Abstract

Chemical flooding, SP or ASP, is of increasing interest due to the need to increase oil production. Design of chemical processes is very project specific and requires case by case studies including various steps among which reservoir data analysis, chemical formulations, coreflood validations and reservoir simulation. Every step is dependent on the preceding ones and the last reservoir simulation step gathers all the information collected during the project. In this paper, we present a chemical simulator describing two phase flow with chemical transport of alkaline, surfactant, polymer and salinity. Two phase flow is related to capillary desaturation curve through the decrease of oil-water interfacial tension. Physical chemistry reactions are described either with a thermodynamic approach or a simplified one using tables or simplified physics to be compatible with large scale reservoir simulations. In this paper, we describe the simulator and present results of numerous experiments specially designed to validate the model: alkaline injections of carbonate and borates, surfactant adsorption experiments at different salinities and pH, systematic effect of salinity on interfacial tension and oil recovery with/without salinity gradient. The good agreement between the experimental and numerical oil recoveries and chemical compositions is very encouraging and supports the validity of the physics implemented in the simulator. In particular, the dominant effect of pH on adsorption and the importance of a salinity gradient on oil recovery is highlighted by the numerical simulation. Finally, a sensitivity study at the reservoir scale is presented to illustrate relevant factors for the implementation of an economic surfactant-based process.

Introduction

Oil mobilization in chemical EOR processes is related to three mechanisms: (1) ultra-low interfacial tension (IFT) for displacement efficiency, (2) mobility control for sweep efficiency, and (3) transport of additives in the formation. The success of a surfactant flooding, or ASP for being general, depends on the simultaneous propagation of a surfactant formulation designed for low IFT, alkaline and polymer at a desired concentration to control oil mobility. The physics is complex and requires to be studied at the laboratory to design the process and to investigate the effect of the main parameters on the oil recovery performance [Moreau et al. (2010)]. The simulator, with the appropriate physics, provides an integration of the determinant parameters. It is emphasized as a tool which can be used in very different ways: as an help for the design of experiments to improve the ASP performances, and as a tool to scale experiments to pilot and finally to the reservoir scale. The process can be analysed and optimized.

Physics of surfactant processes are well-documented. Efficiency is directly related to IFT through the capillary number. Low IFT is obtained from phase behavior studies where the salt concentration is a crucial data for the design of the formulation. Since the salinity inside the reservoir during the ASP injection is varying from formation water to injection water or make-up water salinity, formulation work must be done inside a salinity window by looking for a formulation composition giving the lowest IFT
when the formation brines mixes with the make-up brine. Numerical simulation can be used to reject surfactant systems which become over-optimized just because the surfactant migrates in the oil-rich phase during flow.

Alkaline is added with two targets: (1) to reduce surfactant adsorption, and (2) to generate in situ surfactant generally referred as soap \([\text{Nelson et al. (1984); Martin and Oxley (1985); Bazin et al. (1992)}]\). Alkaline is beneficial for surfactant cost reduction but surfactant needs to be transported behind the alkaline front. However, alkaline is subjected to losses due to three mechanisms: (1) adsorption sometimes referred as hydroxy ion exchange, (2) precipitation when alkaline is carbonate or metaborate, (3) mineral dissolution mainly with the use of caustic at high temperature. The physics of alkaline propagation is well known for carbonates and caustic. Metaborates are promising chemicals, mainly because their tolerance to calcium brines is much higher than carbonates. However, for metaborate the difficulty for modeling the physics leads in the complex chemistry of this additive, with dissociation equilibria involving numerous species. We propose in this paper a particular physics, based on a pseudo representation to calculate the propagation of metaborate, taking into account the adsorption.

Polymer challenge is mobility control. Addition of polymer into the surfactant slug is still a debate whereas injection of polymer behind the surfactant slug is the rule when reservoir permeability is reasonable. Again, beside experiments, modeling may be used to test the gain in oil recovery obtained by polymer addition into the surfactant formulation.

In this paper we give a review of IFP Energies nouvelles R&D simulator, which is named SARIP\textsuperscript{CH} \[\text{Beicip-Franlab (2011)}\].

We first describe ASP model capabilities with emphasis on the physics. Then comes a description of laboratory work performed to validate the various options. Alkaline option is validated with caustic, carbonate and metaborate. Ion exchange and precipitation tested at the laboratory are reproduced by the modeling. Finally, the complete validation of oil recovery efficiency is obtained from an experiment performed with a salinity gradient. In a second part, SARIP\textsuperscript{CH} is used to test sensitivity to various parameters affecting the cost of the process, mainly surfactant adsorption or to test the effect of mobility control inside the formulation. Finally, we present results at the pilot scale, in a tridimensional configuration.

