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# Altering wettability to recover more oil from tight formations

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A B S T R A C T

We describe here a method for modifying the bulk composition (pH, salinity, hardness) of fracturing fluids and overflushes to modify wettability and increase oil recovery from tight formations. Oil wetting of tight formations is usually controlled by adhesion to illite, kerogen, or both; adhesion to carbonate minerals may also play a role when clays are minor. Oil-illite adhesion is sensitive to salinity, dissolved divalent cation content, and pH. We measure adhesion between middle Bakken formation oil and core to verify a surface complexation model of reservoir wettability. The agreement between the model and experiments suggests that wettability trends in tight formations can be quantitatively predicted and that the bulk compositions of fracturing fluid and overflush compositions might be individually tailored to increase oil recovery.

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## Introduction

There is an enormous incentive to improve tight formation oil recoveries from their typically low value of 6–8% of the original oil in place. Increased oil recovery would boost reserves while lowering unit operating costs. Here we examine how oil recovery might be increased by designing the bulk composition of the fracturing fluid (salinity, pH, hardness), or that of "squeeze job" overflushes, to make the formation more water-wet. We focus on chemically enhancing oil recovery, but expect that new physical procedures such as high intensity fracturing, refracturing, and choking will aid the chemical enhancement as well since the chemical and physical processes are largely independent. To do this, we identify the primary wettability-affecting reactions in tight formations and build a geochemical surface complexation model to predict how these reactions respond to changes in fluid chemistry. We then test the model by measuring the effect of salinity and pH on adhesion of middle Bakken oil to core. These measurements are combined to describe how fracturing or squeeze job fluids might be altered to increase water wetting and recover more oil from the middle Bakken. The general approach should apply to other tight formations as well.

Tight formations such as the Bakken and the Eagle Ford are source-reservoir systems primarily made up of quartz, feldspar, calcite, dolomite, illite clay, and as much as 5–10% percent kerogen. Table 1 shows approximate mineralogies of the three largest tight formations/basins in the US.

Oil tends to be associated with illite, or kerogen when present, or both (Bryndzia and Braunsdorf, 2014). A thin layer of water separates oil from the surface of reservoir minerals (Buckley et al., 1989; Dubey and Doe, 1993) as shown schematically in Fig. 1. Illite, the solid in Fig. 1, possesses a negative charge on its basal plane because of heterovalent substitution in the lattice. Illite negative surface charge is balanced by cations from solution, such as $Na^+$, and by positively charged groups present at the oil-water interface, e.g. nitrogen bases, $-NH^+$, and calcium-terminated carboxyls, $-COOCa^+$. Electrostatic attraction between positively charged oil surface groups and negatively charged clay basal planes, is likely to control oil adhesion in sandstones containing clays such as illite or smectite (Brady and Krumhansl, 2013). While the number of negatively charged basal plane clay groups is fixed by lattice composition, the abundance of charged oil surface groups depends upon the history of the oil and chemistry of the oil and the connate fluid (e.g. pH, salinity, Ca + Mg). High numbers of $-NH^+$ and $-COOCa^+$ groups should favor formation of electrostatic "bridges" and oil adhesion – that is increase the degree of oil wetting. Decreasing the numbers of $-NH^+$ and $-COOCa^+$ groups should reduce oil adhesion, making the formation more water wet, resulting in greater oil mobility and recovery.

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**Table 1**
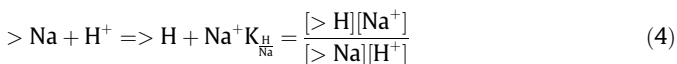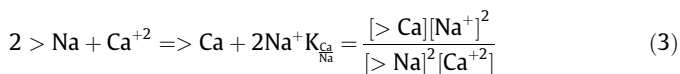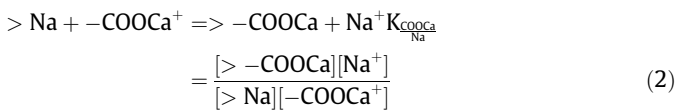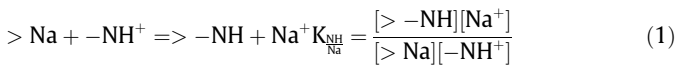Lithology of three largest tight oil formations/basins in the USA.[a]

| Basin | Production (mbbl/d) | % Carbonate | % Clay | % Kerogen | Dominant clay |
|---|---|---|---|---|---|
| Permian | 2040 | 5–40 | 10–40 | 1–10 | Illite |
| Bakken | 1220 | 10–15 | 10–20 | 2–8 | Illite |
| Eagle Ford | 900 | 40–60 | 10–40 | 5–10 | Smec/illite/kaol |

[a] Balance is mostly quartz or biogenic silica.

