# LOW SALINITY OIL RECOVERY - AN EXPERIMENTAL INVESTIGATION

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*This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Trondheim, Norway 12-16 September, 2006*

**Abstract:**
The idea of injecting low salinity water into a petroleum reservoir is not novel and was often used in the 70's prior to the injection of surfactant. Yet, recently it was shown that simply injecting sufficiently low salinity water improves oil recovery (LoSal™). Many possible mechanisms concerning Low salinity waterflood have been proposed in the literature. This paper describes an experimental investigation into some of the factors controlling the increased oil recovery observed when low salinity brine is injected into oil saturated reservoir core samples. Extensive chemical analyses were performed on the effluent showing the extent of interaction between the injected brine, the oil and the rock matrix.

**Introduction:**
It has been 10 years since Yildiz and Morrow [1] pushed forward the research started by Jadhunandan [2-4] and published their paper on the influence of brine composition on oil recovery which showed that changes in injection brine composition can improve recovery. Since then Tang & Morrow [5] progressed the research on the impact of brine salinity on oil recovery, followed by other researchers such as Webb et al. and McGuire et al. [3], which carried out an extensive research programme on low salinity injection (LoSal™). This programme included numerous core floods at ambient and reservoir condition (Temperature and Pressure, with live fluid) both in secondary and tertiary mode, single well tracer tests and log inject log, which resulted in a series of publications [6-8] and the registration of the LoSal™ EOR process trademark.

Numerous hypotheses have been devised to explain the increase in oil production associated with low salinity water injection, including increasing pH leading to In-situ saponification and interfacial tension reduction, emulsion formation, clay migration, and wettability alteration. In this paper the fines migration and pH increase mechanism are reviewed and discussed in the light of new data obtained during ambient and reservoir condition low salinity floods. Also a new mechanism based on the extended DLVO theory and cation exchange is discussed.

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**Experiments:**
All corefloods discussed in this paper were performed on nominally 3” long by 1.5” diameter plug samples from sandstone oil reservoirs. Plug samples were loaded into hydrostatic coreholders and miscibly solvent cleaned with cycles of toluene and methanol, prior to saturation with simulated formation brine. Initial water saturation was acquired by constant pressure oil flood. Values were found to be matched to those corresponding to the height of the sample above the oil water contact. From analyses of sister samples using in-situ saturation data, the distribution of water was uniform across the length of the core samples. In all cases simulated formation water was used for the initial water.

Samples were then loaded into hydrostatic coreholders, prior to taking the samples to the conditions of the test. Refined laboratory oils were displaced with the crude oil, via a slug of toluene to provide a buffer between the lab oil and the crude oil. The sample was then shut in for a period of time (ageing).

Waterfloods were then performed on the samples by injecting brine at constant flow rate at elevated temperature and with nominal back pressure on the plug samples, to ensure no gas production from the oil. For tertiary low salinity waterfloods, high salinity connate brine was first injected. Differential pressure and oil production were continuously monitored, and brine was injected until no further oil production or change in pressure was recorded, at which time low salinity water injection commenced from the low oil saturation achieved after high salinity brine injection. Once again differential pressure and oil production were monitored. Secondary low salinity waterfloods were performed in an identical manner, but low salinity brine was injected into the sample at initial water saturation. During the course of the low salinity injection pH was monitored in the effluent by taking aliquots of effluent brine. In some cases, which are described later, aliquots of the effluent were also taken for ion analyses using inductively coupled plasma mass spectroscopy (ICP).

Mechanistic studies were performed at reduced conditions of pressure and elevated temperature.

**Results & Discussion**

1. **Fines Migration:**

An attempt to explain the LoSal™ mechanism was put forward by Tang and Morrow. They noticed fines (mainly Kaolinite) being eluted during low-salinity waterfloods on Berea core samples. They concluded that fines mobilisation resulted in exposure of underlying surfaces, which increased the water-wetness of the system. (Earlier work had shown that optimum waterflood displacement efficiency occurs under weakly water wet conditions.) In the presence of high salinity brine, clays are undisturbed and retain their oil wet nature leading to poorer displacement efficiency. When contacted with low-salinity water, clay particles detach from the pore surface. Lever and Dawe [9] showed that the released fines migrate with flowing fluid and are subsequently captured at pore

throats or pore constrictions, causing formation damage. Tang and Morrow supposed that the detachment of mixed-wet clay particles from pores mobilised previously retained oil droplets attached to these clays, allowing an increase in oil recovery. They also reported a reduction in permeability when the injection brine salinity was less than 1550 ppm TDS. This reduction in permeability was observed when the low-salinity brine replaced the initially permeating high-salinity brine. Valdya and Fogler [10] showed that the release process is primed by a combination of extremely low-salinity and high pH. They reported little change in permeability when fluids with increasing pH were injected until an injection pH of 9 was reached. At a pH > 11 a rapid and drastic decrease in the permeability was observed implying that sever damage was caused on contact with the high-salinity fluid and the absence of salts in the solution.