**Modeling of chemical EOR processes**

SARIP\textsuperscript{CH} is a in-house two-phase chemical flooding reservoir simulator. Here and below, we assume without any loss of generality that water is the wetting phase and oil is the non-wetting phase, and that all the chemical species — polymer, surfactant and alkaline — live in the water phase, the oil phase being a dead black oil (no dissolved gas). The flow of this two-phase multi-component system is driven by the generalized Darcy equation, bracketed with each phase mass conservation equation,

\[
\mathbf{u}_i = -\frac{k_{ij}}{\mu_i} (\nabla p_i - \rho_i \mathbf{g}) \quad \partial_t (\rho_i \phi) + \nabla \cdot (\rho_i \mathbf{u}_i) = \delta_i
\]

where the subscript \(i = w,o\) labels the oil and water phases, \(\mathbf{u}_i\) is the Darcy velocity, \(k\) is the absolute permeability, \(k_{ij}\) is the relative permeability, \(\mu_i\) is the viscosity, \(p_i\) is the pressure, \(\rho_i\) is the density, \(\mathbf{g}\) is the gravity acceleration, \(\phi\) is the porosity, \(S_i\) is the saturation such that \(\sum S_i = 1\) with \(S_w \in [S_{wir}, 1 - S_{or}]\), \(S_{wir}\) and \(S_{or}\) being the irreducible water and residual oil saturations, and \(\delta_i\) denotes a source or a sink well term. Specifically, water-phase species mass conservation equations are the following:

\[
\partial_t M_{wj} + \nabla \cdot (\rho_w C_{wj} \mathbf{u}_w + j_{wj}) = \delta_{wj} \quad M_{wj} = \alpha_{wj} \rho_w S_w C_{wj} + \rho_r (1 - \phi) C_{r j}
\]

where \(C_{wj}\) is the water-phase \(j\)-species concentration (such that \(\sum C_{wj} = C_w\)), \(C_{r j}\) the \(j\)-species concentration adsorbed on the rock, \(\alpha_{wj}\) the \(j\)-species (polymer) volume factor exclusion, and \(j_{wj}\) the \(j\)-species

\[\text{Beicip-Franlab (2011)}\].

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1 The physics of SARIP\textsuperscript{CH} is currently being implemented in the commercial reservoir simulator PumaFlow\textsuperscript{TM} within the OpenFlow\textsuperscript{TM} platform \[\text{Beicip-Franlab (2011)}\].
Clearly, the oil-water interfacial tension saturation reduction. the interfacial tension exhibits a critical ultra-low minimum at the optimum surfactant concentration, and the logarithmic increase over several orders of magnitude results in a significant residual oil saturation reduction. As we shall see below, because of the surfactant, relative permeabilities are some dynamical functions of the water and oil mobile saturations whose range boundaries $S_{wi}$ and $S_{or}$ may dynamically vary with the capillary number $N_c$:

$$k_{rw}(S_w; N_c) = f[S_w^*(N_c)] \quad \quad \quad \quad \quad S_w^*(N_c) = \frac{S_w - S_{wi}(N_c)}{1 - S_{wi}(N_c) - S_{or}(N_c)}$$

$$k_{ro}(S_w; N_c) = g[S_w^*(N_c)] \quad \quad \quad \quad \quad S_w^*(N_c) = \frac{1 - S_w - S_{or}(N_c)}{1 - S_{wi}(N_c) - S_{or}(N_c)} = 1 - S_w^*(N_c)$$

where $S_w \in [S_{wi}(N_c), 1 - S_{or}(N_c)]$ and $S_w^* \in [0, 1]$. For example, relative permeabilities can be Corey power laws, that is $k_{rw}(S_w; N_c) = k_{ro}(S_w; N_c) = k^0_{ro}(1 - S_w^*)^{n_o}$, the $k^0_{ro}$ and $n_o$ being possibly some functions of $N_c$. However, in most cases relative permeabilities will be some family of numerical tables indexed by the capillary number; the same holds for the capillary pressure (e.g., $p_c(S_w^*) = p_c/S_w^*$ where $p_c$ is the displacement pressure and $\lambda$ some exponent [Standing (1975)], since the irreducible water and residual oil saturations dynamically depend on the capillary number:

$$k_{ri}(S_w; N_c) = k_{ri}[S_w; S_{wi}(N_c), S_{or}(N_c)]$$

$$p_c(S_w; N_c) = p_c[S_w; S_{wi}(N_c), S_{or}(N_c)]$$

Some authors defined the capillary number $N_c$ as the non-dimensional ratio of the phase pressure driving viscous force to the oil-water interfacial tension, that is $N_c = \frac{\mu u_{i}}{\sigma_{ow}}$, where $\sigma_{ow}$ is the oil-water interfacial tension [Moore and Slobod (1956); Taber (1969); Stegemeier (1974, 1977); Lake (1989)]. However, several definitions are possible as long as they are relevant and consistent [Abrams (1975); Taber (1981); Lake (1989); Delshad (1990); Souto et al. (1993); Labrid et al. (1992)]. In SARIPCH we chose $N_c = \frac{R_{m}k_{ro}(N_c) + k_{rw}(N_c)}{\sigma_{ow}}$, where $R_m$ is the polymer mobility reduction.

The capillary desaturation curve relationship (CDC), $S_{or} = S_{or}(N_c)$, relates the residual oil saturation as a function of the capillary number [Stegemeier (1974)]. The lower the interfacial tension is, the lower the residual oil saturation is, the higher the ‘free’ recoverable oil is, and the higher the capillary number is. However, in order to be truly effective, the surfactant has to lower the interfacial tension over several orders of magnitude, say from $\sigma_{ow} = 30 \text{ mN/m}$ without any surfactive agent to $10^{-4} \text{ mN/m}$ with an efficient and cost-effective surfactant [see Figure 3(b)], hence the logarithmic scale in $N_c$ as shown in Figure 3(a): indeed, increase of $N_c$ over several orders of magnitude results in a significant residual oil saturation reduction.

