 1999b; Zhang and Morrow, 2006; Zhang et al., 2007b) and also by researchers at BP (Lager et al., 2007; Webb et al., 2005a; Webb et al., 2005b) have confirmed that enhanced oil recovery can be obtained when performing a tertiary low salinity waterflood, with salinity in the range of 1000-2000 ppm. Based on 14 tests from different sandstone reservoirs, Lager et al. (Lager et al., 2007) have reported that the average increase in recovery was about 14%. The laboratory observations have even been confirmed by single well tests performed in an Alaskan reservoir (Lager et al., 2008b). As increasing amounts of laboratory experiment results have been published in the last decade, various suggestions of the mechanism behind the low salinity process have appeared. Unfortunately, none of the suggested mechanisms have so far been generally accepted as the "true" mechanism. The reason is that many parameters linked to the rock, to the reservoir fluids (oil and brine), and to the injection fluid are involved. In order to give the reader a good background to understand the proposed mechanism in this paper, a list of the accepted experimental conditions is given, followed by a short recap of the previously suggested mechanisms.

Conditions for low salinity effects

The listed conditions for low salinity effects are mostly related to the systematic experimental work by Tang and Morrow (Tang and Morrow, 1999a), but some points has also been taken from the work by BP (Lager et al., 2007; Lager et al., 2008a).

- Porous medium
 - Sandstones.
 - Low salinity effects have not been documented in pure carbonates, but Pu et al. have observed low salinity effects in a sandstone containing dolomite crystals (Pu et al., 2008).
 - Clay must be present
 - The type of clay may play a role.
- Oil
 - Must contain polar components (i.e. acids and bases)
 - No effects have been observed using refined oil free from polar components.
- Formation brine, FW,
 - Formation water must contain divalent cations, i.e. Ca^{2+} , Mg^{2+} (Lager et al., 2008a)
 - Initial FW must be present
 - Efficiency is related to initial water saturation, S_{wi}
- Low salinity injection fluid
 - The salinity is usually between 1000-2000 ppm, but effects have been observed up to 5000 ppm.
 - Appears to be sensitive to ionic composition (Ca^{2+} vs. Na^+)
- Produced water
 - For a non-buffered system, the pH of effluent water usually increases about 1-3 pH units when injecting the low salinity fluid.
 - It has not been verified that increase in pH is needed to observe low salinity effects.
 - In some cases, production of fines have been detected, but low salinity effects have also been observed without visible production of fines (Lager et al., 2008a)
- Permeability decrease
 - Usually an increase in pressure over the core is detected when switching to the low salinity fluid, which may be related to migration of fines or formation of an oil/water emulsion.
 - There is a lack of experimental evidence to say that observed low salinity effects are accompanied by permeability reduction.
 - Waterflood experiments have been performed without any variation in end point relative permeability data between high and low salinity water floods, under both secondary and tertiary flood conditions (Webb et al., 2008).
- Temperature
 - There appears to be no temperature limitations to where low salinity effects can be observed. Most of the reported studies have, however, been performed at temperatures below 100 °C.

In the literature, it has often been reported that low salinity effects have been observed both in a secondary and tertiary flooding mode. In a tertiary flooding mode, the core is first flooded with formation water until the oil production plateau is reached. Thereafter, the injected fluid is switched to low salinity water by diluting the formation water with distilled water until the salinity is in the range of 1000 to 2000 ppm. When performing a secondary low salinity flood, the core is restored after the formation waterflood, and a new flood is performed with the low saline water. The oil recoveries from the two floods are then compared. Very often it is observed that the increase in oil recovery is higher in the secondary flood compared to the tertiary flood. Recently, a study on oil recovery by cyclic waterflooding of mixed-wet sandstone and limestone performed by Loahardjo et al. (Loahardjo et al., 2008) showed increased oil recovery from restored cores using the same formation water as was used in the first flood. In consequence, low salinity effects observed during a secondary flooding mode need not to be linked solely to decrease in salinity of the injected fluid. This is surely new and interesting information about crude oil-brine-rock interactions. Thus, reliable low salinity effects should only be verified under tertiary flooding conditions.

Suggested low salinity mechanisms

It is obvious, that a chemical mechanistic study of the low salinity effect in sandstones, is much more complicated compared to wettability alteration studies in chalk by “Smart Water” (Punternvold et al., 2007; RezaeiDoust et al., 2009b; Strand et al., 2006; Strand et al., 2008; Zhang et al., 2007a). Probably the low salinity effect is a result of different mechanisms acting together, each with its own contribution. Even though it is generally accepted that the low salinity effects are caused by wettability alteration, some physical mechanisms have also been suggested; such as migration of fines and fluid flow due to osmotic pressure caused by salinity gradients. Some of the mechanisms, which have been proposed until today, e.g. fines migration, pH increase, multi-ion exchange (MIE) and “salting in effects”, were briefly discussed in RezaeiDoust et al. (RezaeiDoust et al., 2009b). Recently, Ligthelm et al. (Ligthelm et al., 2009) explained the wettability alteration process by low

salinity in terms of double layer effects. It was suggested that a decrease in salinity will increase the size of the ionic double layer between the clay and oil interfaces, facilitating the release of organic materials. This is a pure physical explanation, and it was illustrated by supposing a Ca^{2+} bridge between the clay and oil both containing negatively charged interfaces, similar to the illustrations put forward by Lager et al. (Lager et al., 2008a). Polar oil components can surely adsorb onto clay minerals without a bridge of divalent cations.

Experimental

Waterflood experiments

Materials

Oils

Prior to use, the oils were centrifuged to remove any possible particles and water. Table 1 includes some of the properties of the oil at room temperature.

Table 1 Oil properties

	AN mg KOH / g	BN mg KOH / g	Density g/cm ³	Viscosity cp
High BN Low AN Oil	0.12	1.78	0.846	17.6
Low BN High AN Oil	1.82	0.54	0.804	-

Brines

The brines used were prepared by dissolving reagent grade salts in distilled water to the compositions given in table 2. All brines were filtered to remove particles if any, and vacuumed to remove dissolved gas.

Table 2 Molar (mol/L) brine compositions

	Connate brine	Low salinity brine
Cl^-	1.72	0.013
Na^+	1.54	0.003
Ca^{2+}	0.09	0.005
TDS (g/L)	100000	710

Cores

Outcrop sandstone core plugs from a quarry in France were used in the experiments. Core plug specifications are listed in Table 3.

Table 3 Core material

Plug Name	Composition of Clay %		Total clay amount wt%	Permeability mD	Porosity %	Pore Volume ml
	Illite and/or micas	Chlorite				
B11	85	15	9.9	1243	20.0	15.9
B15	85	15	10.3	2303	20.4	16.3

Core preparation and test procedure

The dry cylindrical core was evacuated and saturated with connate brine under vacuum. Porosity and pore volume were calculated from weight difference between wet and dry core. The core was mounted in a Hassler core holder and at least 20 PV of the same brine was injected into the core to get a stabilized pH at the outlet and also a constant pressure drop across the core. The pressure drop was then used to calculate the permeability of the core to brine. A water saturation of 20% was established using desiccator, according to the procedure developed by Springer et al. (Springer et al., 2003). The core was again mounted in the Hassler core holder and 2 PV of oil was flooded through the core in both directions at 50 °C. After oil flooding the core was put in an

aging cell, surrounded by fresh oil, and aged at 60 °C for 2 weeks. Waterflooding tests were performed at 40 °C, and sequences of high salinity and low salinity brine was injected at a rate of 4 PV/day, followed by a period of high rate (close to 20 PV day) low salinity brine injection check for end effects. The volumes of produced water and oil were noted down at intervals. The oil recovery factor was calculated as percents of original oil in place (%OOIP). Samples of the effluent water were taken and pH and density were measured. Where a sequential restoration was needed, the core was first cleaned with n-Heptane until a clean effluent was obtained, to remove oil. Then the core was dried at 90 °C over night. Since different low salinity brines containing different ions were used (for different cores) the core was then flooded with 10000 ppm NaCl brine to wash out all the ions and make a baseline by having just NaCl, and again it was dried over night in the oven. The dry core was then subjected to the procedure as described above.