The mechanism of fines migration was explained by the Deryaguin-Landau-Verwey-Overbeek (DLVO) theory of colloids. The permeability reduction occurs if the ionic strength of the injected brine is equal to or less than, the critical flocculation concentration (CFC), which is strongly dependent on the relative concentration of divalent cations such as $Ca^{2+}$ and $Mg^{2+}$ [11, 12]. Divalent cations have been known to stabilise the clay by lowering the Zeta potential resulting in the lowering of the repulsive force. Also Bazin and Labrid [13] indicated that water sensitivity is related to the cation exchange capacity (CEC) of clay sandstones. They concluded that high CEC sandstone will lead to a high potential for permeability reduction.

As Tang & Morrow showed, it is possible to have fines migration during low salinity injection. However, during numerous BP Low salinity reduced condition and full reservoir condition corefloods, which have all shown increased oil recovery, no fines migration or significant permeability reductions have been observed. These results question the link between fines migration and oil recovery.

**2. pH variation:**

Some studies have shown a rise in pH during LoSal™ laboratory experiments (fig 1). This rise in pH is due to two concomitant reactions: carbonate dissolution and cation exchange. The dissolution of carbonate (i.e. calcite and/or dolomite) results in an excess of $OH^-$ and cation exchange occurs between clay minerals and the invading water. The dissolution reactions are relatively slow and dependent on the amount of carbonate material present in the rock

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \quad (1)$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad (2)$$

However, cation exchange occurring on the clay minerals, and to a much lesser extent quartz, is faster. The mineral surface will exchange $H^+$ present in the liquid phase with cations previously adsorbed. This will lead to a decrease in $H^+$ concentration inside the liquid phase resulting in a pH increase.

If a pH above 9 was achieved inside a petroleum reservoir this would be equivalent to an alkaline waterflood. According to Jensen & Radke [14], the mechanisms active at the

front where alkaline water is displacing acidic crude oil include: (1) a reduction of oil/water interfacial tension, (2) wetting alteration of the matrix grains, (3) formation of water drops inside the oil phase, and (4) drainage of oil from the volume between alkaline water drops to produce an emulsion containing very little oil.

The initial results from Tang [5] on Berea sandstone and early experiments performed at Sunbury on a North Sea reservoir system (Fig 1) clearly exhibit a rise in pH. The explanation given at the time for this increase was that carbonate dissolution was sufficient to generate this order of pH. The evidence showing a pH increase during Low salinity floods was cited in a paper [6] to suggest that Low salinity waterflood worked like an Alkaline waterflood.

However, conflicting evidence throws doubt on this mechanism being the cause of the LoSal™ effect. The best Low salinity coreflood results obtained to date come from a North Sea reservoir (ca. 40% increase in oil recovery) which has crude oil with a very low acid number (AN < 0.05). According to the literature [15] on Alkaline waterflooding, a high AN (AN > 0.2) is needed to generate enough surfactant to induce wettability reversal and/or emulsion formation. Also no direct correlation has been found between the increase in oil recovery due to low salinity waterfloods and the acid number of the crude oil (fig. 2). As the number of low salinity waterfloods performed increased, some evidence started to emerge that the benefit of LoSal™ could be achieved at a pH below 7.

Heriot Watt University performed an experiment on a North Slope core sample where the pH rose from 5 to 6 (Fig 3a) with an increase in oil recovery. A geochemical model using PHREEQC, was created simulating a low salinity waterflood. The model gave only an approximation of the pH variation as the organic phase is extremely difficult to model accurately. Interestingly, when the model contains traces of carbonate, the pH rises and then slowly decreases, as observed in the HW experiment (fig 3c) but if the carbonates traces are removed, the pH drops. This disputes the earlier hypothesis that the main drive for the pH variation is the carbonate dissolution.