Clearly, the oil-water interfacial tension $\sigma_{ow}$ is a function of the surfactant concentration. More critically, it is above all a critical function of the water salinity (or total dissolved solids in water concentration, TDS), as can be seen in Figure 3(b) [Shah and Scheckter (1977); Shah (1981)]. Indeed, for one given surfactant concentration, the interfacial tension exhibits a critical ultra-low minimum at the optimum salinity $S^*$, and a logarithmic increase over several orders of magnitude in the vicinity of $S^*$. Therefore, the interfacial tension $\sigma_{ow} = \sigma_{ow}(C_{w}, S, \{C_{w}\})$ dynamically depends on the surfactant concentration $C_{w}$, on the salinity $S$, and on the alkali concentration(s) $\{C_{a}\}$ if any. It should be noted that despite the modeling is two-phase, the interfacial tension encompasses the full Winsor surfactant three-phase critical behavior in an effective and simple manner.

Alkali, polymer and surfactant species adsorptions are Langmuir-like [Souto et al. (1993); Labrid et al. (1992)]. More sophisticated is the case of the surfactant, where the Langmuir plateau is a product function of the water salinity (say chloride and sodium ions concentrations) and pH (say hydroxide ions concentration), in order to take into account the alkali effect on limiting the surfactant adsorption:

$$C_{rj} = C_{wj}^0 \frac{K_{j}C_{wj}}{1 + K_{j}C_{wj}} \quad j = s, p, \{a\} \quad C_{wj}^0 = \text{linear function of (salinity, pH)}$$
where $C_{rj}^0$ is the maximum $j$-species concentration adsorbed on the rock (Langmuir plateau) and $K_j(T)$ is the $j$-species equilibrium constant at temperature $T$.

Additional features are alkaline-rock reactions through ion exchange and dissolution-precipitation. Ion exchanges reactions involving calcium, magnesium, potassium and sodium cations are written below [Bazin and Labrid (1991)]. Ion exchanges equilibrium constants and solubility products used in the simulation were close to equilibrium constants found in the litterature (see Table 1):

$$\frac{C_{rCa}^+ C_{wNa}^+}{C_{rNa}^+ C_{wCa}^{2+}} = K_{21}$$
$$\frac{C_{rCa}^+ C_{wNa}^+}{C_{rNa}^+ C_{wCa}^{2+}} = K_{25}$$
$$\frac{C_{wMg}^{2+} C_{wCO_3}^-}{C_{wNa}^+ C_{wMg}^{2+}} = K_{61}$$

Table 1: Ion exchanges equilibrium constants and solubility products (see the text).

**Ion exchange in the context of a high salinity preflush**

This simulation addresses a realistic strategy of surfactant injection in a context of high divalent cation concentration. Preflush injection can be recommended when surfactants with limited tolerance to divalent cations are used. Injection of high salinity brine is a way to decrease divalent cation concentration ahead of the surfactant slug owing to ion exchange mechanisms.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>576</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>96</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>46</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1193</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2: Composition of reservoir water for preflush validation in SARIP$^{CH}$. 

In the initial situation, the core is equilibrated with reservoir water, clays are saturated with the four cations (Table 2). Ion exchange capacity of the reservoir sandstone is 7.2 meq/100 g (Table 1). This high cation exchange capacity is related to a high clay content, which is mainly made of smectites. When potassium chloride is injected, calcium, magnesium and sodium cations are replaced by potassium. Figure 1 shows comparison of simulation and experimental results. Release of calcium and magnesium occurred at one PV according to the chromatographic theory for ion exchange. A very large preflush size is necessary if a complete release of divalent cations is required. Addition of alkaline additive is a way to shorten the cation release.

**Alkali transport: the ‘pseudo-OH’ model for simplified pH calculation**

In the case of alkali transport, the pH (i.e. the concentration in OH$^-$ ions) of the water phase in the zones of the reservoir contacted with the alkali-surfactant slug is a key parameter. Indeed, its determination is
needed to predict the amount of alkali to be injected to achieve a satisfactorily reduction of surfactant adsorption, which directly impacts the oil recovery. The pH is controlled by the chemical equilibriums associated to the injected alkali agent and by the adsorption of OH− ions on the rock surface. For the simulation, it is useful to consider separately the case when the alkali is caustic soda (NaOH) and the general case of an alkali being a base which leads to a buffer effect.

**Case #1:** If the alkali is NaOH, transport of the OH− ions and hence pH can be rather straightforwardly determined, provided the Langmuir isotherm adsorption parameters (equation 7) for the OH− ions are known.

**Case #2:** If the alkali is a more complex base, the OH− concentration is controlled both by OH− adsorption and by the relevant chemical equilibriums corresponding to the base used. As a consequence, pH determination requires solving a system of equations in each grid block. This method is described in particular in Mohammadi et al. (2008) for carbonate (reactions 5) and in Flaaten et al. (2008) (reactions 3 and 4) for metaborate. As will be shown with the first example below, it gives satisfactorily results when compared to experimental data. However, the corresponding computation times can be significantly long. In addition, such full calculations require to input the chemical equilibriums thermodynamic constants, which are not always well known, for example in the case of metaborate. This method can thus potentially lead to erroneous pH calculation and/or entail over-lengthy simulations. Furthermore, in the case of some complex base (like tetraborate), the relevant chemical equilibriums involved may not be known, rending the simulation impossible. For these reasons, a complete calculation method is not always practically applicable.