Adsorption studies

Materials

Solid material

Kaolinite clay powder provided by VWR International was used as the solid phase. The clay powder has been purified through washing by the manufacturer. The point of zero charge (PZC) for kaolinite has been measured to pH ~ 4 (Stumm and Morgan, 1996), above which it is negatively charged.

Organic material

A known amount of Quinoline, $pK_a = 4.9$, delivered by Merck, was dissolved in distilled water and pH was adjusted to ~5. The quinoline solution had a concentration of ~0.07M. The fraction of protonated base increases as the pH of the solution decreases below the pK_a value and reaches about 100% around pH 3.5 (Standal et al., 1999).

The 4-tert-butyl benzoic acid (PTBBA), $pK_a = 4.4$, was delivered by Fluka. The acid was dissolved in distilled water and the pH was adjusted to X by concentrated NaOH solution. The concentration of the PTBBA stock solution was ~0.07M.

Brines

The brines used were artificially made by dissolving desired amounts of salts in distilled water. The salts NaCl, $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 2H_2O$ were delivered by Merck. A 30000 ppm stock solution was made containing mostly NaCl in addition to 0.045M of both Ca^{2+} and Mg^{2+} . From this stock solution a 25000 ppm and a 500 ppm brine solution were made by dilution with distilled water.

Adsorption measurements

Adsorption of organic material onto kaolinite at room temperature was measured by a batch method. Kaolinite powder, 30 wt%, was rotated and equilibrated with brine for 2 hrs before addition of organic acid or base, and rotated and equilibrated for another 24 hrs. If necessary, pH was adjusted with HCl or NaOH. After equilibration, the ~10 ml samples were centrifuged at 2500 rpm for 20 min. 100 μ l of the supernatant was pipetted out and diluted 100 times. A Shimadzu UV-1700 PharmaSpec UV-VIS spectrophotometer was used to measure the absorbance at wavelength 312.5 nm for quinoline and at 235 nm for PTBBA. A calibration curve using known concentrations of acid/base was used to determine the acid/base concentration in the supernatant. The calibration curve varied with pH, therefore different calibration curves were used for different pH values. It was assumed that the calibration curves were similar regardless of salinity. Adsorption is reported as mg acid/base adsorbed per gram of kaolinite, and it is plotted versus equilibrium solution concentration of acid/base. Desorption was attempted by removing parts of the supernatant and replacing it with fresh brine, either of high salinity or low salinity. The salinity remained constant in the samples used for desorption with high salinity brine, while in the low salinity samples the salinity was gradually reduced in each desorption step. The samples were rotated for 24 hrs to re-establish equilibrium, and then adsorption was again measured.

Simulations

OLI systems stream analyzer 3.0 was used as software for the simulation studies. It is chemical model software based on thermodynamic equilibrium conditions using published experimental data. pH of Varg reservoir brine was calculated on the basis of increasing CO_2 or H_2S amount in the brine. The temperature was 75 °C and the pressure was kept at 100 atm to keep the CO_2 or H_2S gas in solution. Varg reservoir brine composition is given in table 4.

Table 4 Molar (mol/L) composition of Varg brine

	Varg
Cl ⁻	3.526
Mg ²⁺	0.144
Ca ²⁺	0.536
Na ⁺	2.086
K ⁺	0.051
Ba ²⁺	0.007
Si ²⁺	0.008
TDS (g/L)	201.56

Results and discussion

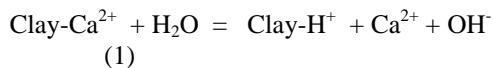
In this section, the suggested chemical mechanism for low salinity EOR will be presented first, and then, short experimental documentations for each step will be given. More detailed experimental documentation will be presented in forthcoming papers. Finally, based on the proposed mechanism, some criteria for evaluation of the potential for low salinity EOR effects are listed.

Proposed chemical low salinity mechanism

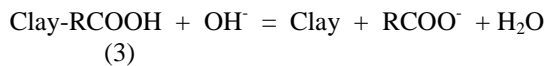
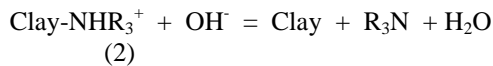
Regarding the observed experimental conditions for low salinity effects, it is assumed that the following parameters will play a major role:

- Clay properties/type and the amount present in the rock.
- Polar components in the crude oil, both acidic and basic.
- The initial formation brine composition and pH.
- It is further assumed that the EOR effect of low salinity flooding is caused by improved water wetness of the clay minerals present in the rock.

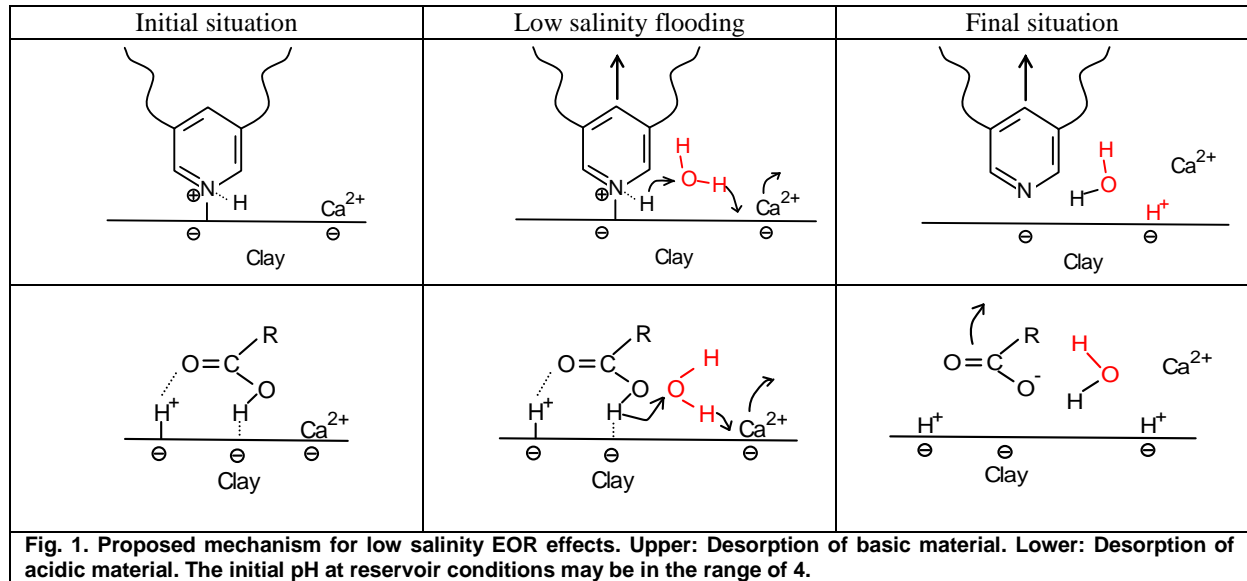
The clay acts as a cation exchanger with a relatively large surface area. Initially, both basic and acidic organic materials are adsorbed onto the clay together with inorganic cations, especially Ca²⁺, from the formation water. A chemical equilibrium is then established at actual reservoir conditions regarding pH, temperature, pressure etc. Remember that the initial pH of the reservoir formation water may be even below 4 due to dissolved CO₂ and H₂S. When the low saline water is injected into the reservoir with an ion concentration much lower than that in the initial formation brine, the equilibrium associated with the brine-rock interaction is disturbed, and a net desorption of cations, especially Ca²⁺, occurs. To compensate for the loss of cations, protons, H⁺, from the water close to the clay surface adsorb onto the clay, a substitution of Ca²⁺ by H⁺ is taking place. This creates a local increase in pH close to the clay surface as illustrated by the following equation using Ca²⁺ as an example:



The local increase in pH close to the clay surface causes reactions between adsorbed basic and acidic material as in an ordinary acid-base proton transfer reaction, as shown by eqs. 2 and 3.

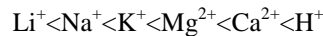


As will be illustrated later in the paper, the adsorption of basic and acidic materials onto clay minerals is very sensitive to changes in pH. Thus, desorption of initially adsorbed cations onto the clay is the key process in increasing the pH of the water that is localized close to the clay surface. An increase in pH is needed to remove some of the adsorbed organic material on the clay surface. The suggested mechanism is schematically illustrated in Fig. 1 for adsorbed basic and acidic material.



