

Introduction

Production of incremental oil from large carbonate reservoirs can supply humankind with crude oil for several decades. Injection of lowered or modified salinity brine, which can imbibe into bypassed zones and perhaps with a slight pressure push produce the trapped oil, is the most desired solution to the problem of increasing water cut in the reservoirs. Other solutions exist, but they are more expensive. The recovery mechanism starts by wettability alternation through lowering of water advancing contact angle, which enables spontaneous imbibition. The wettability alternation is caused by weakening rock-oil interaction, which is manifested by multi-component ion exchange Lager et al. (2008); Chen et al. (2018); Yutkin et al. (2018); Hu et al. (2018).

Crude oil-brine interface is charged with several polar functional groups dangling into the brine. These originate from asphaltenes – a collection of small-to-large aromatic molecules – that reside at the interface and form polymer-like structures owing to π - π -stacking. Both positively and negatively charged groups can be found at the interface making it amphoteric. Amphoteric polymer-like interfaces interact with almost any surface once protecting water film is broken, which readily happens on a rough surface. Then the charged groups at the oil-brine interface will reach the surface and substitute ions in the β -plane of the rock generating oil wet surface. This process must be reversed to produce oil. Once exchanged, the process can be reversed. However, the polymer-like nature of the adsorbed asphaltenes greatly impedes the reversal.

Using a classic 2-1 ion-exchange isotherm, we study the appropriate strategies for reversing the ion-exchange process in the above context of incremental oil recovery. For practical reasons we focus on highly saline brines, like seawater, and its dilutions. We account for the effects of bulk chemical speciation on the ion exchange. Next, we consider ion exchange coupled with 1D transport model and demonstrate that simple seawater dilution does not favor asphaltene detachment. Finally, we compose a seawater-based flood that is efficient in reversing the exchange process and weakening rock-oil bond.

Methods

In this work we use a classic adsorption isotherm for a nonlinear 2-1 ion exchange in dimensionless form Equation 1

$$\frac{Y_{Ca^{2+}}}{(1-Y_{Ca^{2+}})^2} = \left[\frac{K_{ex}CEC}{C_{Cl^-}} \right] \frac{X_{Ca^{2+}}}{(1-X_{Ca^{2+}})^2} \quad (1)$$

where $Y_{Ca^{2+}} = 2n_{Ca^{2+}}/CEC$, $X_{Ca^{2+}} = 2C_{Ca^{2+}}/C_{Cl^-}$, K_{ex} is the ion-exchange equilibrium constant, $C_{Cl^-} = 2C_{Ca^{2+}} + C_{Na^+}$, $2n_{Ca^{2+}} + n_{Na^+} = 1$, $n_i = \bar{C}_i/CEC$, \bar{C}_i is a surface concentration in moles per unit of specific surface area, and CEC is cation exchange capacity expressed in equivalents per specific surface area.

This isotherm analytically describes 2-1 cation or anion exchange with the salinity term defined as C_{Cl^-} or C_{Na^+} , respectively. Solving for concurrent aqueous chemical equilibrium requires a numeric solver. We use PHREEQC code to obtain solutions for such cases Parkhurst and Appelo (1999).

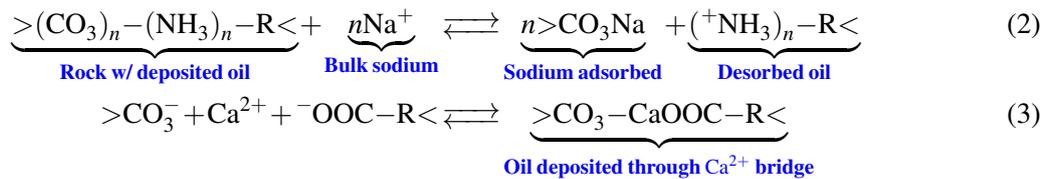
We assume that both positive and negative functional groups reside at crude oil-brine interface. Indeed, total acid or total base numbers routinely obtained for crude oils indicate the presence of proton donors and acceptors, some of which can attain charge in aqueous environment. On top of the list of functional groups are amines (aliphatic or aromatic) and acids (carboxylic or sulphate). Charge on these groups depends on reservoir pH. Carbonate reservoirs are pH buffers, with a typical pH range 7 – 8. At such pH, amino, carboxylate, and sulphate groups exist in charged form. 1D dispersive transport coupled with a non-linear process, like 2-1 ion-exchange, has no analytic solution. We use PHREEQC 1D transport module in our numerical approach.

Results

Reaction 2 below describes the multi-component ion exchange mechanism of oil desorption. The leftmost species in reaction 2 represents asphaltene at crude oil-brine interface attached to carbonate rock. The

index “n” emphasizes the polymer-like structure formed by asphaltenes at the interface. Many bonds form between the oil-water interface and the rock making it harder to separate. The reaction itself hypothesizes a detachment process of oil caused by sodium cations.