According to Appelo [16] the injection of fresh water in a saline aquifer is accompanied by a loss of $Na^+$ and $Mg^{2+}$ from the exchanger and an increase in $Ca^{2+}$ at the exchanger surface. In principle the loss of $Ca^{2+}$ from solution is sufficient to drive the dissolution reaction which should increase the pH up to 10. However, this is not observed in an aquifer due to proton buffering, which will keep pH at about 7 to 8. Proton buffering is due to the desorption of proton ($H^+$) from oxides and organic matter. It is also due to the desorption of complexes, in combination with reactions from oxides [17]. Furthermore, due to technical limitations, none of the experiments showing a change in pH were performed at reservoir conditions with live fluids. The majority of petroleum reservoirs contain $CO_2$ which will act as a pH buffer, rendering an increase of pH up to 10 unlikely if not impossible in most reservoirs.

The results obtained, unequivocally prove that despite previous evidence, high pH is not responsible for the increase in oil recovery due to the injection of low salinity water. This is important as it would have been very unlikely that such an increase would have been

sustainable in a petroleum reservoir due to the proton buffering from oxides present in the reservoir rocks and the significant amount of $CO_2$ present in some petroleum reservoirs.

### 3. Multicomponent Ionic Exchange (MIE):

At the same time as pH measurements were carried out, geochemical analysis of the low salinity effluents were performed. These highlighted the predominant role of multicomponent ionic exchange (MIE) chromatography on the water chemistry during waterflooding. Multicomponent ionic exchange is the basis of geochromatography. It involves the competition of all the ions in pore water for the mineral matrix exchange sites. Because natural exchangers show different selectivity for different cations, the ratio of sorbed over solute concentration is variable for individual cations. This theory was applied to enhanced oil recovery in the 70's by Pope et al. [18] but the best application of this theory was done by a Hydrogeologist who studied the invasion of saline aquifers by fresh water. Valocchi et al. [19] injected fresh water in a brackish water aquifer and noticed that the concentration of $Ca^{2+}$ and $Mg^{2+}$ in different control wells were lower than the invading water and the connate brine. Similar results were witnessed during low salinity floods done at BP and Heriot Watt (Fig 4a & 4b). The evidence of MIE came from the effluent analysis of a North Slope low salinity coreflood. The injected brine and the connate water had similar $Mg^{2+}$ concentration (55 ppm). However the effluent analysis showed a sharp decrease in $Mg^{2+}$. This indicates that $Mg^{2+}$ was strongly adsorbed by the rock matrix. Similar results were obtained by Heriot Watt University on two different floods performed on the same system. $Ca^{2+}$ and $Mg^{2+}$ were strongly adsorbed until the rock matrix was fully saturated.

Following these results a mechanism was formulated around the possibility that MIE was responsible for the increase in oil recovery. According to the extended DLVO theory [20] and Sposito [21] , 8 different possible mechanisms of organic matter adsorption onto clay mineral (table 1) are possible depending on the organic function of the organic matter and the condition of the clay surfaces. Out of those 8 mechanisms, 4 will be strongly affected by cation exchange occurring during a low salinity brine injection; cation exchange, ligand bonding and cation and water bridging (fig 5)

| *Mechanism* | *Organic functional group involved* |
|---|---|
| Cation exchange | Amino, ring NH, heterocyclic N (aromatic ring) |
| Protonation | Amino, heterocyclic N, carbonyl, carboxylate |
| Anion exchange | Carboxylate |
| Water bridging | Amino, Carboxylate, carbonyl, alcoholic OH |
| Cation bridging | Carboxylate, amines, carbonyl, alcoholic OH |
| Ligand exchange | Carboxylate |
| Hydrogen bonding | Amino, carbonyl, carboxyl, phenolic OH |
| Van der Waals interaction | Uncharged organic units |

**Table 1, Mechanism of association between organic functional groups and soil minerals (from Sposito, 1989)**

Adsorption by cation exchange occurs when molecules containing quaternized nitrogen or heterocyclic ring replace exchangeable metal cations initially bound to clay surface. Ligand bonding refers to the direct bond formation between a multivalent cation and a carboxylate group. These bonds are stronger than cation bridging and cation exchange bonds and lead to the detachment of organo-metallic complexes (RCOO-M; where M represents the multivalent cation) from the mineral surface. Cation bridging is a weak adsorption mechanism between polar functional group and exchangeable cations on the clay surface. It is to note that on some occasion if the exchangeable cation is strongly solvated (i.e $Mg^{2+}$) water bridging will occur. It involves the complexation between the water molecule solvating the exchangeable cation and the polar functional group of the organic molecule. In several studies regarding organic matter adsorption onto clay minerals in seawater [12, 20, 22, 23], it has been found that van der waals interactions, ligand exchange and cation bridging are the dominant adsorption mechanisms.