Properties of clay minerals

The presence of active clay minerals is necessary to obtain low salinity EOR effects. The crystal structure of common sandstone reservoir clays is made up of sheets of tetrahedral silica and octahedral aluminium layers. Clay minerals are often characterized as cation exchange material, because of structural charge imbalance, either in the silica or in the aluminium layer and also at the edge surfaces, causing a negative charge on the clay surface. The relative replacing power of cations is generally believed to be:



At equal concentrations, Ca^{2+} will displace more Na^+ than vice versa. The magnitude of the selectivity of different cations towards different clays varies considerably (Kleven and Alstad, 1996). It is also important to note that the proton, H^+ , has the strongest affinity towards the clay surface, but the concentration of H^+ is usually much lower than the concentration of cations present in the formation water at pH= 4-5.

Kaolinite is characterized as a 1:1 clay, that is, one unity consists of one tetrahedral silica layer and one octahedral aluminium layer. The unities are bonded together by strong hydrogen bonds, and kaolinite is known as a non-swelling clay, as indicated by the low surface area of 15-25 m²/g, Table 1. The charges within the structure are well balanced, which is also indicated by a relative low cation exchange capacity, 3-15 meq/100g, Table 1. The cation exchange mechanism for kaolinite is mainly linked to the edge surfaces. Kaolinite has a tendency to transform into illite and chlorite at greater depths.

Mica and Illite are characterized as 2:1 clays, that is, one unity consists of three sheets where the octahedral aluminum layer lies between two tetrahedral silica layers. The charge imbalance is located in the silica layers (Si^{4+} is replaced by Al^{3+} , which creates a negatively charged surface). The difference between mica and illite is only related to the degree of charge imbalance in the silica layers causing a lower negative surface charge on illite compared to mica. The structural units are bonded together by cations, and the clay may swell in a low saline environment. Both the cation exchange capacity and the surface area are much larger compared to kaolinite, Table 1. In this case, it is assumed that lattice substitution is the main mechanism for ion exchange, and the cation exchange capacity is in the range of 10-40 meq/100g.

Montmorillonite is similar in structure to mica and illite; a 2:1 clay. In this case, the charge imbalance is located in the octahedral aluminum layer in between the two tetrahedral silica layers (Al^{3+} may be replaced by Mg^{2+}). The clay has a very high cation exchange capacity, 80-150 meq/100g. As for mica and illite, the lattice substitution is believed to be the cation exchange mechanism for montmorillonite. Montmorillonite clay data are summarized in Table 1.

Chlorite is characterized as a 2:1:1 clay. The negatively charged mica structure units, 2:1, are bonded together by a “polymeric cation” brucite layer. It is an octahedral aluminum layer with charge imbalance (Al^{3+} may be

substituted by Si^{4+} , giving a positive charge). The surface area of chlorite is very large, $140 \text{ m}^2/\text{g}$, but the cation exchange capacity is in the same range as for mica/illite, 10-40 meq/100g. As for kaolinite, the edge surfaces will be the active place for cation exchange reactions. Chlorite clay data are summarized in Table 5.

Table 5 Properties of actual clay minerals (International Drilling Fluids (IDF), 1982)

Property	Kaolinite	Illite/Mica	Montmorillonite	Chlorite
Layers	1:1	2:1	2:1	2:1:1
Particle size (micron)	5-0.5	large sheets to 0.5	2-0.1	5-0.1
Cation exchange cap. (meq/100g)	3-15	10-40	80-150	10-40
Surface area BET- N_2 (m^2/g)	15-25	50-110	30-80	140

Polar components present in crude oil

The polar components in the crude oil, which are most suitable to adsorb onto reservoir minerals, are believed to have acidic or basic properties. The acids are often termed naphthenic acids, in which the carboxyl group is part of large molecules mostly present in the resin and asphaltene fraction, but also pure fatty acids are present in crude oil. The organic naphthenic acids have pK_a values around 4.9 as reported by Havre et al. (Havre et al., 2003). When pH is equal to the pK_a value, the concentration of the dissociated anionic form and the non-dissociated acid is equal. Depending on the conditions, both the anionic and the neutral form of the acid are able to adsorb onto reservoir minerals. The relative adsorption activity is surely depending on the pH.

The most active basic material in crude oil is cyclic nitrogen compounds of the pyridine type, containing a cyclic aromatic six-carbon ring. Like the carboxyl groups, most of the basic groups are also located in the heavy end fraction of the crude oil. Pyridines are weak bases with pK_a values of the protonated acidic form in the range of 4.7. Thus, carboxylic groups and the acidic form of the basic material have comparable pK_a values. Therefore, the fraction of undissociated acid and protonated base will show a very similar variation with the pH of the solution. This is important to be aware of when discussing adsorption/desorption of bases and acids from crude oil onto reservoir clay minerals.

Adsorption onto clay minerals

It is documented in the literature that the reservoir rock must contain active clay minerals, that the oil must contain polar components, and that the initial formation water must contain active cations, especially Ca^{2+} in order to observe low salinity effects. Furthermore, Lager et al. (Lager et al., 2008a) observed no correlation between the acid number of the crude oil and low salinity EOR effects. Very often in sandstone reservoirs at high temperatures, the base number is significantly higher than the acid number. The key to understanding the chemical mechanism of low salinity EOR is to obtain detailed knowledge about the interactions between polar components, clay and active cations in the brine.

Adsorption of basic compounds

Earlier adsorption studies of quinoline, a base of the pyridine type, onto kaolinite and montmorillonite showed great variation in adsorption capacity between the two clays, Fig. 2 (Burgos et al., 2002). The adsorption was strongly depending on the pH of the solution, and there appeared to be an adsorption maximum at pH of about 4. The maximum adsorption onto montmorillonite was about 100 times higher compared to kaolinite in CaCl_2 solutions. There is no doubt that it is the protonated cationic form of quinoline that is the most active species because the adsorption becomes very low as the pH increases to 8. It is interesting to note that the adsorption profile vs. pH is quite different for kaolinite and montmorillonite in the pH window between 4 and 8. For kaolinite, the adsorption is very low at $\text{pH} > 5$, less than 1 mmol/kg, while the adsorption onto montmorillonite is still above 100 mmol/kg at $\text{pH} = 7$, even though the fraction of the cationic form is very low at this pH. This indicates that also the neutral form of quinoline will adsorb onto montmorillonite, which is a 2:1 clay with charge imbalance in the octahedral layer in between the two tetrahedral silica layers. Obviously, there is a competition between the protonated base and the proton itself for the negatively charged adsorption sites on the clay. As the pH decreases, the concentrations of both species increase, and the adsorption of both components increases until the pH is about 4. At this pH, the fraction of protonated base is about 0.75, and at lower pH values, H^+ will even displace the protonated base from the clay surface. According to the cation exchange order listed above, the proton has the highest affinity towards the clay surface. Calcium, which has the second

strongest affinity to clay, will also compete with the protonated base for the adsorption sites on clay. Decrease in adsorption of quinoline is observed upon increasing the concentration of Ca^{2+} from 0.4 mM to 4.0 mM, Fig. 2 (Burgos et al., 2002). The decrease in adsorption of quinoline was, however, more significant for kaolinite compared to montmorillonite.

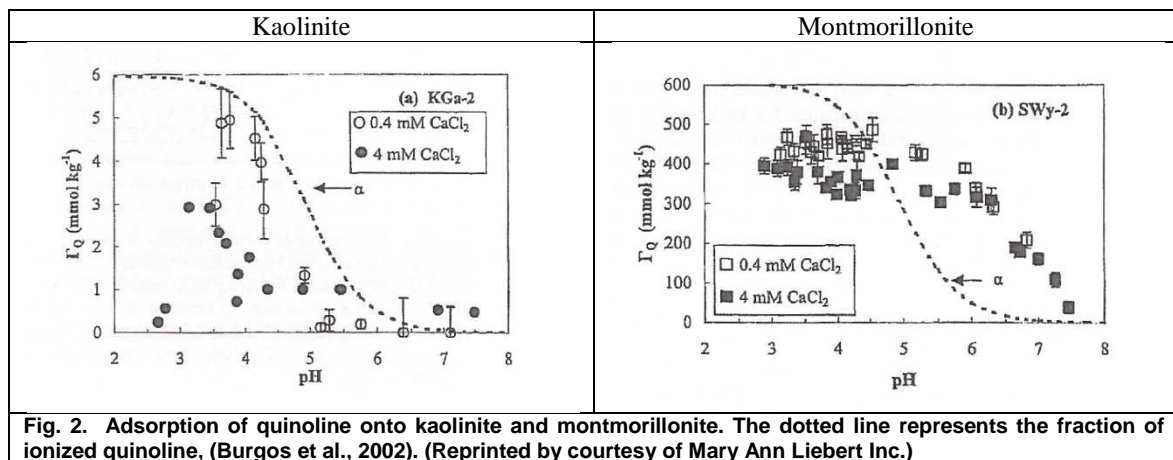


Fig. 2. Adsorption of quinoline onto kaolinite and montmorillonite. The dotted line represents the fraction of ionized quinoline, (Burgos et al., 2002). (Reprinted by courtesy of Mary Ann Liebert Inc.)