Another mechanism that allows charged groups at the oil-brine interface interact with carbonate surface is ion-bridging. It is described by reaction 3. In this case, calcium ions serves as a bridge between two negatively charged groups forming $>\text{CO}_3-\text{CaOOC}-\text{R}<$ complex. Analogous reactions can be devised for calcium sites at a carbonate surface and negatively charged functional groups at the oil-water interface including anion bridging, but we limit our discussion to reactions 2 and 3.



Reaction 2 with $n = 2$ is a 2-1 ion exchange, and its extent can be understood by solving Equation 1. Oil deposition path offered by reaction 3 depends on the species $>\text{CO}_3-\text{Ca}^+$ that in turn exchanges with sodium. Therefore, a waterflood that reduces calcium ion concentration at the rock surface ($n_{\text{Ca}^{2+}}$) should also favor oil-rock bond(s) weakening.

Figure 1a shows three ion-exchange processes for a 2-1 system exemplified by Ca^{2+} and Na^+ : 1) dilution of artificial seawater with DI water (dashed green line); 2) dilution of artificial seawater with NaCl brine having higher sodium concentration than the seawater (dotted blue line); and 3) dilution of artificial seawater with NaCl brine having the same sodium concentration as the seawater (solid red line). Our goal is to achieve the lowest $n_{\text{Ca}^{2+}}$ by exchanging it with sodium.

We start with the analysis of the most impractical first case. Indeed, dilution of seawater with deionized water is expensive. What is worse, such dilution does not result in a decrease of $n_{\text{Ca}^{2+}}$. Instead, as indicated by the arrows, $n_{\text{Ca}^{2+}}$ increases. The second and third cases are functionally similar and give similar results. In the second case, one can efficiently decrease $n_{\text{Ca}^{2+}}$, but at the cost of adding extra NaCl and increasing salinity of already saline brine. Finally, the third case is most optimal and allows one to decrease $n_{\text{Ca}^{2+}}$ to 0, but it is impractical.

We next study the effect of calcite chemical equilibrium on cation exchange isotherm at constant salinity for cation and anion exchanges exemplified by $\text{Ca}^{2+}/\text{Na}^+$ and $\text{SO}_4^{2-}/\text{Cl}^-$ respectively. This case requires a numerical solver. We solve for both cation and anion exchange reactions simultaneously using the same parameters for both processes. One can regard $\text{Ca}^{2+}/\text{Na}^+$ ion pair as a proxy for $(+\text{NH}_3)_2-\text{R}</\text{Na}^+$ pair and $\text{SO}_4^{2-}/\text{Cl}^-$ for $(-\text{OOC})_2-\text{R}</\text{Cl}^-$, respectively.

Figure 1b shows the result of the modeling with solid circles indicating the end of dilution. First, the isotherms differ because of calcium carbonate and sulphate chemistry. Second, sulphate is less represented on the surface than calcium. Finally, sulphate surface concentration is less impacted by the dilution than calcium concentration. Therefore, we conclude that both $n_{\text{Ca}^{2+}}$ and $n_{\text{SO}_4^{2-}}$ decrease with dilution *i.e.* respond to the treatment.

Discussion

We study and discuss two tertiary recovery waterflood cases and their efficiency in reducing the number of rock-oil bonds. The cases considered are simplified with a number of assumptions and therefore only provide a basis for qualitative comparison of waterflood designs and results.

First, we consider injection of 2x diluted artificial seawater. A carbonate core initially contains artificial seawater ($C_{\text{Na}^+} = 1.5 \text{ M}$, $C_{\text{Ca}^{2+}} = 0.25 \text{ M}$, and $C_{\text{Cl}^-} = 2 \text{ M}$) as in Yousef et al. (2012). Then a 2x diluted