On an oil-wet surface, multivalent cations at a clay surface will bond to polar compounds present in the oil phase (resin and asphaltene) forming organo-metallic complexes. Such complexes have been shown to promote oil-wetness in petroleum reservoirs [24]. At the same time, some organic polar compounds will be adsorbed directly to the mineral surface displacing the most labile cations present at the clay surface, enhancing the oil wetness of the clay surface. During the injection of low salinity brine, MIE will take place, removing organic polar compounds and organo-metallic complexes from the surface and replacing them with uncomplexed cations. In theory, the desorption of polar compounds from the clay surface should lead to a more water-wet surface, resulting in an increase in oil recovery .

To test this mechanism, an experiment was devised to replace all the multivalent cations present on the mineral surface by $Na^{+}$. A North Slope core sample was flushed repeatedly with a brine containing only NaCl until the effluent showed only traces of $Ca^{2+}$ and $Mg^{2+}$. Two shut ins were performed to make sure that no carbonates was left undissolved. Once the core surface was fully saturated with $Na^{+}$, oil was flooded until a Swi of 12% was obtained. After aging, high salinity brine, containing only NaCl was flushed through the core followed by low salinity brine containing only NaCl. Finally a tertiary flood was performed using low salinity brine containing $Ca^{2+}$ and $Mg^{2+}$.

By doing so, the formation of organo-metallic complexes on the mineral surfaces due to the presence of multivalent cations on the mineral surface, was prevented and only van der Waals interactions occured. If MIE is the predominant mechanism, the primary high salinity flood should yield a higher oil recovery due to the absence of oil adsorption by ligand formation and multivalent cation bridging and exchange. Also the secondary LoSal flood should not produce any oil as all the “mobile” oil would have been displaced by the primary flood and no organo-metallic complexes are present to be desorbed. Finally a tertiary LoSal flood containing divalent cations should not produce any oil as only non-complexable monovalent cations (i.e. $Na^{+}$) will be desorbed from the mineral surface by the divalent cations present in the invading brine.

The results of the experiments matched the predictions. Firstly the North slope core sample was prepared to a representative initial water saturation and aged in dead crude oil. The initial screening experiments were conducted at 25$^{o}$C. A conventional high salinity waterflood gave a recovery of 42% OOIP and a tertiary Low salinity flood resulted in a total recovery of 48% OOIP (i.e. an additional 5% OOIP). A second suite of experiments were conducted at reservoir temperature (102$^{o}$C). A conventional high salinity waterflood resulted in a recovery of 35% OOIP. The core was flushed with a brine containing only high salinity NaCl until $Ca^{2+}$ and $Mg^{2+}$ was effectively eluted from the pore surface. Initial water saturation was re-established and the sample aged in crude oil. A high salinity waterflood consisting of NaCl (no $Ca^{2+}$ and $Mg^{2+}$) resulted in a recovery of 48% OOIP. A tertiary low salinity flood was then conducted (again no $Ca^{2+}$ and $Mg^{2+}$) and no additional recovery observed (fig. 6). This was followed by a low salinity flood with $Ca^{2+}$ and $Mg^{2+}$ present and again no additional recovery was observed. This sequence indicated that high salinity connate brine containing $Ca^{2+}$ and $Mg^{2+}$ resulted in poor recovery. Removing the $Ca^{2+}$ and $Mg^{2+}$ from the rock surface before waterflooding led to higher recovery irrespective of salinity and it is to note that it is the first time that no improve oil recovery is observed when low salinity is injected into a clastic reservoir where the mineral structure has been preserved. This has confirmed the importance of MIE in the LoSal™ mechanism.

**Conclusion:**

In conclusion, pH induced IFT reduction or emulsification and fines migration are not ubiquitous during LoSal floods. They are an effect rather than the cause. Cation exchange between the mineral surface and the invading brine has been demonstrated to be the primary mechanism underlying the improved waterflood recovery observed with LoSal waterflooding. This mechanism explains many of the results that have been reported during 10 years of research on low salinity injection. It explains why LoSal™ does not work when a core is acidised and fired as the cation exchange capacity of the clay minerals is destroyed. It explains why low salinity water injection has no effect on mineral oil as no polar compounds are present to strongly interact with the clay minerals. Also it explains why there is no direct correlation between the oil acid number and the amount of oil recovered as quaternized nitrogen and heterocyclic ring also play a role in the adsorption mechanism. Finally it explains why LoSal™ does not seem to work on carbonate reservoirs.