The ‘pseudo-OH’ model is an alternative to the complete calculation method for the injection of bases which are not NaOH. It relies on a simplified (but practically relevant) determination of the pH in each grid block which assumes that, instead of the actual alkali agent, only pseudo OH− ions with specific adsorption parameters are transported in the porous medium. Determination of these parameters is achieved through a fit of the effluent pH results of a reference monophasic alkali-injection coreflood. The whole process for simulating a given reservoir case hence involves 3 steps:

a) Reference monophasic coreflood experiment on a rock sample representative of the reservoir under study: injection of the actual alkali agent to be used in the case, measurement of the injected solution pH and of the pH in the effluents (called effluent pH in the following);

b) Simulation of this experiment with the NaOH model (case #1) with an injected OH− concentration corresponding to the pH of the actual solution injected in the experiment. Several simulations are performed to fit the effluent pH experimental data, by adjusting the adsorption parameters C0 and

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Figure 1: Comparison of ions exchange simulation and experimental results (see the text).
\( K \) (equation 7) for the adsorption of the pseudo-OH\(^-\) ions;

c) Simulation of the full-scale reservoir case, the alkali transport being computed with the NaOH model, with, for the pseudo-OH\(^-\) ions, a concentration being the concentration corresponding to the pH of the actual alkali agent solution and the adsorption parameters being the parameters determined in step b).

**Implementation of the ‘pseudo-OH’ model**

In this section, we present two examples of the implementation tests of steps a) and b) of the ‘pseudo-OH’ model.

**Example 1: Sodium carbonate (Na\(_2\)CO\(_3\)) injection**

The experimental conditions are detailed in Table 3. The core (a synthetic granular pack made of 95 wt-% silica and 5 wt-% kaolinite) is initially saturated with 10 g/L NaCl brine. A volume of 5.5 mL (corresponding to 1 PV) of 10 g/L Na\(_2\)CO\(_3\) solution in the same 10 g/L NaCl brine is then injected. After the alkali injection, 35.7 mL (6.5 PV) of 10 g/L brine is then injected as chase water. The pH of the alkali solution is 11.4. The concentration of OH\(^-\) ions can be determined graphically from plots such as those presented in Figure 2(a), analytically from the resolution of the chemical equilibriums involved with Na\(_2\)CO\(_3\) or directly from the pH of the injected alkali solution. For the present experiment, the injection concentration of OH\(^-\) ions to be used for the ‘pseudo-OH’ model is \([\text{OH}^-] = 0.092 \text{ g/L} \). In the numerical simulations, the same injection sequences as in the experiment are performed. The alkali slug in particular must have the same size as in the experiment (1 PV).

<table>
<thead>
<tr>
<th>Alkali agent injected</th>
<th>Na(_2)CO(_3)</th>
<th>Sodium Tetraborate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous medium</td>
<td>synthetic granular pack with 95 wt-% silica and 5 wt-% kaolinite</td>
<td>synthetic granular pack with 95 wt-% silica and 5 wt-% kaolinite</td>
</tr>
<tr>
<td>Diameter</td>
<td>2 cm</td>
<td>2 cm</td>
</tr>
<tr>
<td>Length</td>
<td>7 cm</td>
<td>7 cm</td>
</tr>
<tr>
<td>Porosity</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>Brine initially in place</td>
<td>NaCl 10 g/L</td>
<td>NaCl 10 g/L</td>
</tr>
<tr>
<td>Alkali concentration in the injection slug</td>
<td>10 g/L</td>
<td>10 g/L</td>
</tr>
<tr>
<td>NaCl concentration in the injection slug</td>
<td>10 g/L</td>
<td>10 g/L</td>
</tr>
<tr>
<td>pH of the injection slug</td>
<td>11.4</td>
<td>9.5</td>
</tr>
<tr>
<td>Volume of the injection slug</td>
<td>1 PV</td>
<td>1 PV</td>
</tr>
<tr>
<td>Volume of 10 g/L NaCl chase water injected</td>
<td>6.5 PV</td>
<td>7 PV</td>
</tr>
<tr>
<td>Darcy velocity</td>
<td>80 cm/d</td>
<td>80 cm/d</td>
</tr>
<tr>
<td>Temperature</td>
<td>40 °C</td>
<td>ambient</td>
</tr>
</tbody>
</table>

Table 3: Core properties and main experimental parameters for the reference monophasic coreflood injections of sodium carbonate (Na\(_2\)CO\(_3\)) and sodium tetraborate.

On Figure 2(b) are presented the experiment effluent pH data (dots) and the ‘pseudo-OH’ numerical results (curves) versus the total volume of liquid injected (normalized in PV). To illustrate the adjustment procedure implemented, several curves are shown, each of them corresponding to the result of a simulation run performed with a given pair of \( C_0 \) and \( K \) values. The criterion for best fit here is qualitative: correct representation of the pH breakthrough and of the pH maximum value are privileged rather than least-square minimization. This approach is justified by the fact that reservoir-scale simulations involve alkali-surfactant slug always lower than 1 PV and chase water slug volumes of 1 PV maximum. For this experiment, the best fit is obtained with \( C_0 = 1.8 \mu g/g \) and \( K = 900 \text{ L/g} \). For this simulation, and for all simulations resulting in a correct adjustment of the pH breakthrough, it appears that the simulated pH
decrease faster than the experimental pH. This is due to the lack of buffer effect when directly injecting OH$^\text{-}$.