## Methods

### Thermodynamic Modeling

Sorption of $-NH^+$ and $-COOCa^+$, and competing $Na^+$ and $Ca^{+2}$, onto illite basal planes can be described by the following chemical reactions (Brady and Krumhansl, 2013):

$$> Na + -NH^+ => -NH + Na^+ \quad K_{\frac{NH}{Na}} = \frac{[> -NH][Na^+]}{[> Na][-NH^+]} \tag{1}$$

$$> Na + -COOCa^+ => -COOCa + Na^+ \quad K_{\frac{COOCa}{Na}}$$
$$= \frac{[> -COOCa][Na^+]}{[> Na][-COOCa^+]} \tag{2}$$

$$2 > Na + Ca^{+2} => Ca + 2Na^+ \quad K_{\frac{Ca}{Na}} = \frac{[> Ca][Na^+]^2}{[> Na]^2[Ca^{+2}]} \tag{3}$$

$$> Na + H^+ => H + Na^+ \quad K_{\frac{H}{Na}} = \frac{[> H][Na^+]}{[> Na][H^+]} \tag{4}$$

where ">" is a negatively charged site on the clay basal plane and brackets denote aqueous activities and surface concentrations.

Reactions (1) and (2) promote oil-illite linking. Reactions (3) and (4) indirectly affect oil-illite attraction by affecting the amounts of competing exchangeable Na and Ca on the basal planes, and pH. Oil linking through sorption of $-NH^+$ oil surface groups to illite (Reaction (1)) will be most important at pH values where oil $-N$ groups are protonated and positively charged (pH < 5–6 at 25 °C); and when $Na^+$ and $Ca^{+2}$ concentrations are low, limiting competition with $-NH^+$ groups for illite basal plane sites. Electrostatic linking of $-NH^+$ groups can be decreased, and oil recovery enhanced, by raising the pH (Fig. 1a→b), and/or by increasing the salinity (Fig. 1a→c). Oil linking through $-COOCa^+$ exchange onto basal planes (Reaction (2)) will be most important at pH > 5 where some oil carboxylate groups are deprotonated and can become Ca-terminated. Low $Na^+$ will favor oil-illite linking through $-COOCa^+$ sorption (Reaction (2)) because there will be less competition for illite surface sites. Increased pore water $Ca^{+2}$ will have a mixed effect on oil-illite adhesion; while $Ca^{+2}$ promotes formation of the potentially bridging $>-COOCa^+$ complex on the oil surface, $Ca^{+2}$ also effectively competes with $-COOCa^+$ for exchange sites on the illite surface.

Fig. 2 illustrates general oil-illite adhesion trends by showing the number of electrostatic bridges calculated to form between oil and illite as a function of pH and salinity; calculated values are listed in Table 2. The calculation relies on a diffuse layer model
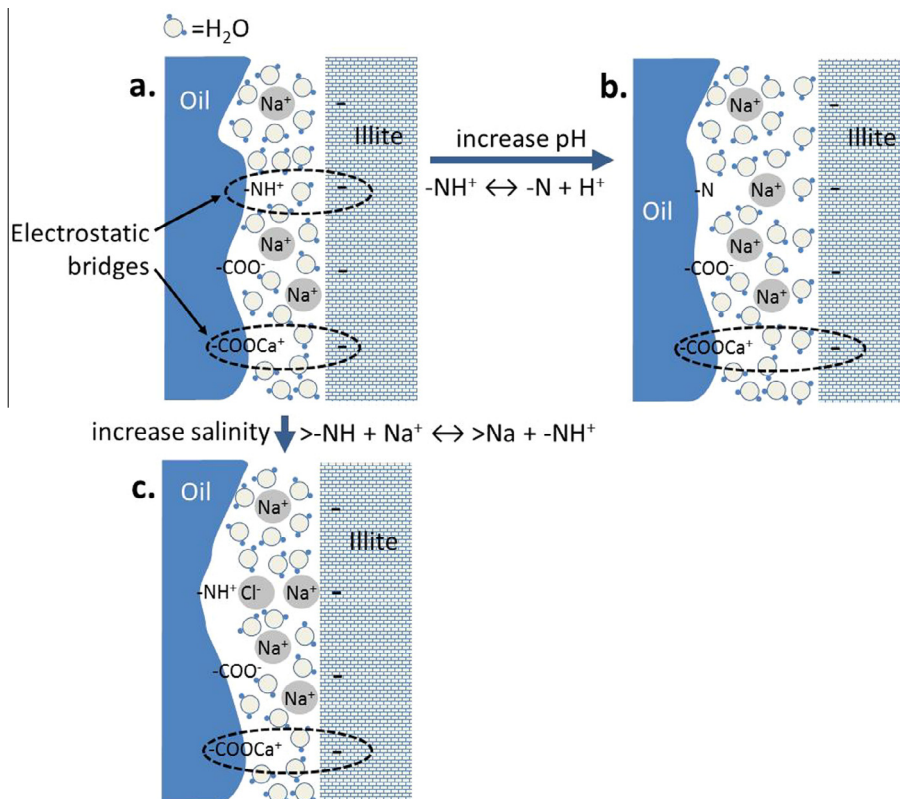


**Fig. 1.** Schematic of the oil-illite interface showing effects of increased pH (a→b) and increased salinity (a→c) on electrostatic bridging, and the relevant reactions for each change.