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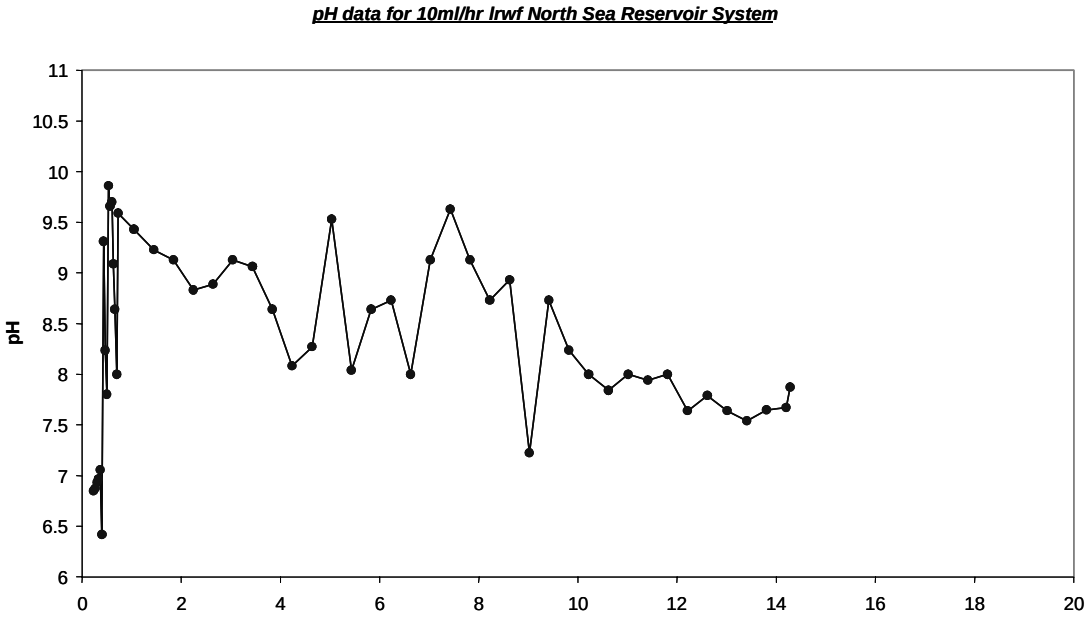



Figure 1. pH variation during a low salinity flood (pH vs. pore volumes)

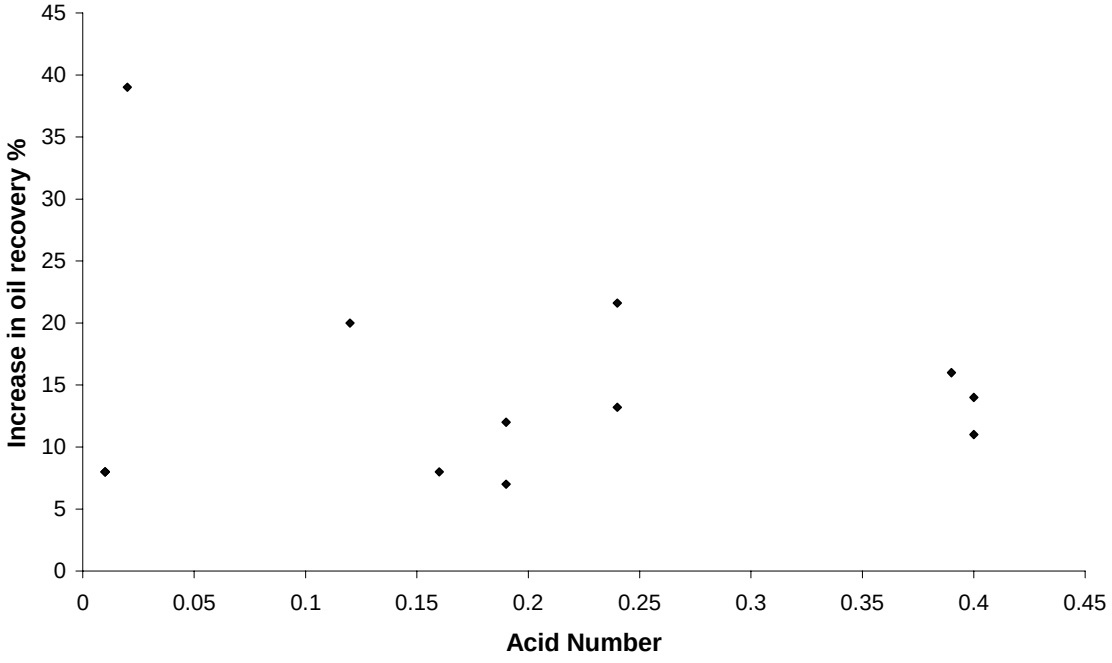



Figure 2. Lack of correlation between Acid Number and the increase in oil recovery due to low salinity waterflood