A very small decrease in adsorption of quinoline onto montmorillonite was observed when increasing the temperature from 4 to 60 °C (Doehler and Young, 1960). The fraction of protonated base is not very sensitive to changes in temperature because acid-base reactions with proton transfer are very fast having low activation energy.

The relative adsorption of quinoline onto actual clays has been found to increase in the following way; Kaolinite < Illite < Montmorillonite (Doehler and Young, 1960), which is consistent with the order of increased cation exchange capacity as shown in Table 1. In other words, the cation exchange capacity appears to be more important than the BET N_2 specific surface area, which is in the order: Kaolinite < Montmorillonite < Illite.

The salting in mechanism was tested by performing adsorption and desorption studies of quinoline onto kaolinite at room temperature. Adsorption was performed in high salinity brine, and desorption was performed with both high and low salinity brine. No significant difference between high saline and low saline condition in the desorption process was observed, Fig. 3.

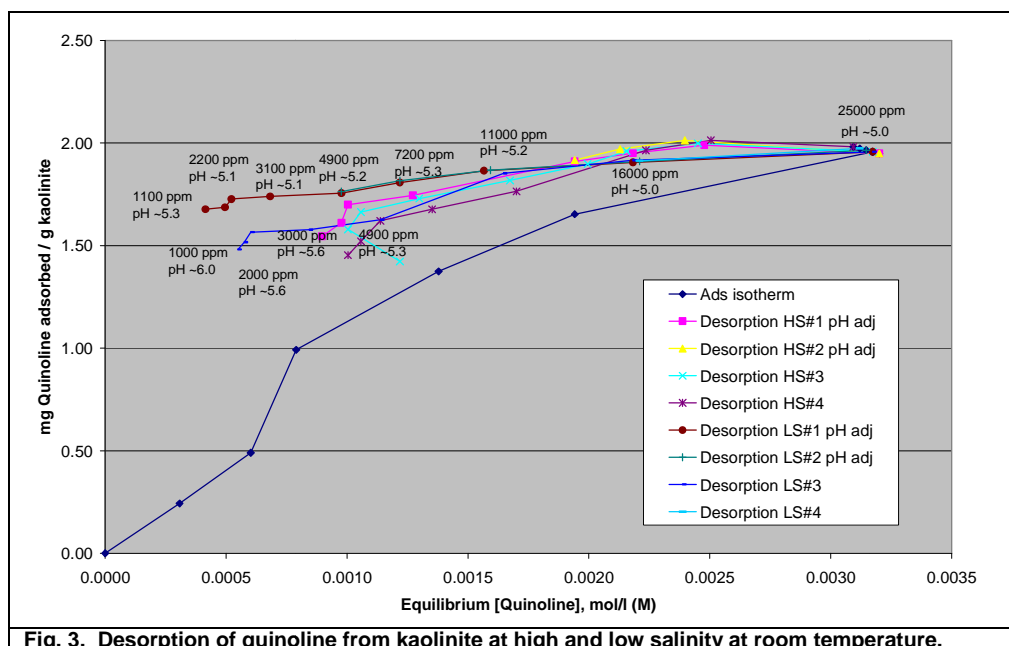
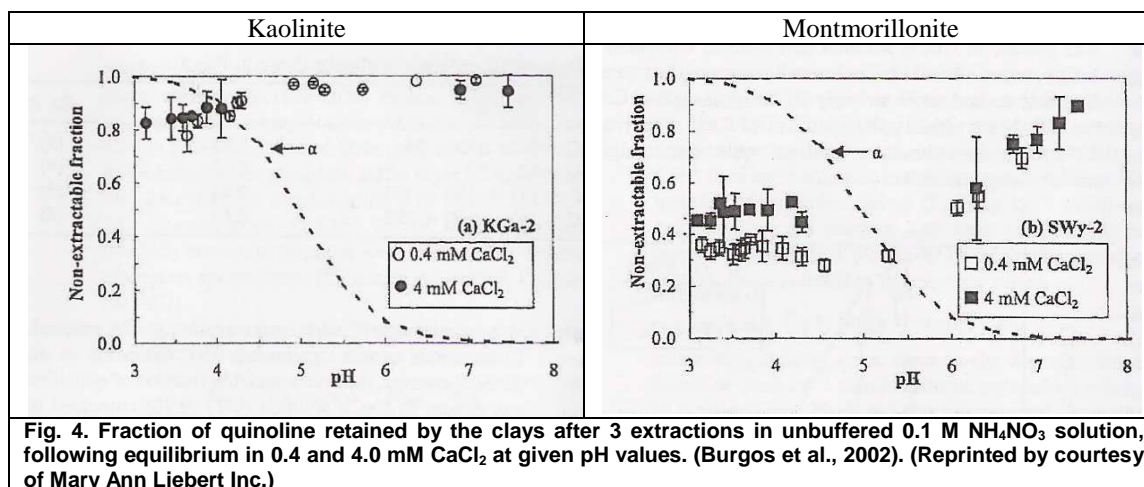


Fig. 3. Desorption of quinoline from kaolinite at high and low salinity at room temperature.

In the desorption tests, the pH was quite constant, and in the range of 5.0-6.0. Thus no significant desorption of quinoline due to salting in effects at low saline conditions could be observed, and for both high and low salinity conditions desorption was low. This is also in line with a previous study stating that the fraction of sorbed

quinoline that was retained by kaolinite following three sequential extractions in unbuffered 0.1 M NH_4NO_3 following equilibrations in 0.4 and 4.0 mM CaCl_2 was between 0.8 and 1.0 in the pH range of 3 to 7.5, Fig. 4 (Burgos et al., 2002).



In the case of montmorillonite, a similar study showed that a fraction of about 0.4 of quinoline was retained at pH values below the pK_a value, but as the pH increased to 7.5, the retained fraction increased to about 0.9. Thus, it appears that the adsorption of the base, which probably takes place by hydrogen bonding, is strong on both kaolinite and montmorillonite, and it is hard to remove it. If the pH at reservoir conditions drops to pH \sim 4-5, the cationic form of quinoline will be the most active species for adsorption. It is of interest to note that the effect of salinity in terms of CaCl_2 concentration was negligible for kaolinite, while for montmorillonite it appeared that quinoline was somewhat more retained at high CaCl_2 concentration at pH values below 5-6, while the salt effects were negligible at higher pH values.

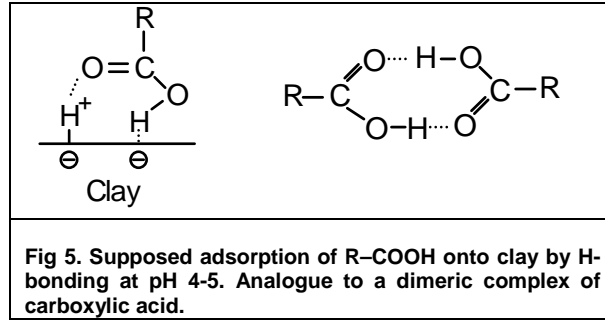
Adsorption of acidic compounds

Carboxylic material will also adsorb onto clay minerals as observed by Madsen and Lind in their studies of adsorption of benzoic acid onto kaolinite in a NaCl solution (Madsen and Lind, 1998). It is of great interest to note that the adsorption process also in this case is very sensitive to pH, and the adsorption increased as pH decreased, Table 6.