Figure 2(c) shows a comparison between simulations of the experiment with the ‘pseudo-OH’ model and a model involving the complete calculation of the carbonate acid-base equilibriums (Na$_2$CO$_3$ model). It appears that, disregarding the pH value before the breakthrough (discrepancies are due to different model initializations), the two simulations satisfactorily reproduce the experimental results up to about 2 PV, which is largely sufficient for the simulation of real field cases.

Example 2: Sodium tetraborate injection

For the injection of complex alkali agents or of alkali slugs with multiple constituents, using a ‘pseudo-OH’ model can be the only way to perform a simulation. The example experiment presented in this paper consists in the injection of a sodium tetraborate solution at 10 g/L concentration, with a pH of 9.5. The other conditions of this experiment, reported in Table 3, are comparable to those for the Na$_2$CO$_3$ injection. For this experiment, the injection concentration of OH$^\text{-}$ ions in the ‘pseudo-OH’ simulations is determined from the measurement of the pH of the injected solution, namely [OH$^\text{-}$] = 0.0014 g/L. However, to generalize the method and speed-up the process, standard curves linking alkali concentration and pH or OH$^\text{-}$ concentration could be built. In the numerical simulations, again, the same injection sequences as in the experiment are performed and the alkali slug must have the same size as in the experiment (1 PV).

On Figure 2(d) are presented the experiment effluent pH data (dots) and the best-fit ‘pseudo-OH’ numerical results (curve) versus the total volume of liquid injected (normalized in PV). This best fit was obtained with $C^0_r = 0.075$ µg/g and $K = 30000$ L/g. The figure shows that, similarly as with the Na$_2$CO$_3$ injection, the pH breakthrough and the maximum pH value are satisfactorily reproduced by the ‘pseudo-OH’ model. It also appears that the discrepancy between the simulated and the experimental pH during long-term chase water injection is less marked than with Na$_2$CO$_3$. This originates in the fact that, due to the lower pH value obtained, the model is less sensible to the absence of buffer effect with OH$^\text{-}$ injection.

ASP salinity gradient coreflood

Results presented below illustrate a ASP salinity gradient process to maximize oil recovery. Surfactant phase behavior, surfactant adsorption, and polymer viscosity data were obtained from a parallel study reported in a companion paper \cite{Moreau2010}. Experiments with synthetic representative crude, reservoir formation brine, and surfactant solutions were performed to determine the optimum solubilization ratio and optimum salinity, as well as to screen surfactants and polymer for compatibility. Based on the laboratory measurements, the optimum interfacial tension is about $5 \times 10^{-4}$ mN/m using the Huh relation \cite{Huh1979}; see Figure 3(b)]. The polymer selected by laboratory testing was a hydrolyzed polyacrylamide (SNF’s Flopaam 3330S). The injection flow rate is 3 cm$^3$/h. The properties of this coreflood are summarized in Table 4 and include porosity, permeability, fluid volumes and relative permeabilities.

The salinity is continuously decreased from 50 g/L in the waterflooding water up to 25 g/L in the chase water (see Table 5). The surfactant slug is 0.5 PV at a surfactant concentration of 8 g/L in 30 g/L NaCl and 10 g/L Na$_2$CO$_3$. The surfactant slug is in a Winsor I type. The polymer drive is at a salinity of 25 g/L NaCl + 10 g/L Na$_2$CO$_3$. The optimal salinity is at 36 g/L NaCl + 10 g/L Na$_2$CO$_3$. The schedule of this coreflood and its pseudo companion are summarized in Tables 5 and 6.

Coreflood measurements and simulation results are summarized in Figures 3(c)-(f). Surfactant concentration has been determined by Hymaine titration. It must be emphasized that a mass balance on surfactant effluents shows retention of 160 µg/g of rock. The simulated oil bank breakthrough [see Fig-
Figure 2:  (a) Graphical illustration of the determination of the equivalent concentration in OH\(^-\) as a function of Na\(_2\)CO\(_3\) concentration and temperature. (b) Na\(_2\)CO\(_3\) injection, determination of the \(C_0\) and \(K\) parameters of the pseudo-OH\(^-\) ions by adjustment of effluent pH experimental data. The pseudo-OH\(^-\) concentration used is \([\text{OH}^-]\) = 0.092 g/L. The best fit is obtained for \(C_0 = 1.8 \mu\text{g/g}\) and \(K = 900 \text{ L/g}\). (c) Na\(_2\)CO\(_3\) injection, effluent pH. Comparison between the Na\(_2\)CO\(_3\) model, the ‘pseudo-OH’ model and the experimental data. ‘Pseudo-OH’ model parameters are: \([\text{OH}^-]\) = 0.092 g/L, \(C_0 = 1.8 \mu\text{g/g}\) and \(K = 900 \text{ L/g}\). Both the Na\(_2\)CO\(_3\) and the ‘pseudo-OH’ model satisfactorily predicts the breakthrough and the maximum pH value. (d) Sodium tetraborate injection, effluent pH. Comparison between the ‘pseudo-OH’ model and the experimental data. ‘Pseudo-OH’ model best-fit parameters are: \([\text{OH}^-]\) = 0.0014 g/L, \(C_0 = 0.075 \mu\text{g/g}\) and \(K = 30000 \text{ L/g}\). The ‘pseudo-OH’ model satisfactorily predicts the breakthrough and the maximum pH value.