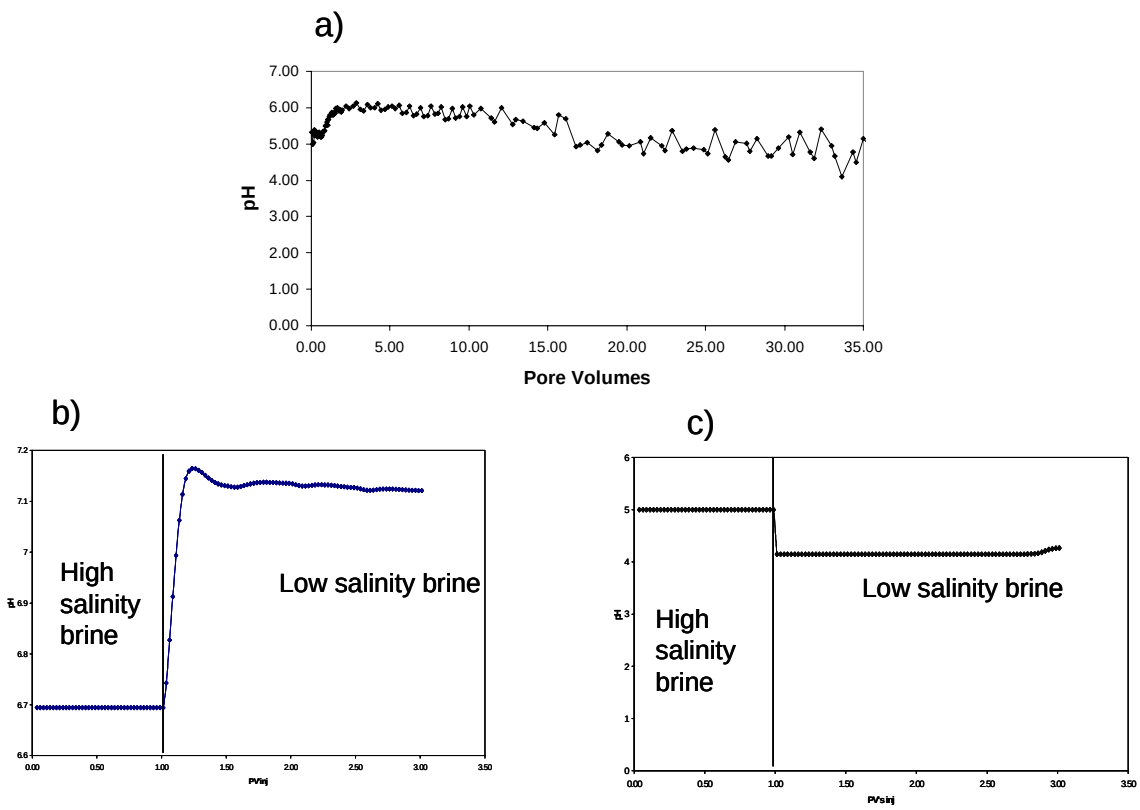
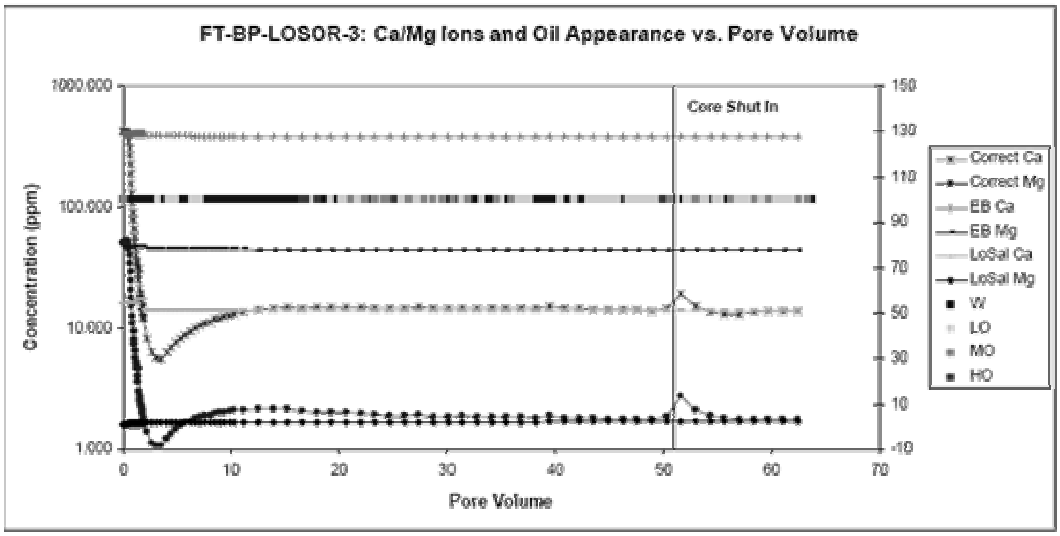