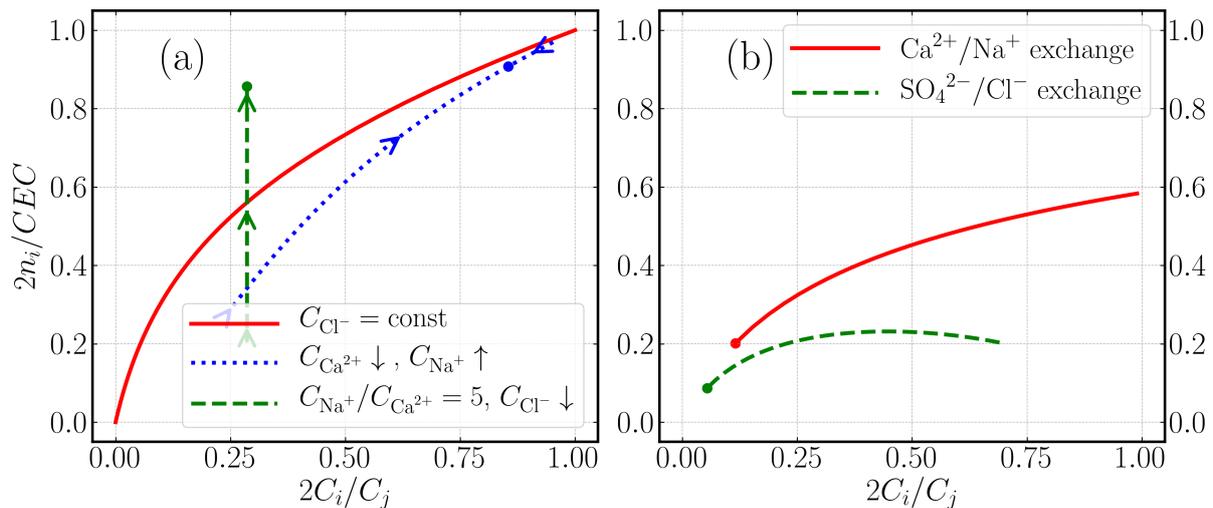


Figure 1: Various exchange isotherms. $C_{i,j}$ corresponds to bulk ionic concentration of exchanging ions, n_i corresponds to ion concentration on the surface, where $i = Ca^{2+}$ or SO_4^{2-} , and $j = Na^+$ or Cl^- . Arrows indicate direction of salinity decrease, circles indicate points of lowest salinity. **(a)**: Green dashed line: a constant ratio isotherm ($C_{Na^+}/C_{Ca^{2+}} = 5, C_{Cl^-}$ follows electroneutrality). Blue dotted line: an isotherm with all three concentrations varying. Red solid line: constant salinity isotherm, *i.e.* $C_{Cl^-} = \text{const}$. **(b)**: Cation and anion exchange on $CaCO_3$ surface with bulk chemical equilibrium. Red solid line shows Ca^{2+}/Na^+ isotherm; green dashed line shows SO_4^{2-}/Cl^- exchange isotherm at constant salinity (*i.e.* $C_{NaCl} = \text{const}$). $CaSO_4 \cdot xH_2O$ phases were allowed to reach saturation index of 3 without precipitation.

artificial seawater flushes for 0.5 pore volumes. We calculate concentrations of all major species as well as equivalent fraction of adsorbed calcium at the surface. The goal is to observe a decrease of $n_{Ca^{2+}}$, which is a proxy for $(^+NH_3)_n - R <$.

Figure 2a shows the result of such modeling. Chloride is a tracer; sodium and calcium almost exactly follow chloride step concentration change. However, we observe that after injection of 0.5 PV (see zone to the left of 0.5 PV mark), $n_{Ca^{2+}}$ increases rather than decreases. We cannot comment on the magnitude of the ion exchange effects because of simplicity of the model. This effect is predicted by the ion-exchange adsorption isotherm (see green dashed line in Figure 1a). Therefore, we conclude that such approach does not favor detachment of $(^+NH_3)_n - R <$. The same conclusion can be made about anion exchange (not shown here).

Next, we consider a lowered salinity waterflood that corresponds to the third case pictured in Figure 1a (solid red line). As previously, the core is initially filled with the artificial seawater. Then a modified salinity brine is injected for 0.5 PV. The brine is derived from the artificial seawater by replacing half of calcium with sodium but keeping chloride concentration fixed ($C_{Na^+} = 1.75$ M, $C_{Ca^{2+}} = 0.125$ M, and $C_{Cl^-} = 2$ M), which roughly corresponds to 2x dilution.

Figure 2b shows the result of such simulation. Chloride concentration is a straight line as by design. Calcium and sodium profiles show step changes with hardly noticeable retention. The most important feature in the figure is the positive response of calcium surface concentration to the treatment. Indeed, $n_{Ca^{2+}}$ decreases (and so would do $(^+NH_3)_n - R <$) as a result of the waterflood. Again, this outcome is as predicted by the ion exchange isotherm in Figure 1a. We, therefore, conclude the efficiency of the selected approach.