The surfactant breakthrough shown in Figure 3(c) is also well reproduced within a 10% error. The simulated pressure drop reported in Figure 3(d) reasonably fits the measured one; they both share the well known one-dimensional constant flow rate waterflooding behavior [Willhite (1986)]. Finally, as reported in Figure 3(f), the pH amplitude and its PV threshold are well reproduced, apart a noticeable time lag regarding the reach of the final
GEOMETRY
Core length \( L = 9.78 \times 10^{-2} \) m
Core diameter \( D = 4.92 \times 10^{-2} \) m
Core cross sectional area \( A = 1.9 \times 10^{-3} \) m²

VOLUMETRICS
Irreducible (connate) water saturation \( S_{wi} = 0.253 \)
Residual oil saturation (waterflooding) \( S_{orw} = 0.568 \)
Residual oil saturation (chemical flooding) \( S_{orc} = 0.018 \)
Porosity \( \phi = 0.159 \)
Porous volume \( V_p = 2.9564 \times 10^{-5} \) m³
Residual oil in place \( \text{ROIP} = 1.6792 \times 10^{-5} \) m³

POLYMER PROPERTIES
Mobility reduction \( R_m = 1.8 \)

CORE CONDITIONS
Core temperature \( T_c = 60 \) °C
Core pressure \( p_c = 2 \) bar

FLOW PROPERTIES
Water density at core conditions \( \rho_w(T_c, p_c) = 983.28 \times 10^{-3} \) kg/m³
Oil density at core conditions \( \rho_o(T_c, p_c) = 719.95 \times 10^{-3} \) kg/m³
Water viscosity at core conditions \( \mu_w(T_c, p_c) = 0.46642 \) cP
Oil viscosity at core conditions \( \mu_o(T_c, p_c) = 0.80123 \) cP
Horizontal absolute permeability \( k = 850 \) mD
Maximum water relative permeability (waterflooding) \( k_{rw}(1 - S_{orw}) = 0.580 \)
Maximum water relative permeability (chemical flooding) \( k_{rw}(1 - S_{orc}) = 0.048 \)
Maximum oil relative permeability (waterflooding) \( k_{ro}(S_{wi}) = 0.690 \)
Maximum oil relative permeability (chemical flooding) \( k_{ro}(S_{wi}) = 0.690 \)

FLOW RATE
Water phase injection rate \( Q_{inj} = 3 \) cm³/h = \( 7.2 \times 10^{-5} \) m³/d
Water & oil phases total production rate \( Q_{prod} = Q_{inj} \)

Table 4: Coreflood and simulation model properties.

<table>
<thead>
<tr>
<th>Water (PV)</th>
<th>NaCl (g/L)</th>
<th>Na₂CO₃ (g/L)</th>
<th>Surfactant (g/L)</th>
<th>Polymer (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water in place</td>
<td>–</td>
<td>50</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Surfactant slug</td>
<td>0.55</td>
<td>30</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>Polymer slug</td>
<td>1.72</td>
<td>25</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Flush water</td>
<td>2.52</td>
<td>25</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5: ASP coreflood injection schedule.

plateau value.

Quarter 5-spot chemical displacement sensitivity analysis

The goal of this section is to give by a reservoir simulation sensitivity analysis realistic tertiary SP flood recovery factor estimates on the basis of a tridimensional vertically heterogeneous quarter 5-spot ‘toy model’ (taken from a previous study), and to show how the tertiary oil recovery performance may depend on surfactant adsorption, surfactant concentration, surfactant slug size, capillary desaturation curve, and eventually how a pre-existent secondary waterflood of variable duration may affect the tertiary recovery factor.
Table 6: ASP coreflood pseudo injection schedule. The Langmuir hydroxide ions adsorption is such that $C_{rOH^-}^0 = 0.12 \mu g/g$ and $K_{OH^-} = 900 L/g$.

The reservoir investigated in this study is 924 m deep and 13 m thick. The reservoir is currently undergoing waterflood and is producing about 98% water cut, which is close to the economic limit. The properties of this reservoir are summarized in Table 7 and include porosity, permeability, fluid volumes and relative permeabilities. The residual saturations, relative permeability end points and relative permeability Corey exponents were derived from laboratory data and are typical of a water-wet reservoir. In addition, the reservoir fluid properties were also obtained from the field operator and are listed in Table 7.

The simulation model is a quarter five-spot symmetry element with a pressure-constrained injector and producer within a $2.8676 \times 10^5 m^2$ pattern (70 acre). Well test measurements indicated that the reservoir can be described as layered with one bottom high permeability layer stacked with two lower permeability layers (see Table 7). In lack of any other available operator data, we assumed the planar permeability field to be homogeneous in each layer.