Table 6 Adsorption of benzoic acid onto kaolinite using a 0.1 M NaCl solution at 32 °C (Madsen and Lind, 1998)

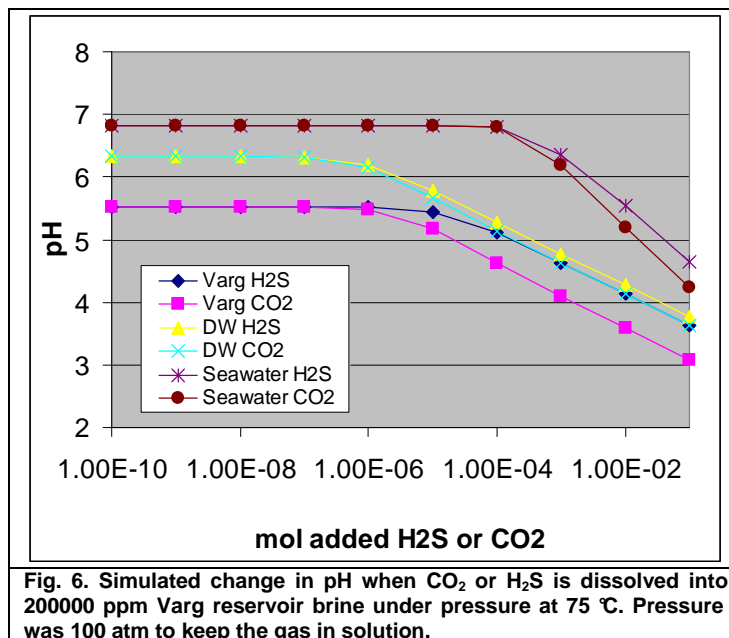
$\text{pH}_{\text{initial}}$	Γ_{max} $\mu\text{mole}/\text{m}^2$
5.3	3.7
6.0	1.2
8.1	0.1

Thus, the adsorption behavior of acidic and basic materials in crude oil appeared to have similar adsorption properties toward clay minerals regarding variation in pH. As pH decreases towards the pK_a value of the carboxylic material, usually in the range of 4-5, the fraction of the non-dissociated form of the carboxyl group increases, and it becomes equal to the anionic form. There is no doubt that non-dissociated carboxylic material will adsorb strongly onto clay minerals at pH values in the range of 4-5. The carboxylic acid group may bond to the clay surface by means of hydrogen bonding between the carbonylic oxygen and an adsorbed proton, and the proton of the carboxylic acid group can be attracted to a negatively charged site of the clay as illustrated in Fig. 5. The bonding is then similar to the bonding in a dimeric acid complex, which is regarded to be quite stable.



As pointed out by Buckley et al. (Buckley et al., 1998), the wetting behavior of carboxylic material may be more complex in the presence of divalent ions in the formation water. It was suggested that adsorbed Ca^{2+} may form a bridge between the clay and the carboxylate group. The MIE-mechanism suggested by Lager et al. (Lager et al., 2008a) was discussed in terms of such a bonding mechanism for organic material. Besides acting as a bridge between clay and acid in the adsorption process, carboxylic material can also be precipitated onto clay minerals as calcium carboxylate and in that way change wetting conditions.

The pH of the initial formation brine may vary more than 1 pH unit depending on the composition. The pH of the high saline Varg brine, which contains a high concentration of Ca^{2+} (Table 4) is about 5.5, while the pH of seawater is about 6.8, as shown by the modeling listed in Fig. 6. At reservoir conditions, and due to dissolved CO_2 and H_2S in the formation brine, the pH will decrease, but the decrease in pH is related to the composition of the water. The difference in the pH between the Varg brine and seawater, when the fluids contain 10^{-4} mole/l of CO_2 , is slightly more than 2 pH units, Fig. 3. A decrease in pH to about 4-5 will favor adsorption of the non-dissociated carboxylic acid onto clay on the expense of a bridging mechanism and precipitation caused by Ca^{2+} . It is of interest to note that adsorption of humic acids onto kaolinite and montmorillonite increases with increasing ionic strength and decreasing pH. It was also observed that the presence of Ca^{2+} enhanced adsorption compared to the presence of Na^+ (Feng et al., 2005).



Salting in effects were tested by studying the adsorption/desorption of 4-tert-butyl benzoic acid (PTBBA) onto kaolinite. The adsorption/precipitation isotherm at high salinity is shown in Fig 7. Four samples underwent desorption, two of them were desorbed with high salinity water and the remaining two with low salinity water. Significant differences in desorption curves were observed. At low salinity, the hysteresis between the adsorption/precipitation and desorption/dissolution curves was very small compared to the result obtained for the

high salinity tests. These observations indicate that salting in effects may have some contribution in improving the water wetness, especially if precipitation of calcium carboxylates is part of the wetting properties. This effect is relevant for oils with high AN. The pH of the initial samples was 6.3, while the final pH of high and low salinity desorption ended at 5.4 and 6.1, respectively, these differences may influence the results to some extent.

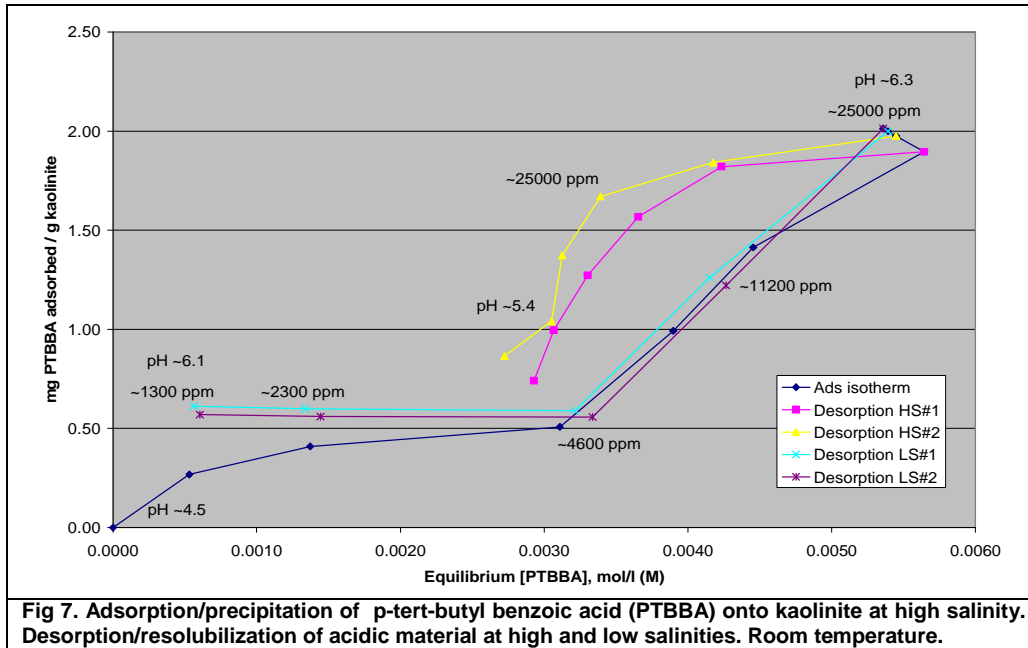
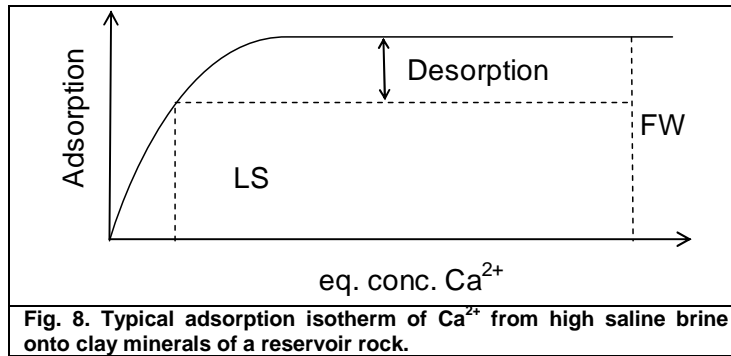


Fig 7. Adsorption/precipitation of p-tert-butyl benzoic acid (PTBBA) onto kaolinite at high salinity. Desorption/resolubilization of acidic material at high and low salinities. Room temperature.