Figure 3. a) pH variation during a low salinity waterflood in an Endicott core. b) PHREEQC model of the pH variation during a low salinity waterflood with the presence of calcite. C) PHREEQC model of the pH variation during a low salinity waterflood without the presence of calcite.



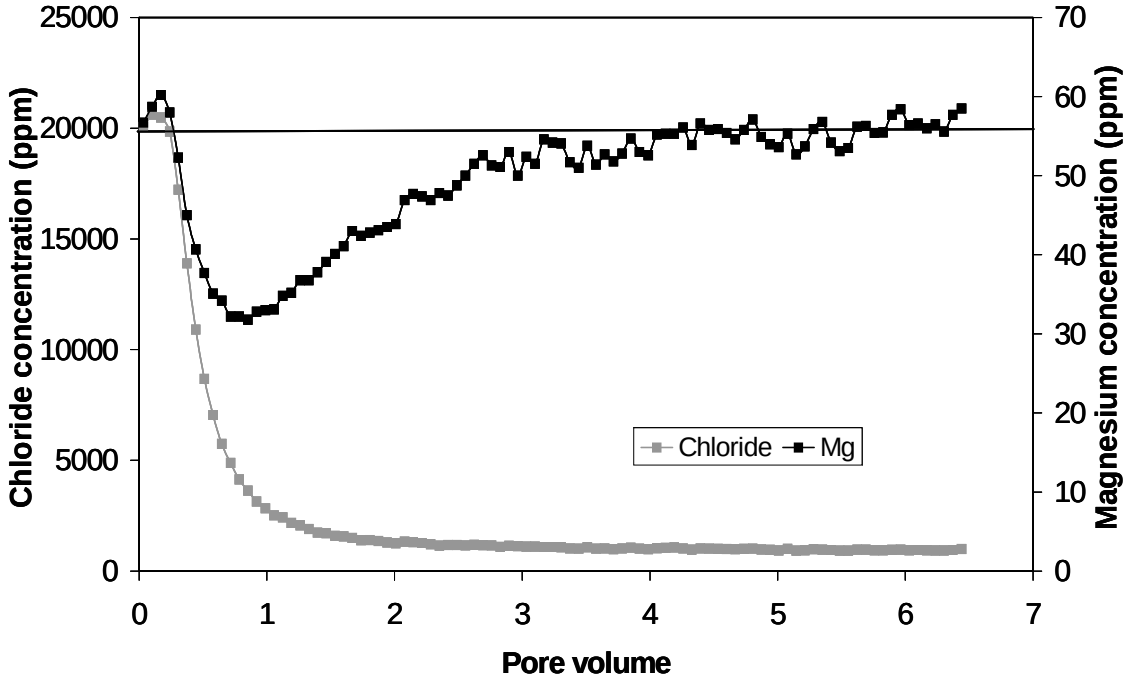




Figure 4. Variation in $Ca^{2+}$ and $Mg^{2+}$ in the effluent during low salinity corefloods.