The reservoir has had a very long history of primary and secondary recovery. We did not try to obtain a realistic post-waterflood oil saturation and pressure distribution; rather, we adopted a very phenomenological two-fold approach: first, we crudly assumed that all the oil that could be displaced by waterflood had been produced, that is we did not simulate nor match the waterflood and started from scratch the tertiary chemical injection from a ‘perfect’ tertiary initial state $[i.e. S_w(x,t=0^-) = 1 - S_{orw} at any point x of the reservoir]$. This case is probably highly unrealistic but is also the most defavorable scenario regarding the chemical injection, since there is no remaining ‘free’ oil in the reservoir that could be ultimately produced by waterflooding and that could be eventually produced by the chemical injection. In a second approach, a waterflood of variable duration was simulated with known well constraints and ceased at several realistic water cuts; in this case the simulated post-waterflood conditions were used as the initial conditions for all SP simulations.

Surfactant phase behavior, surfactant adsorption, and polymer mobility reduction were obtained from a previous study. Experiments with reservoir crude and formation brine, and surfactant solutions were performed to determine the optimum salinity and solubilization ratio, as well as to screen surfactants and polymer for compatibility. Based on the laboratory data, the optimum interfacial tension is about $3.6 \times 10^{-3} mN/m$ using the Huh relation $[Huh (1979)]$. In addition, experimental corefloods were conducted to measure the performance of the surfactant and polymer. In particular, the surfactant adsorption was measured in several corefloods and ranged from 100 to 400 $\mu g/g$ with an average value of 200 $\mu g/g$. Measurements also shown that polymer adsorption could be neglected.

Measurements also shown that polymer adsorption could be neglected.

The base case simulation was designed by utilizing known field conditions and laboratory coreflood designs. The known field conditions included a maximum bottom-hole injection pressure of 150 bar and a minimum bottom-hole production pressure of 15 bar. The injection well constraint is due to the reservoir fracture pressure and the producer constraint is due to facility constraints from the field of...
Table 7: Reservoir and simulation model properties.

interest. The laboratory coreflood designs were utilized to develop the base case injection scheme for the chemical flood. The SP design for the base case simulation is summarized in Table 8: a 0.3 PV surfactant with polymer slug is followed by a 1.7 PV polymer drive slug; of course, thumb’s rule for the polymer drive slug size is rather 0.5 PV, but here our phenomenological goal is only to give rough recovery estimates and relative variations on a ‘large’ time scale.

<table>
<thead>
<tr>
<th>Water (PV)</th>
<th>Surfactant (g/L)</th>
<th>Polymer (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant slug</td>
<td>0.3</td>
<td>10</td>
</tr>
<tr>
<td>Polymer slug</td>
<td>1.7</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 8: Quarter 5-spot base case tertiary SP injection schedule (surfactant adsorption is 200 µg/g).
Figure 4 reports the tertiary recovery factor sensitivity to surfactant adsorption [Figures 4(a)-(b)], surfactant concentration [Figures 4(c)-(d)], and surfactant slug size [Figures 4(e)-(f)]; in that case, the polymer drive slug varies accordingly to the surfactant slug size so that the total injection run duration is 2 PV, reminding that the base case surfactant adsorption is 200 $\mu$g/g, surfactant concentration is 10 g/L and surfactant slug size is 0.3 PV. The base case capillary desaturation curve is shown in Figure 5(a) and (d).

As shown in Figure 4(b), where each curve is a snapshot at some time (injected PV) for several surfactant adsorptions ranging from 0 to 900 $\mu$g/g, the recovery factor decreases quasi-linearly in the surfactant adsorption. This is an important trend because of its non-saturating feature, contrary to an asymptotic logarithmic variation, e.g., as we shall see below. Base case final recovery factor is 20% ROIP; 2% additional ROIP can be gained if the surfactant is assumed not to adsorb on the rock, which is unlikely. On the other hand, the more pessimistic 400 $\mu$g/g surfactant adsorption leads to a 16% ROIP final recovery factor. A noticeable gap of about 3% ROIP appears in the oil recovery between the 400 and the 300 $\mu$g/g surfactant adsorption cases.

Figures 4(c)-(d) report the recovery factor sensitivity to the surfactant concentration, ranging from 2 to 40 g/L, 10 g/L being the base case and leading to a 20% ROIP recovery factor. In that case, the recovery factor increases non-linearly with the surfactant concentration; there is a noticeable change in the recovery factor — almost 4% ROIP — if the surfactant concentration is increased from 10 to 15 g/L. Of course, higher surfactant concentrations lead to better recoveries, but since the recovery process is non-linear in the surfactant concentration, the additional recovered oil is not proportional to the increase of the surfactant concentration. Besides, large time scale injection also seems to play a key role: indeed, the recovery factor exhibits a large gap between 0.75 and 1 injected PV, after what the recovery factors amplitudes are translated from each other, which is not the case below 1 injected PV.

Finally, Figures 4(e)-(f) report the recovery factor sensitivity to the surfactant slug size, ranging from 0.1 to 1 injected PV, 0.3 injected PV being the base case and leading to a 20% ROIP recovery factor. This case exhibits a strong non-linear dependence of the recovery factor in the surfactant slug size, with a large gap between 0.2 and 0.3 injected PV (4% ROIP). This gap is by far larger between 0.1 and 0.2 injected PV (8-9% ROIP).