Adsorption of cations

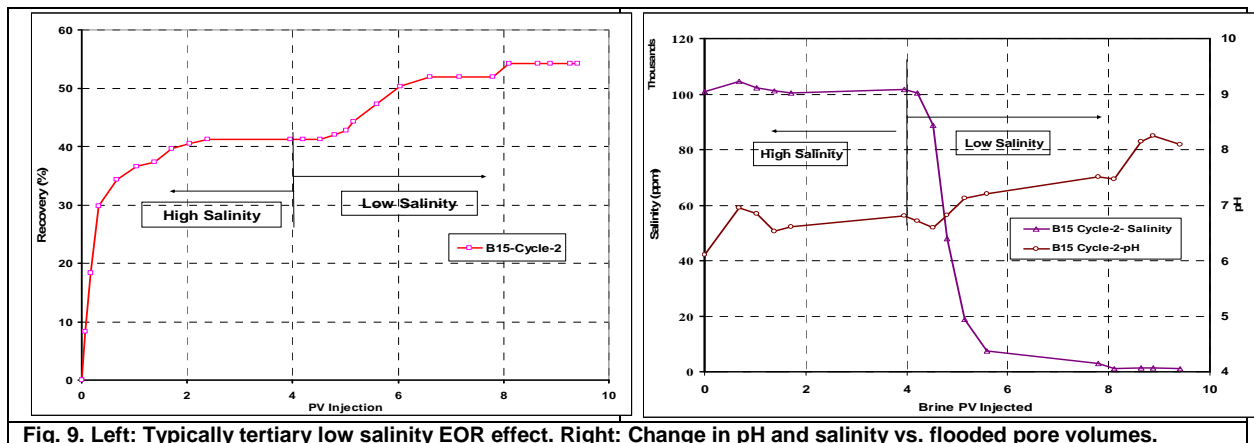
The proton, H^+ , has the strongest affinity toward the clay surface. The concentration of H^+ in the pH range 4-7 varies between 10^{-4} to 10^{-7} M, which is usually much lower than the concentration of Na^+ , Ca^{2+} and Mg^{2+} found in initial formation water. In a 200 000 ppm formation brine, the concentration of Ca^{2+} may be as high as 0.54M. At reservoir conditions, with a pH buffered formation water close to pH 4, both acidic and basic material are co-adsorbed onto the clay together with active cations like Ca^{2+} . If the concentration of the actual adsorbing material is high, and the number of potential negatively charged adsorption sites on the clay is limited, the adsorption isotherm for Ca^{2+} may have a large and nearly flat area as illustrated by Fig. 8. Thus, in order to observe a significant desorption of Ca^{2+} from the clay surface, the water must be diluted 10-100 times, as is the case for observing low salinity EOR effects. A local increase of pH at the water-clay interface that is needed to desorb the organic matter, will only take place if desorption of cations occurs.

As pointed out earlier, the mechanism for ion exchange is mainly linked to the edge surfaces for kaolinite and chlorite, and for illite/mica and montmorillonite it is assumed that the lattice substitutions are the main mechanism. Therefore, the selectivity characteristics of different cations vary for different clays. Concerning Na^+ and Ca^{2+} , kaolinite shows a strong selectivity for Ca^{2+} over Na^+ . For montmorillonite, however, the selectivity of Ca^{2+} is only slightly higher than for Na^+ (Kleven and Alstad, 1996). Due to the structural similarities between montmorillonite and illite/mica, it is reasonable to believe that the selectivity characteristics for Ca^{2+} and Na^+ towards illite/mica is more similar to montmorillonite than kaolinite. The structural similarity between kaolinite and chlorite regarding adsorption of cations indicates that the selectivity for Ca^{2+} towards chlorite is much higher than for Na^+ . Based on the suggested mechanism for observing low salinity EOR effects, the cations in the formation water must be able to compete with basic and acidic organic matter and H^+ for the adsorption sites on the clay surface. Therefore, a reservoir rock containing mostly kaolinite and/or chlorite as clay materials should contain significant amount of Ca^{2+} in the formation water, while a reservoir rock containing mostly illite/mica and/or montmorillonite may show low salinity effects even without divalent cations present in the initial formation water.

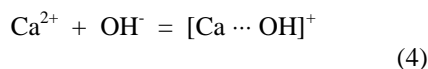


Local pH changes at the water-clay interface

When performing lab experiments, both formation water and injected water are usually prepared without adding a pH buffer like CO_2 , which is always present at reservoir conditions. Thus, the pH of the initial formation water in typical lab experiments is often in the range of 6-7, and the pH of the diluted formation water used as injection fluid in the low saline flood is approximately the same. Under such conditions, a sudden increase in pH of the produced water is always noticed provided that the formation water contained active cations like Ca^{2+} and clay minerals were present. The reason for the increase in pH is due to a sudden desorption of active cations as illustrated by Eq. (1). Because of the substitution of Ca^{2+} by H^+ , the pH is increased close to the clay surface, causing a fast desorption of basic and acidic material according to traditional acid-base reactions by proton transfer, as illustrated in equations (2) and (3). During a low salinity flooding laboratory test, a typical change in pH of the effluent may be from 6.5 to 8, as shown in Fig. 9.



For a given composition of the formation brine, the increase in pH of the effluent is depending to some extent on the composition of the injected brine. The presence of divalent cations in the injected fluid may give somewhat smaller increase in pH of the effluent due to complex formation of the type:



It is very important to note, that for a pH buffered system, the effluent pH may not show any increase at all. Low salinity EOR effects will, however, be observed because a local increase in pH close to the clay surface will still cause desorption of organic material according to the above listed reactions because the acid-base reactions are very fast. It has been stated in the literature that the activity of H^+ in the bulk solution as described by pH measurements may be quite different from the activity of H^+ close to interfaces between water and minerals. According to Bailey et al. (Bailey et al., 1968) the “*apparent surface acidity/basicity at the mineral-water interface of negatively charged clay minerals may be 2-4 pH units different from the bulk solution*”. Similar effects of pH have also been observed at liquid-liquid interfaces (Havre et al., 2003). Because of a dynamic flow condition, the desorbed material is transported away from the adsorption sites in an irreversible process. As a result, re-adsorption of desorbed material will not take place, and the desorbed surface area becomes more water-wet.

Based on the proposed chemical mechanism, the key to observing low salinity EOR effects is linked to desorption of adsorbed active ions by introduction of the low salinity fluid. At initial reservoir conditions the clay must not only contain adsorbed organic material, but in addition a significant amount of cations must be

adsorbed. Lager et al. (Lager et al., 2008a) observed no low salinity effects when the formation water did not contain divalent cations. Co-adsorption of polar components, cations and protons onto clay minerals is depending on type of clay and maybe most of all on the pH. The composition of the low saline injection water is not important, as long as the concentration of active ions is low enough to promote significant desorption from the clay surface (RezaeiDoust et al., 2009a).

At pH values above 2, silica is negatively charged (Buckley et al., 1998), and protonated cationic basic material will adsorb onto the surface. Silica is, however, not acting as a cation exchanger, and local increase in pH close to the water-silica interface will not take place during a tertiary low salinity waterflood. This is in line with experimental observations that active clay material must be present in the sandstone in order to obtain low salinity effects.

Is multi ion exchange, MIE, the low salinity mechanism?