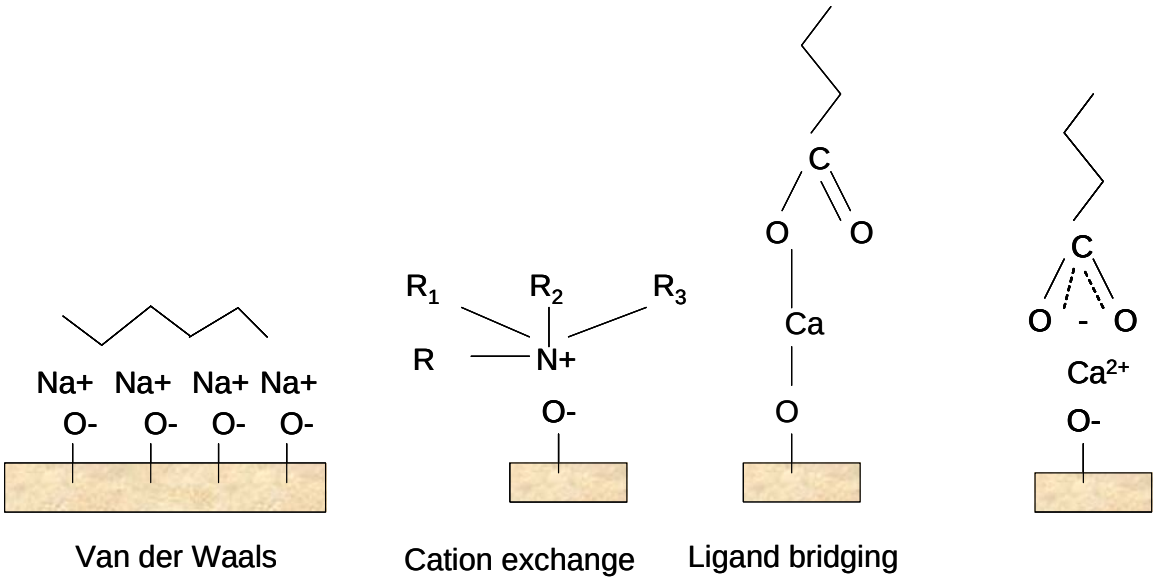



Figure 5. Representation of the diverse adhesion mechanism occurring between Clay surface and crude oil

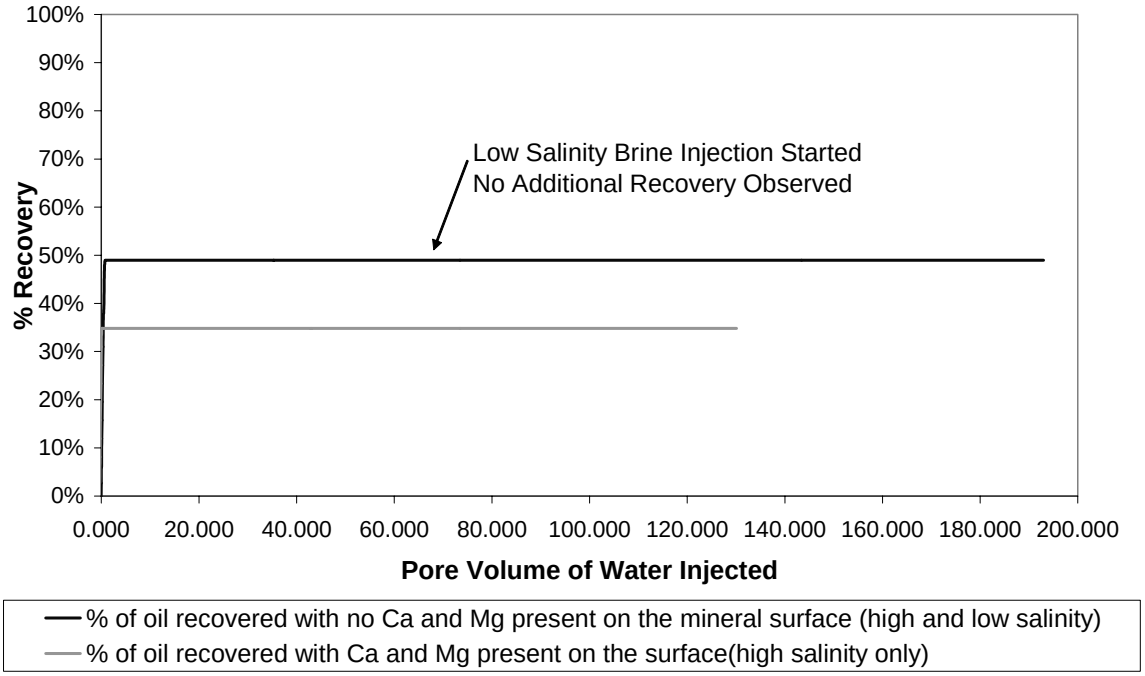



Figure 6. Effect of MIE on the % of oil recovery