The last part of this sensitivity study is dedicated to the tertiary recovery factor dependence in the capillary desaturation curve, and in a pre-existent waterflood of variable duration. We start with the capillary desaturation curve [see Figures 5(a)-(c)], the tertiary reservoir initial conditions and injection schedule being the same as the ones which have been previously used and reported in Table 8. The base case capillary desaturation curve is shown in Figure 5(a) (red symbols are measured CDC while its fitting companion curve is continuous line, curve [1] in the figure). We first translate this base CDC without modifying its shape (nor the independent IFT table) to lower capillary number values twice half an order of magnitude successively, which leads to CDCs [2] and [3]. Secondly, the base CDC slope is increased, which leads to CDC [4], then shifted half an order of magnitude to the left (CDC [5]), and finally one more order of magnitude to the left (CDC [6]). Corresponding recovery factors in % ROIP and % OOIP are reported in Figures 5(b)-(c): comparison between recovery factors [1] and [3] shows that a one order of magnitude $N_c$-shift of the CDC results in a doubling of the recovery factor in % ROIP or % OOIP. Comparison between recovery factors [2] and [6], and [1] and [2] approximately gives the same estimate; in the latter case, half an order of magnitude $N_c$-shift of the CDC results in multiplying the recovery factor by 1.75.

Next, we investigate the ‘benefit’ of a secondary pre-existing waterflood of variable duration on the tertiary oil recovery expressed in % OOIP in the case of the two extreme capillary desaturation curves [1] and [6], which are reported in Figure 5(d). In that case, the tertiary injection schedule reported in Table 8 is completed with a waterflood of three durations: 0.5, 1.0 and 1.5 injected PV. The corresponding full recoveries are reported in Figure 5(e). The 0.5, 1.0 and 1.5 PV waterfloods respectively lead to a quite
realistic water cut of 90, 95 and 98%, independently of the CDC. While the CDC [1] leads to a 55% OOIP final recovery, the CDC [6] leads to a 75% OOIP final recovery; these recoveries seem far from being unlikely or unrealistic.

Finally, we ‘separate’ in each flood the waterflood oil recovery contribution from the one due to the chemical flood. To do so, we redefine in each flood (three floods for CDC [1] and three floods for CDC [6]) the time origin as the end of the waterflooding, that is 0.5, 1.0 and 1.5 injected PV respectively, and we reset accordingly the oil recoveries. Tertiary recovery factors are reported in Figure 5(f), and should be compared with the ones reported in Figure 5(c), where there is no waterflood. While CDC [1] leads in the case of a perfect tertiary displacement to a 8% OOIP recovery factor, it leads respectively to a 29, 23 and 20% OOIP recovery factor with a pre-existing waterflood of 0.5, 1.0 and 1.5 injected PV duration. While CDC [6] leads in the case of a perfect tertiary displacement to a 28% OOIP recovery factor, it leads respectively to a 44, 38 and 35% OOIP recovery factor with a pre-existing waterflood of 0.5, 1.0 and 1.5 injected PV duration. Table 9 summarizes these results.

<table>
<thead>
<tr>
<th>CDC</th>
<th>no WF</th>
<th>1.5 PV WF</th>
<th>1.0 PV WF</th>
<th>0.5 PV WF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recovery factor (% OOIP) [1]</td>
<td>8%</td>
<td>20%</td>
<td>23%</td>
<td>29%</td>
</tr>
<tr>
<td>Relative variation (from no WF case) [1]</td>
<td>–</td>
<td>+150%</td>
<td>+188%</td>
<td>+263%</td>
</tr>
<tr>
<td>Recovery factor (% OOIP) [2]</td>
<td>28%</td>
<td>35%</td>
<td>38%</td>
<td>44%</td>
</tr>
<tr>
<td>Relative variation (from no WF case) [2]</td>
<td>–</td>
<td>+25%</td>
<td>+36%</td>
<td>+57%</td>
</tr>
</tbody>
</table>

Table 9: Quarter 5-spot tertiary recovery factor sensitivity study to capillary desaturation curve, and to a pre-existent waterflood of variable duration (see Figure 5).

Conclusions

The following conclusions are drawn:

- The fundamental mechanisms for tertiary displacement of oil by surfactant enhanced alkaline and polymer flooding are successfully introduced in a C-EOR reservoir simulator.
- Good agreement is obtained between coreflood experiments using alkaline/surfactant/polymer chemicals to recover residual oil and our chemical simulator.
- Various options as ion exchange with precipitation/dissolution and a pseudo-representation of alkaline propagation are validated with dedicated experiments.
- Sensitivity studies show the drastic effect of adsorption on oil recovery which has a crucial impact on C-EOR economics.
- Scaling to pilot size is determinant to demonstrate the efficiency of C-EOR. This can be done using SARIPCH with physical data fully validated at core scale.

Acknowledgements

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References


Taber, J.J. [1969] Dynamic and static forces required to remove a discontinuous oil phase from porous media containing both oil and water. SPE 2098.


Figure 3: Coreflood measurements and simulation results comparison. (a) Measured capillary desaturation curve (blue symbols), (b) measured IFT as a function of salinity for several surfactant concentrations, (c) recovery factor (blue symbols are experimental measurements and red continuous lines are simulation outputs), (d) pressure drop, (e) surfactant concentration in the effluent, (f) produced water pH.
Figure 4: Quarter 5-spot tertiary recovery factor sensitivity study to surfactant adsorption [(a)-(b)], surfactant concentration [(c)-(d)], and surfactant slug size [(e)-(f)]. (See the text.)
Figure 5: Quarter 5-spot recovery factor sensitivity study to capillary desaturation curve [(a)-(c)], and to a pre-existent waterflood of variable duration [(d)-(f)]. (See the text.)