It was stated by Lager et al. (Lager et al., 2008a) that cation exchange between the mineral surface and the invading low salinity brine was the primary mechanism underlying the improved waterflood recovery observed with low salinity waterflooding. When divalent ions, from the invading low saline brine, exchange with either cationic organic complexes or with bases due to the change in ion exchange equilibria, bound oil becomes mobile and an increase in oil recovery ensues. This mechanism was termed Multi Ion Exchange, MIE, by Lager et al. (2006 SCA Trondheim) A decrease in the concentration of multivalent cations, especially in the concentration of Mg^{2+} , in the effluent of core floods even below the concentration present in the injected low saline water, was a very important documentation of the MIE mechanism. In a recent paper Lager et al. (Lager et al., 2008b) observed that the concentration of Mg^{2+} changed dramatically in the produced water during a low salinity field test in Alaska. These results were in line with earlier observations in the laboratory. A similar, but much smaller change in the concentration of Ca^{2+} was also noticed. Lager et al. interpreted this observation as a field documentation of the MIE mechanism. It should be noticed that the concentrations of Mg^{2+} and Ca^{2+} in the injected low saline waters were $(0.78 - 1.35) \times 10^{-3}$ and $(1.77 - 2.52) \times 10^{-3}$ mol/l, respectively. Furthermore, initial pH of the produced water was about 8.0. The following question was asked: "Will Mg^{2+} and possibly Ca^{2+} precipitate as $Mg(OH)_2(s)$ and $Ca(OH)_2(s)$ as the pH is increased due to the desorption of cations from the clay surface at the front of the invading low saline fluid as indicated in Eq. (1)?" The solubility of $Mg(OH)_2$ and $Ca(OH)_2$ was modeled in a 50 000 ppm NaCl solution at 50 and 100 °C and at a pressure of 6 bars, Fig. 10. The solubility of both $Mg(OH)_2$ and $Ca(OH)_2$ decreases drastically as the temperature increases at given pH, about a factor 100 when increasing the temperature from 50 to 100 °C. At $pH \approx 8$, the solubility of $Mg(OH)_2$ is about 10^{-3} mole/l, and by increasing the pH just one pH unite to 9, the concentration of Mg^{2+} drops to about 10^{-5} mole/l due to precipitation of $Mg(OH)_2$. Thus, a local increase in pH above 8 will will precipitate $Mg(OH)_2$ from a 10^{-3} molar low saline solution of Mg^{2+} . A much larger increase in pH , $pH \approx 11$, is needed to precipitate $Ca(OH)_2$ from a solution of 10^{-3} mole/l of Ca^{2+} .

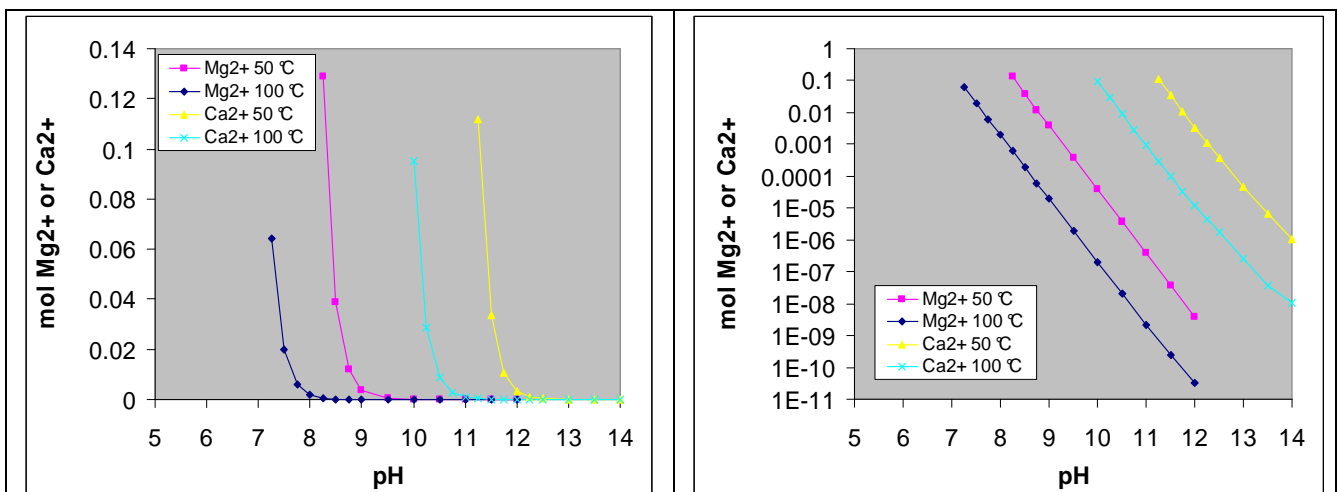
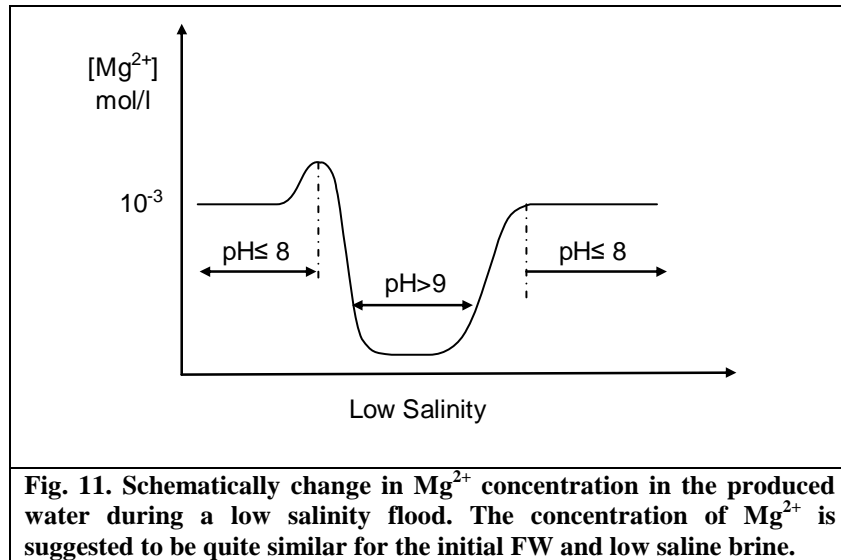


Fig. 10. Solubility of $Mg(OH)_2$ and $Ca(OH)_2$ versus pH at 50 and 100 °C in a 50 000 ppm NaCl brine and 6 bars. Logarithmic scale to the right.



Generally, the variation in the Mg^{2+} concentration in the produced water is illustrated in Fig. 11 (Lager et al., 2008b). First, the concentration is constant and similar to the concentration of the formation water, and then an increase in the concentration is observed probably due to desorbed Mg^{2+} present in the bank of the formation water ahead of the injected low saline fluid. Next, the strong decrease in the Mg^{2+} concentration to a concentration that is much lower than in the injected low saline water, is caused by precipitation of $Mg(OH)_2$. The pH increases because cations adsorbed onto the clay are transferred into the low saline brine as shown by Eq. 1. The subsequent increase in the Mg^{2+} concentration occurs, when the equilibrium between the low saline water and the clay has been established, and the pH has decreased again. Thus, the change in the concentration of Mg^{2+} is not necessarily caused by a MIE process, as stated by Lager et al. (2006 SCA in Trondheim). It can also be explained by precipitation of $Mg(OH)_2$ as a result of a local increase in pH in the injected low saline water. Precipitation of $Mg(OH)_2$ will decrease the local alkalinity, which may have impact on the desorption of organic material from the clay surface. Therefore, the concentration of Mg^{2+} in the low saline fluid should be low or absent. It is, however, no chemical reason, that the strongly hydrated Mg^{2+} ion should have a superior reactivity towards the active sites on the clay surface compared to Ca^{2+} . It is documented by laboratory tests, that similar tertiary low salinity EOR effects are obtained without any divalent cations present in the low saline fluid (RezaeiDoust et al., 2009a).

Optimal conditions for observing low salinity EOR effects

Based on the suggested description of the chemical mechanism for low salinity EOR effects, some important notations concerning laboratory test procedure and some criteria for optimal low salinity EOR effects can be put forward. Detailed parametric studies on each of the involved steps concerning oil properties, salinity and composition of formation water, composition and salinity of injected low salinity water, temperature, etc. are in progress and have partly been performed and will be presented in forthcoming separate papers in order to verify the suggested mechanism.

Initial wetting properties/core preparation

The strong pH dependence on adsorption and desorption of acidic and basic material onto different clay minerals is very important. In many cases, the potential of low salinity effects related to a specific reservoir is first tested at laboratory conditions, at given reservoir temperature, with stabilized oil with reasonable high AN and/or BN, and with a given composition of formation water without dissolved CO_2 . At these conditions, the initial pH of the formation water is too high compared to reservoir conditions, which means that the adsorption of polar components onto clay minerals becomes too low compared to reservoir conditions. Suppose a situation where the lab pH is 6 and an actual reservoir pH is 4. If the main clay mineral is kaolinite, there is a great difference in wetting properties between lab and reservoir to be expected. In an equivalent situation with montmorillonite as the main clay material, the difference in wetting properties is probably lower, Fig. 2. It is therefore important to perform the tests under pressure to include CO_2 as a pH buffer in order to obtain initial wetting properties as close to reservoir conditions as possible.