Conclusions

In this work using 2-1 ion-exchange isotherm we studied multi-component ion exchange, which is believed to explain crude oil interactions with the rock surface. Our goal was to find the general waterflooding strategies that favor reversal (partial or full) of the exchange reactions responsible for oil attachment to the surface. We considered several exchange isotherms and their effects on solute transport. Our study

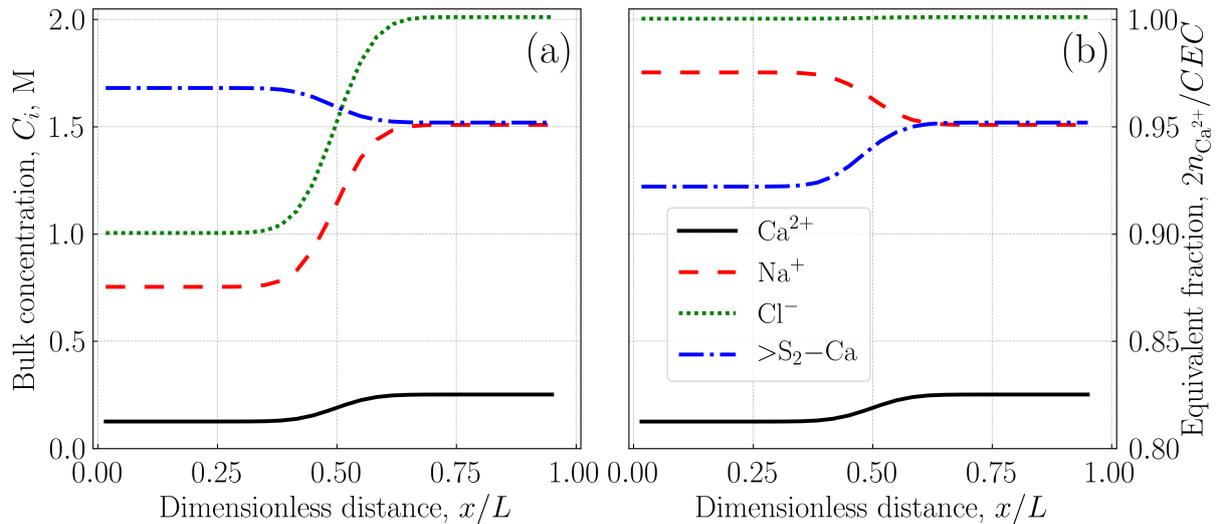


Figure 2: Simulated concentration profiles at $ut/\phi L=0.5$ for (a): a diluted seawater injection accompanied by cation exchange. Initial concentration is an artificial sea water composition from Yousef et al. (2012). Injected brine is 2 times diluted seawater. Calcite dissolution is assumed to be fast; (b): an optimal waterflood composition that favors desorption of calcium. Initial concentration in the core is as above. The injected brine is a modified salinity seawater. It was adjusted according to the ion-exchange isotherm that results in lower $n_{Ca^{2+}}$. $Pe_L = 100$

provides useful guidelines for designing a modified salinity brine that is successful in detaching crude oil from rock surface. For example, we found that a direct salinity reduction of seawater or formation brine is not an efficient strategy. A more efficient strategy is the maintenance of constant salinity accompanied by increase of one of exchange-active ions. Additionally, we found that bulk chemical speciation strongly affects ion exchange process and must be taken into account when designing a modified salinity waterflood. The suggested strategy, however, has not been verified experimentally. This is the subject of future work.

Acknowledgements

This project was funded by prof. Patzek's baseline research grant.

References

- Chen, Y., Sari, A., Xie, Q., Brady, P.V., Hossain, M.M. and Saedi, A. [2018] Electrostatic Origins of CO_2 -increased Hydrophilicity in Carbonate Reservoirs. *Scientific Reports*, **8**(1), 17691.
- Hu, X., Yutkin, M.P., Hassan, S., Wu, J., Prausnitz, J.M. and Radke, C.J. [2018] Calcium Ion Bridging of Aqueous Carboxylates Onto Silica: Implications for Low-Salinity Waterflooding. *Energy & Fuels*, **33**(1), 127–134.
- Lager, A., Webb, K.J., Black, C.J.J., Singleton, M. and Sorbie, K.S. [2008] Low Salinity Oil Recovery - An Experimental Investigation I. *Petrophysics*, **49**(1), 28–35.
- Parkhurst, D. and Appelo, C. [1999] Water-resources investigations report 99-4259. *US Geological Survey*, **67**(Version 2), 312.
- Yousef, A.A., Al-Saleh, S. and Al-Jawfi, M.S. [2012] Improved/Enhanced Oil Recovery from Carbonate Reservoirs by Tuning Injection Water Salinity and Ionic Content. In: *SPE Improved Oil Recovery Symposium*.
- Yutkin, M.P., Mishra, H., Patzek, T.W., Lee, J. and Radke, C.J. [2018] Bulk and Surface Aqueous Speciation of Calcite: Implications for Low-Salinity Waterflooding of Carbonate Reservoirs. *SPE Journal*, **23**(01), 084–101.