In order to see the effect of increased adsorption of both acidic and basic components onto the clay materials, the same outcrop core was treated in two different ways, Fig. 12. The same high salinity formation water and low salinity injection fluid were used.

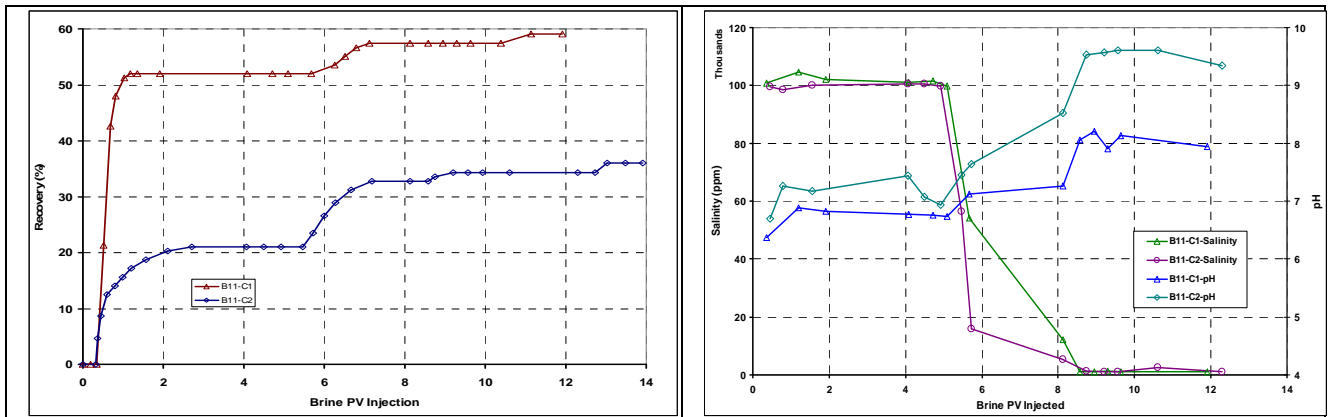


Fig. 12. Left: Tertiary low salinity effects for the same core treated in two different ways. Right: Increase in pH and decrease in salinity vs. flooded pore volumes.

First, the core was treated with an oil with high AN and low BN (C1 – cycle 1), and the high salinity secondary recovery was slightly above 50%. Low salinity waterflood increased the recovery to nearly 60%, an increase in oil recovery of about 20%. The core was not cleaned in the ordinary way with toluene and methanol, but only flooded with n-heptane followed by 10 000ppm NaCl solution to remove the low salinity brine and residual oil. Heptane decreases the solubility of active polar carboxylic material and promotes increased adsorption onto reservoir minerals, especially clays. Thereafter, in cycle 2 (C2) the core was treated with formation water and an oil with low AN and high BN, followed by aging. Obviously, the core became much less water wet, and only slightly more than 20% of the oil was recovered in the secondary high salinity flood. However, in the tertiary low salinity flood the oil recovery increased to about 35%, i. e. an increase in oil recovery of about 75% relative to the recovery after the secondary waterflood. It was also noted that the increase in pH was significantly higher in the second case, ΔpH 2.5 versus ΔpH 1.4 units in the first case.

Properties of the clay present

The suggested chemical mechanism presented in this paper requires both polar components and active cations to be initially adsorbed onto the clay. Thus, clay minerals of high cation exchange capacity appear to favor low salinity effects. Among the clays usually present in reservoir sandstones, kaolinite has the lowest cation exchange capacity according to Table 1 (International Drilling Fluids (IDF), 1982), and is therefore probably the least favorable clay material for low salinity flooding. Based on the cation exchange capacity, the order of favorable type of clay minerals should be: kaolinite < illite/mica < montmorillonite.

Crude oil

Polar components must be present, and the AN and BN give a good quantitative indication of the content of active polar components. Both basic and acidic material will adsorb onto clay at pH values of about 4. The total wetting conditions are different for a crude oil with high AN and low BN compared to a crude oil with low AN and high BN, because in the latter case, basic components are also able to adsorb onto negatively charged silica, Table 1. Therefore, in the former case, the high saline secondary oil recovery is significantly higher than in the latter case, but the tertiary low salinity EOR effects were quite similar, as shown in Fig. 13. Thus, there appears to be no restrictions to the type of polar components present in the crude oil provided that a significant amount is present.

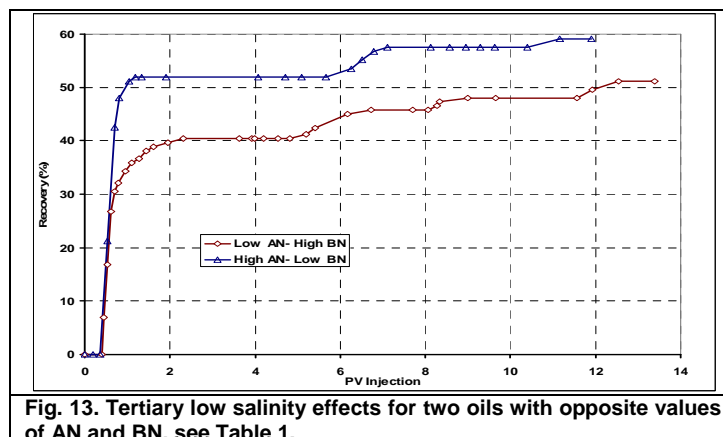


Fig. 13. Tertiary low salinity effects for two oils with opposite values of AN and BN, see Table 1.

Formation water

The formation water must contain active cations, especially Ca^{2+} . Optimal low salinity EOR effects are depending on a balanced initial adsorption of active cations, protons, and organic material onto the clay surface. Thus, for a given crude oil and reservoir rock, both pH and the composition and amount of divalent cations are determined by the properties of the formation water. If the amount of adsorbed organic material is low, which may be the case at pH 6-7, and even though the adsorption of active ions is high, which will give an increase in pH during the low salinity flood due to desorption, the low salinity EOR effect will be low because the rock is already too water-wet. It appears that as long as the concentration of active ions is above a certain level, the initial pH will play a very important role for optimal initial adsorption conditions of the mentioned active species.

Injection fluid

The composition of the low saline injection water appears to be of less importance, as long as the concentration of active ions, are low enough to promote significant desorption from the clay surface. Studies with different composition of the low saline water but at similar ionic strength gave similar tertiary low salinity EOR effects (RezaeiDoust et al., 2009a). Ligthelm et al. discussed the low salinity EOR effect in terms changes in the ionic double layer close to the clay surface. This may be a secondary effect, but the primary effect appears to be a local increase in pH at the water-clay interface related to desorption of active cations.

Conclusions

Based on previous published work on the effect of pH on the adsorption of acidic and basic components relevant to crude oils and new studies on adsorption and core flooding, a new chemical mechanism has been suggested for the tertiary low salinity EOR effect, which can be shortly summarized in the following way:

- Initially there is a balanced adsorption onto the clay minerals of organic material, active cations and protons, preferentially at a reservoir pH of about 4.
- Injection of low salinity brine will cause desorption of adsorbed cations, which will increase the pH close to the water-clay interface because Ca^{2+} is substituted by H^+ on the clay surface.
- An ordinary acid-base reaction takes place between OH^- and the adsorbed acid and protonated base which promotes desorption of organic material. The water wetness increases and increased oil recovery is observed.
- The cation exchange capacity of the clay, which is in the order: kaolinite < illite/mica/chlorite < montmorillonite, appears to be an important parameter for low salinity effects.
- Different clays have different adsorption/desorption pH window. It is therefore important to prepare the cores at relevant reservoir pH, usually around 4.
- At low water-wet conditions, great increase in oil recovery, 75%, can be obtained in the laboratory if the core preparation is optimized.
- Previously, the documentation of the MIE mechanism has very much linked to the change in the concentration of Mg^{2+} in the produced low salinity water. It is shown by modeling that the change in the Mg^{2+} concentration can also be explained by precipitation of $\text{Mg}(\text{OH})_2$ due to a local increase in pH of the low saline fluid.

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